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RHEOKINETICS AND NETWORK FORMATION IN CROSSLINKING STEP-GROWTH POLYMERIZATION

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*Rheokinetics and network formation in crosslinking step-growth polymerization*

**Abstract**

Since the discovery of polyurethane reaction consisting out of isocyanates and polyols, in 1937 up until today, this material has been studied and applied. By combining different monomers and reaction environments several different materials can be made with varied applications like foams, fiber composites matrix, paints, coatings and adhesives. Like in other polymers there is an intimate relation between the structure-processing-property relationships, starting from the monomers building up the network, viscous and the mechanical properties, but due to the fast reaction kinetics of polyurethanes is not well-known and therefore less controllable.

The goal of this work was to gain in-depth knowledge and insight in the reaction kinetics of polyurethane resins and to link it to the changing rheological properties, consequently gaining insight in the use of these resins to produce polyurethane materials. To accomplish this, first the reaction mechanism behind the urethane formation, which is still up for debate, was investigated. Using the concentration profiles obtained from this reaction mechanism and knowing the structure of the monomers, the molecular structure development, such as the average molar mass and crosslink density, can be predicted using a recursive algorithm. Using the average molar mass, the viscosity evolution, gelation and mechanical properties can be predicted. To help facilitate this, a software was developed for simulating and optimizing reaction kinetic mechanisms in a first step and calculate the structure development in a second step.

The developed methods and rheokinetic models are useful for industry as their application can aid in improving the design and process conditions of existing processed and help create and develop new ones.
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<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$A$</td>
<td>pre-exponential factor</td>
</tr>
<tr>
<td>$a_T$</td>
<td>shift factor</td>
</tr>
<tr>
<td>$C_i$</td>
<td>concentration of species $i$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>heat capacity at constant pressure</td>
</tr>
<tr>
<td>$DF$</td>
<td>diffusion factor</td>
</tr>
<tr>
<td>$DP_n$</td>
<td>degree of polymerization</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimeter</td>
</tr>
<tr>
<td>$d\gamma/dt$</td>
<td>shear rate</td>
</tr>
<tr>
<td>$E$</td>
<td>activation energy</td>
</tr>
<tr>
<td>$E_x$</td>
<td>activation energy a extent of conversion $x$</td>
</tr>
<tr>
<td>$f$</td>
<td>functionality of a monomer</td>
</tr>
<tr>
<td>$g$</td>
<td>$g$-factor</td>
</tr>
<tr>
<td>$G_e$</td>
<td>equilibrium modulus</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>$\dot{H}$</td>
<td>reaction heat flow</td>
</tr>
<tr>
<td>$\dot{H}_C$</td>
<td>reaction heat flow expressed in heat capacity units ($\text{J.g}^{-1}.\text{K}^{-1}$)</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant</td>
</tr>
<tr>
<td>$k_i$</td>
<td>reaction rate constant of reaction $i$</td>
</tr>
<tr>
<td>$\log A$</td>
<td>10-based logarithm of the pre-exponential factor</td>
</tr>
<tr>
<td>$\log k_{Tr}$</td>
<td>10-based logarithm of the reaction rate constant at reference temperature $T_r$</td>
</tr>
<tr>
<td>$M_c$</td>
<td>critical molar mass</td>
</tr>
<tr>
<td>MDI</td>
<td>mixture of MDI44 and MDI24 (see materials and techniques)</td>
</tr>
<tr>
<td>MDI24</td>
<td>2,4'-methylene diphenyl diisocyanate</td>
</tr>
<tr>
<td>MDI44</td>
<td>4,4'-methylene diphenyl diisocyanate</td>
</tr>
<tr>
<td>$M_e$</td>
<td>entanglement molar mass</td>
</tr>
<tr>
<td>$M_i$</td>
<td>molar mass of a molecule</td>
</tr>
<tr>
<td>$M_n$</td>
<td>number-average molar mass</td>
</tr>
<tr>
<td>MTDSC</td>
<td>modulated temperature differential scanning calorimetry</td>
</tr>
<tr>
<td>$M_w$</td>
<td>mass-average molar mass</td>
</tr>
<tr>
<td>$M_z$</td>
<td>$z$-average molar mass</td>
</tr>
<tr>
<td>$N_0$</td>
<td>initial number of molecules</td>
</tr>
<tr>
<td>NCO</td>
<td>isocyanate</td>
</tr>
<tr>
<td>$N_i$</td>
<td>number of molecules with a molar mass of $M_i$</td>
</tr>
<tr>
<td>$n_w$</td>
<td>weight-average number of branching units per molecule</td>
</tr>
<tr>
<td>OH</td>
<td>alcohol</td>
</tr>
<tr>
<td>OH$_p$</td>
<td>primary alcohol</td>
</tr>
<tr>
<td>OH$_s$</td>
<td>secondary alcohol</td>
</tr>
<tr>
<td>PDI</td>
<td>polydispersity</td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>heat flow</td>
</tr>
<tr>
<td>TAM</td>
<td>microcalorimeter</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>$T_{g0}$</td>
<td>glass transition temperature of the uncured polymer</td>
</tr>
<tr>
<td>$T_{gl}$</td>
<td>glass transition temperature of the full cured polymer</td>
</tr>
</tbody>
</table>
$T_{g\infty}$: glass transition temperature for polymer with an infinite molar mass

$T_r$: reference temperature

TTT: time-temperature-transformation diagram

$v$: reaction rate

$v_j$: reaction rate of reaction $j$

WLF: Williams, Landel and Ferry law

$x$: extent of reaction

$\gamma$: shear

$\Delta H(t)$: reaction heat generated from the start to time $t$

$\Delta H_{tot}$: total reaction heat

$\Delta_e H$: molar enthalpy of reaction

$\Delta_e H_i$: molar enthalpy of formation of specie $i$

$\eta$: viscosity

$\eta^*$: complex viscosity

$\eta_0$: zero-shear viscosity

$\mu$: crosslink density

$v$: concentration of elastic effective junctions

$v_i$: stoichiometric coefficient of specie $i$

$v_{ij}$: stoichiometric coefficient of specie $i$ in the elementary reaction $j$

$\rho$: density

$\sigma_s$: shear stress

$\tau$: relaxation time

$\tau_r$: relaxation time at reference temperature $T_r$
CHAPTER I

GENERAL INTRODUCTION: AIM & OUTLINE

1 Intro and aim

In historical studies, the prehistorical eras are named after the materials used to make tools, namely the stone age and the bronze age. Using this naming convention, the current age might be described as the ‘plastic age’.\(^1\) Since WW II has there been a great growth in the synthesis methods, the production and applications of synthetic polymers, which might warrant this claim.\(^2\)

One of these applications is composite materials. These are currently of great interest for the automotive and aerospace industries because of the need for materials that have good mechanical properties and light weight, allowing for a reduction in fuel consumption. One of the processing techniques used to make composite materials is resin transfer molding. In this technique a reactive mixture flows through a fiber matrix within a closed mold, after which due to reaction a fiber reinforced composite is produced. With this technique, large and complex shaped composites can be made at a high production rate with a relatively low cost.\(^3\)–\(^5\) Epoxy resins are one of the most used types of resins to make composite materials, because their reactions are well known and can be well controlled. However, epoxy resins have the disadvantage that they are brittle, which makes them unsuitable for certain applications.\(^6\)

Therefore other resins, like polyurethanes, have become of interest because of their higher toughness.\(^6\)–\(^8\)

The urethane bond is formed when an isocyanate group and an alcohol group react with each other. This reaction was first discovered and patented by dr. Otto Bayer in 1937.\(^9\) When people use the term ‘polyurethane’, it is often implied that the starting materials contained the isocyanate group. When reacted with molecules bearing alcohol functional groups urethane groups are formed indeed, however polymers resulting from reactions with many other functional groups, like amines, amides, and epoxies, are often mistimed polyurethanes as well. This is mainly due to the ability to tailor these materials by changing the monomers and to the numerous possible reactions. PU can be made into a thermoplastic, elastomer and thermoset, thus enabling its use in different applications, like paints, hard and soft foams, coatings, adhesives and fiber-reinforced composites.\(^10\) Due to its versatility a turnover of US$ 50 billion was realized with polyurethane in 2014. The expectation by Ceresana, a market research company, is that polyurethane revenues will increase annually by 4.8 % to amass to an approximate value of US$ 74 billion by 2022.\(^11\)

The disadvantage of using polyurethanes is that their reaction kinetics are quite fast, which combined with high reaction heats results in self-heating, which can lead to thermal degradation
During production. Although the urethane reaction is known for quite some time, the detailed mechanism behind the urethane formation is still up for debate. This complicates the use of polyurethanes resins in resin transfer molding and other composite productions techniques. To obtain a high-quality composite material in resin transfer molding, the resin must flow through the fiber matrix, filling the whole cavity. In case of incomplete wetting, air encapsulation or due to a complex shape, this is not always the case, causing reduced mechanical properties and an inferior product.\textsuperscript{3–5} This can be avoided with a good knowledge of the rheological behavior of the resin. This rheological behavior will change depending on the temperature and the degree of polymerization of the resin, which are strongly coupled during a molding process, making the prediction of the chemorheology rather difficult.

The aim of this work is to gain advanced knowledge in the reaction kinetics of polyurethanes and couple these to the changing rheological properties of the material, aiming to gain insight in the production of polyurethane based composite materials. The first step in achieving this goal is an experimental study of the urethane formation kinetics. These results will be used to obtain a mechanistic kinetic model that can describe and predict the urethane formation for a wide range of conditions. The kinetics and the rheology are coupled with one another due to the increase in molar mass of the growing polymer, which affects the viscoelastic behavior. A recursive algorithm was developed that allows to couple the extent of reaction to the average molar mass and some network properties.\textsuperscript{12,13} With this information, the evolution of the viscous behavior of the resin can be predicted as function of the temperature and reaction progress. This results in a model coupling the structure – process – property relationships of polyurethanes.

2 Outline

This work is structured in the following way. First an introduction and a state of the art of the current research concerning the polymerization kinetics, molar mass and viscosity calculation are given, with an emphasis on polyurethanes (Chapter II). This is followed up by a chapter describing the materials and equipment used during this work, accompanied with a brief summary of the innerworkings of the developed software, its tools, and uses (Chapter III).

In Chapter IV, the protocols for how to perform a kinetic polyurethane experiment using thermal analysis techniques is explained. This includes the difficulties that can arise in working with fast curing systems, with long reaction tails, and methods of how to improve the measurement quality and analysis procedure, providing approaches and methods that will be used throughout the rest of the work.

In order to predict molar mass and viscosity evolutions for polyurethanes accurately, a good in-depth knowledge of their reaction kinetics is needed. In Chapter V, the urethane formation kinetics are studied experimentally using reactions with monofunctional alcohols as model systems. Using these results a kinetic model capable of predicting the polyurethane reaction
Introduction

kinetics is developed. In a next step, the kinetics are investigated using bifunctional alcohols, leading to linear polymers (Chapter VI). This also includes studying the impact of using a catalyst (Chapter VII). These systems more closely resemble industrially relevant polymers, but are accompanied with other difficulties not observed in monofunctional systems. A mechanistic model sufficiently able to describe the polyurethane reaction kinetics is developed.

In Chapter VIII, a method to calculate molar mass averages, crosslink densities, viscous and mechanical properties based on polymers with a step-growth mechanism is derived. This method is based on previous work first published by Macosko and Miller.\textsuperscript{12,13} The developed method is then applied on polyurethane systems by implementing the kinetic model and comparing the theoretical results with the experimental measurements (Chapter IX).

Finally, Chapter X will recap the main conclusions drawn from this work and will briefly discuss some future perspectives.
3 References


CHAPTER II

INTRODUCTION

1 Structure and properties of polymers

A polymer or macromolecule is a long chain, linear or branched, or a network built-up out of a large number of monomer units. The properties of a polymer will depend on its architecture and the units it is constituted of. The different polymer architectures can be found in Figure II-1. The development of these architectures during polymerization will mainly depend on the monomers used and the polymerization kinetics by which the polymer chains are formed, which will be further elaborated in section 2 of this chapter. First, the linear and branched polymers and their properties will be discussed, next the polymer networks.

1.1 Linear and branched polymers

The simplest architecture is a linear polymer chain. One of the most used polymers worldwide, high-density polyethylene (HDPE), is synthesized using a Ziegler-Natta catalyst and has almost no branching. Branched polyethylene can be created in a controlled way by adding small amounts of alpha-olefins, like 1-butene and 1-hexene. These molecules will introduce short branching arms on the otherwise linear chain. The resulting polymer is a linear low-density polyethylene (LLDPE). When using pure ethylene and a different catalyst, a branched structure with long branching arms will form, the formed polymer being termed a low-density polyethylene (LDPE). Polyethylene is a semi-crystalline polymer and can therefore be characterized by melting temperature (amorphous polymers are characterized by their glass transition temperature). The different polyethylene architectures result in different properties of the final materials, like the ability to form chain entanglements (see section 1.1.4) and melting temperature. The melting temperature of HDPE is about 135°C, while for LDPE the melting temperature is about 110°C. The melting temperature of LLDPE is in between the those of HDPE and LDPE and can be tuned according to the amount of branching.
1.1.1 Molar mass distributions and molar mass averages

Some polymer properties, like viscosity and glass transition temperature ($T_g$), will vary strongly with the length of the polymer chain. As the polymer chains in a polymer material have very seldom all the same length, there is a distribution in the chain length, which is mainly the result of the synthesis method. Thus, the (average) length of the polymer or its (average) degree of polymerization ($DP$), and thus its (average) molar mass, need to be defined in order to discuss how these affect the polymer properties. In principle, the length distribution is discontinuous, as only an integral amount of monomer units can be part of the chain. Based on this distribution, different molar mass averages can be defined. The number-average molar mass, represented by $M_n$ is defined as follows:\textsuperscript{3}

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$  \hspace{1cm} (eq. II-1)

Figure II-1 An illustration of the different polymer architectures that can be obtained through synthesis. Taken from\textsuperscript{2}
Where \( N_i \) is the number of molecules with a molar mass of \( M_i \). In a similar way, the mass-average molar mass \( M_w \) and the z-average molar mass \( M_z \) are defined by equations (eq. II-2) and (eq. II-3), respectively. An example of a distribution and its molar mass averages is given in Figure II-2. Although the distribution is discrete, if the chains are long enough, this distribution can be described by a continuous function. This is the case for vinyl polymers with a molar mass higher than \( 10^5 \) g/mol.\(^2\) The polydispersity (PDI) is defined as the ratio \( M_w \) and \( M_n \). To characterize the width of a polymer molar mass distribution, the standard deviation is required and can be calculated using the PDI (eq. II-4).

\[
M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}
\]

(eq. II-2)

\[
M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}
\]

(eq. II-3)

\[
PDI = \frac{M_w}{M_n}
\]

(eq. II-4)

\[
\sigma = M_n \sqrt{PDI - 1}
\]

(eq. II-5)

The different averages are needed for describing the different properties, for example, the number average molar mass is used to determine the glass transition temperature (see section 1.1.3) while of the viscous properties the mass average molar mass is used. The molar mass distribution can be measured directly using gel permeation chromatography (GPC).

Based on the monomer structure and concentrations, the reaction mechanism and kinetics, and the extent of reaction, the distribution or its averages can (often) be predicted, which aid in predicting the properties of polymers resulting from certain reaction conditions without actually measuring the distribution. This approach will be further developed in section 2.
1.1.2 Chain dimensions and gyration radius

One way of describing a polymer chain dimension is via the so-called contour length, which is the length along the backbone of the polymer.\(^3\) If the length of its monomer unit is \(l\) then the contour length of a linear polymer chain containing \(n\) backbone bonds is \(nl\). Considering that most polymer chains are quite flexible, having limited energy barriers against rotation around its backbone bonds, and tend to coil up in a solution or in a polymer melt, a better representation of the dimension of a polymer chain is the end-to-end distance \(r\) (Figure II-3 (left)). In a freely jointed chain, this end-to-end distance is not fixed due to the changing rotation around the backbone bonds, implying that there is a range of \(r\) values (from next to each other to a fully stretched chain) with certain \(r\) values being more probable than others. Hence, the root-mean-square (RMS) end-to-end distance \((r^2)^{1/2}\) is more representative for the size of the polymer coil. The radial distribution \(W(r)\) of the end-to-end distance can be calculated using a generalized gamma distribution and is given by (eq. II-6). This distribution is plotted in Figure II-3 (right). Using the distribution the \(\langle r^2 \rangle\) can be calculated (eq. II-7) and the RMS end-to-end distance as well (eq. II-8).

\[
W(r) = 4\pi \left(\frac{\beta}{\pi^{3/2}}\right)^3 r^2 \exp(-\beta^2 r^2) \quad \text{(eq. II-6)}
\]

With \(\beta^2 = 3/(2nl^2)\)

\[
\langle r^2 \rangle = \int_0^\infty r^2 W(r) dr = \frac{3}{2} \beta^{-2} = nl^2 \quad \text{(eq. II-7)}
\]

\[
\langle r^2 \rangle_1 = \frac{1}{n^2 l} \quad \text{(eq. II-8)}
\]

Figure II-3 (left) Schematic representation of the end-to-end distance \(r\) and the distance \(s_i\) between the center of mass (C. M.) and a monomer unit of mass \(m_i\) of a linear coiled polymer molecule. (right) the radial distribution function \(W(r)\) for a chain of \(10^4\) links with a length of 0.25 nm. Taken from 4
Another measurement of the size of a polymer chain is the radius of gyration $s$ and the root-mean-square radius of gyration $\langle s^2 \rangle^{\frac{1}{2}}$. The former is defined as the square-root of the mass average of $s_i^2$ over all monomer units, where $s_i$ is the distance between a monomer unit and the center of mass of a macromolecule composed out of $n$ monomer units with masses $m_i$ with $i=1,2,\ldots,n$ (eq. II-9) (see also Figure II-3). The RMS radius of gyration is defined analogously, but with mean-square distances of the monomer units $\langle s^2 \rangle$ (eq. II-10)

$$s = \left( \frac{\sum_{i=1}^{n} m_i s_i^2}{\sum_{i=1}^{n} m_i} \right)^{\frac{1}{2}} \quad (eq. II-9)$$

$$\langle s^2 \rangle^{\frac{1}{2}} = \left( \frac{\sum_{i=1}^{n} m_i \langle s_i^2 \rangle}{\sum_{i=1}^{n} m_i} \right)^{\frac{1}{2}} \quad (eq. II-10)$$

A linear polymer chain build up out of a certain number of monomers will have a larger $\langle s^2 \rangle$ compared to branched polymers $\langle s_b^2 \rangle$ of the number of monomers assuming they are similar monomer units in length and flexibility. By taking the ratio of RMS radios of the branched and its corresponding linear polymer with the same number of monomer units, the radius of gyration contraction factor or the $g$-factor can be calculated (eq. II-11). The $g$-factor is used for characterizing the effects of branches on the properties of polymers and is used for predicting viscosities (see section 1.1.5).

$$g = \frac{\langle s_b^2 \rangle}{\langle s_l^2 \rangle} \quad (eq. II-11)$$

Zimm and Stockmayer have developed a method for calculating the $g$-factor directly based on the number of branching units and functionality of the branching unit $f$, without calculating the mean-square radii of the branched and linear polymers. Of special interest here are the results for the average $g$-factor when the branching units are randomly distributed along the polymer chain, because they are representative for what happens during step-growth polymerization. The different polymerization mechanisms are discussed in section 2. The solutions for branching units having $f=3$ and $f=4$ are given by (eq. II-12) and (eq. II-13). The mathematical development of these result can be found in the paper from Zimm and Stockmayer.

$$\langle g_3 \rangle = \frac{3(1-2\alpha)}{\alpha} \left\{ \frac{1}{2} \left( 1 - \frac{\alpha}{\alpha} \right)^{\frac{1}{2}} \ln \left( \frac{(1-\alpha)^{\frac{1}{2}} + \alpha^{\frac{1}{2}}}{(1-\alpha)^{\frac{1}{2}} - \alpha^{\frac{1}{2}}} \right) \right\} \quad (eq. II-12)$$

$$\langle g_4 \rangle = \frac{1-3\alpha}{2\alpha} \ln \left( \frac{1-\alpha}{1-3\alpha} \right) \quad (eq. II-13)$$

With $\alpha = \frac{n_w}{2+(f-1)n_w}$

Where $n_w$ is weight-average number of branching units per molecule.
Chapter II

1.1.3 The glass transition temperature

The glass transition is one of the most important thermal transitions of an amorphous polymer. Below its glass transition temperature \((T_g)\), the polymer has glass-like properties, while above \(T_g\), it has a viscous or rubbery behavior. The modulus of a glassy amorphous polymer is of the order of several GPa, while its only at the MPa level for rubbery polymers. The stiffness of the polymer backbone will affect the \(T_g\): a stiffer backbone will lead to a higher \(T_g\). Also the molar mass will influence the \(T_g\), with longer chains leading to higher \(T_g\). For linear amorphous polymers, this can be described by Flory-Fox relation\(^7\):

\[
T_g = T_{g\infty} - \frac{B}{M_n}
\]  

(\textit{eq. II-14})

Where \(T_{g\infty}\) is the glass transition temperature of an infinitely long polymer and \(B\) is a fitting parameter. As a polymer chain becomes longer, the \(M_n\) becomes higher and the \(T_g\) will approach \(T_{g\infty}\).

1.1.4 Motions in polymers

The motions of a linear polymer in its melt are quite different from the molecular motions in other more common liquids. Due to the threadlike structure of polymers, the movement of a polymer chain through surroundings is mainly governed by coordinated thermal motion (or also called Brownian motion) of shorter segments of the polymer chain.\(^8\) To describe the movements of a polymer chain in its melt, the reptation model was developed by de Gennes.\(^9\) In this model, a polymer chain moves in a wormlike fashion through a thin tube surrounding the backbone and formed by its entanglements with other chains. The tube walls, consisting of other polymer chains, are considered to be fixed when compared to the timescale of the wormlike movement.\(^3\) The timescales of the reptation movement of the chain segments and the disentanglement of polymer chains are different and thus will lead to different relaxation times. If a polymer melt has a relaxation time that is much smaller than the measurement time, classical viscous behavior will be observed, following Newton’s law:

\[
\sigma_s = \eta \frac{dy}{dt} = \eta \dot{y}
\]  

(\textit{eq. II-15})

Where \(\sigma_s\) is the shear stress, \(\eta\) is the (shear) viscosity and \(dy/dt\) is the shear rate. Liquids behaving according to (\textit{eq. II-15}) are called Newtonian fluids. In contrast, if the relaxation time is much higher than the measurement time, an elastic, solid-like behavior will be observed, following Hooke’s law:

\[
\sigma_s = G\gamma
\]  

(\textit{eq. II-16})

Where \(G\) is the shear modulus and \(\gamma\) is the shear strain. Hookean solids behave according to (\textit{eq. II-16}). If the relaxation time and measuring time are of the same order of magnitude, a polymer will behave in a viscoelastic manner. The rheology of a material - its viscous, elastic or
viscoelastic behaviour - can be measured using a (dynamic) rheometer, which will be discussed in section 5.1.

1.1.5 Viscosity

The viscosity of a polymer in the melt is directly related to its $M_w$: the zero-shear viscosity $\eta_0$ is given by the following formula:

$$\eta_0 = K M_w^\alpha$$  \hspace{1cm} (eq. II-17)

With $K$ being a proportionality factor. For linear polymers $\alpha$ can have two values, which correspond with different regimes dependent on the molar mass. Below a critical molar mass $M_c$, the value for $\alpha$ is 1 and above $M_c$ it is 3.4. The value of $M_c$ is related to the entanglement molar mass $M_e$ by a factor $f$:

$$M_c = f M_e$$  \hspace{1cm} (eq. II-18)

For many polymers the value of $f$ is 2,\textsuperscript{10} although some researchers\textsuperscript{11,12} found values of $f$ ranging from 1.6 to 3.5. By adapting (eq. II-17) with the $g$-factor, defined in (eq. II-11), the formula (eq. II-19) can be used for branched polymers. A requirement is that the length of the branches is smaller than $M_e$:\textsuperscript{5}

$$\eta_0 = K (g M_w)^\alpha$$  \hspace{1cm} (eq. II-19)

As the relaxation time is temperature dependent, this will lead to a temperature dependent viscosity. The zero-shear viscosity for a certain temperature is related to the zero-shear viscosity at a reference temperature $T_r$ and a temperature dependent factor $K$.

$$\eta_0(T) = K(T, T_r)\eta_0(T_r)$$  \hspace{1cm} (eq. II-20)

The temperature evolution of the factor $K$ will be determined by how close the operating temperature is compared to the glass transition temperature of the polymer. When the temperature is between the $T_g$ and $T_g + 100$ K, the factor will follow the WLF-law (eq. II-21), named after the developers Williams, Landel and Ferry.\textsuperscript{13} When $T_g$ is used as reference temperature the constants $C_1$ and $C_2$ in (eq. II-21) become universal. If the temperature is greater than $T_g + 100$ K, the factor will follow an Arrhenius-like behavior (eq. II-22).

$$\ln\left(K(T, T_r)\right) = \frac{C_1(T - T_r)}{C_2 + T - T_r}$$  \hspace{1cm} (eq. II-21)

$$\ln\left(K(T, T_r)\right) = \ln(A) - \frac{E}{RT}$$  \hspace{1cm} (eq. II-22)

1.1.6 Viscoelasticity

The rheology of a material is considered to become viscoelastic if it starts to deviate from Newtonian behavior (eq. II-15). At low shear rates or equivalently low rates of deformation, polymers will behave as Newtonian fluids and polymer chains will have entangled and coiled-up conformation. As it is hard for the polymer chains to slide past one another, a relatively high
viscosity $\eta_0$ will be observed (Figure II-4). The low shear rate range at which the viscosity does not change is called the first Newtonian plateau. As the shear rate increases, the polymer chains will start to disentangle. The disentangled chains will be able to slide more easily past each other, lowering the viscosity. This effect is called shear-thinning. The relation between the shear stress and the shear rate changes from (eq. II-15) to a power law.

$$\sigma_s = K\dot{\gamma}^n$$  \hspace{1cm} (eq. II-23)

Where $K$ and $n$ are constants. Note that if $n$ is equal to 1, $K$ is equal to the viscosity $\eta$. Based on (eq. II-23), the viscosity can be derived:

$$\eta = K' \dot{\gamma}^{(n-1)}$$  \hspace{1cm} (eq. II-24)

When the shear rate is increased to higher values, the polymer chains will become (nearly) fully disentangled and stretched out (chain alignment). At this point the polymer will again follow a Newtonian behavior, the viscosity no longer changing with increasing shear rate. This is the lowest the viscosity the polymer can have. This viscosity level is called the second Newtonian plateau.

![Figure II-4 Viscosity as function of shear rate illustrating shear-thinning and the changes in chain conformation. Taken from 14](image-url)

There are several parameters that will influence the shape of the viscosity evolution as a function of the shear rate. Firstly, higher molar mass polymers will have more entanglements, resulting in a higher resistance for moving past other chains.\textsuperscript{14–16} This in turn will lead to higher levels of the first Newtonian plateau and $\eta_0$ according to (eq. II-17). Secondly, polymers that are highly branched with branches smaller than $M_e$ will have a lower level of $\eta_0$ compared to
Introduction

their linear equivalents, this because the side chains will have lubricating effect.\textsuperscript{14} This in agreement with (eq. II-19). Branched polymers with long branches (longer than $M_e$) higher viscosities are measured, as these branches cause entanglements.\textsuperscript{5,15} A Thirdly, as the molar mass distribution becomes broader, the shear-thinning effect will be observed a lower shear rates because the lower molar mass chains will first disentangle. These effects are summarized by Figure II-5.

The viscoelastic effects are not only seen on the viscosity, but also on the modulus. This can be illustrated by a stress relaxation test. In such a test, a fixed deformation is applied, and the stress required to keep the deformation is measured as a function of time. The stress is highest at the start and will slowly relax with time. The cooperative chain movement in polymers is hindered by the entanglements and intramolecular forces, but given enough time, the polymer chains will slide past one another, thus releasing the stress built up. The time needed to relax those stresses is called the relaxation time $\tau$. The stress relaxation modulus is given by following formula:

$$G(t) = \frac{\sigma(t)}{\gamma_0}$$ \hspace{1cm} (eq. II-25)

![Figure II-5 Schematic representation the effects of the molar mass, branching and molecular weight distribution on the viscosity as function of the shear rate. Adapted from 14](image)

Where $\gamma_0$ is the applied shear deformation and $\sigma(t)$ is the measured shear stress. The relaxation time is temperature dependent, with lower temperatures corresponding with longer relaxation times. This is called the time-temperature superposition principle. With this principle the modulus can be predicted for a time scales (larger or smaller) at a certain temperature based on measurements done at another time scale and temperature. By doing so the modulus can be predicted for conditions where measuring it is unfeasible. This is done by introducing a shift
factor $a_T$. The relaxation time at a certain temperature $T$ is calculated by measuring the relaxation time, $\tau_r$, at a certain reference temperature, $T_r$, and applying a shift factor $a_T$, defined as:

$$a_T = \frac{\tau(T)}{\tau_r(T_r)} \quad (eq. \text{II-26})$$

This shift factor $a_T$ follows the WLF – law:

$$\ln(a_T) = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \quad (eq. \text{II-27})$$

By measuring the stress-relaxation behavior of a polymer over a broad range of temperatures, a so-called master curve of the relaxation times at the reference temperature can be constructed. An example of such a master curve is given in Figure II-6 for polyisobutylene.

Figure II-6 Using the time-temperature superposition principle, a stress relaxation modulus versus relaxation time master curve is constructed for polyisobutylene at 25°C, over a much larger time scale than can typically be measured. Taken from

1.2 Polymer networks

Polymer networks are different from linear and branched polymers as they are one giant molecule interconnected with itself with numerous links, the so-called crosslinks. A schematic representation of a network structure with a lot of crosslinks is given in Figure II-7. Polymer networks are also called thermosets. The mechanical behavior of these materials is different according to the relative position of the glass transition of the thermoset and the operating temperature. Thermosets having a $T_g$ below the operating temperature will behave like rubbers,
while thermosets having a $T_g$ far above room temperature will behave like a glassy material. The value of the $T_g$ of a thermoset will largely depend on the structure of the network: as the crosslink density increases, $T_g$ also increases. In the network in Figure II-7, there are also some entangled polymer chains forming a physical crosslink. These are important to describe the viscoelastic behavior of the thermoset. In addition, some network defects can be noted. A first one is a dangling chain end which can be formed due to incomplete reaction. A second network defect is a loop. In order to study the network behavior in depth, the network formation must be understood.

![Figure II-7 Schematic representation of a polymer network. Taken from²](image)

1.2.1 Network formation and gelation

Using monomers or prepolymers having an average functionality that is higher than two, networks can be formed. This reaction is often called curing when describing polymerization reactions leading to networks. The rate and the mechanism behind the formation of these networks will influence their properties, which will be discussed in section 2.4.3.

Due to the curing, monomers will combine, forming bigger molecules (Figure II-8 from (a) to (b)). As they grow, their molar mass increases and, as was described for linear molecules, the viscosity will increase. At a certain point, the by this time hyperbranched polymers will form a macromolecular network (Figure II-8 from (b) to (c)), implying that there is a transition from a soluble material into an insoluble network. This network constitutes the fraction of the monomers that forms a percolating structure, called the gel fraction. The remaining fraction of monomers, oligomers, and polymers not (yet) connected to the network is called the sol fraction. At that point, a percolating network is formed, the material will stop flowing as a liquid and will behave as a (visco-)elastic material. The transition from a liquid to solid behavior is called the gelation or the gel point. At the gelation, the molar mass distribution of the polymer becomes infinitely broad, the DPI becomes infinite, and according to (eq. II-4), $M_w$ becomes infinite.
Figure II-8 Schematic representation of a network formation for a typical step growth polymer. (a) The start with a mixture of monomer units. (b) Partially reacted forming branched and hyper branched chains. (c) The formation of continuous network or gelation, with still some soluble material. (d) A fully cured network

Figure II-9 Schematic representation of zero shear viscosity $\eta_0$, gel conversion $x_c$ and equilibrium modulus $G_e$ of a network forming polymer. Adapted from
The increase of the viscosity as function of the extent of reaction, also termed the conversion, is represented schematically in Figure II-9. As the conversion increases, the viscosity increases until gelation occurs, when it becomes infinite. The conversion corresponding with the gel point is the gel conversion. From the gel point onward the polymer will behave elastically and mechanical properties can develop. Just after the gel conversion, the network is only very slightly crosslinked and thus very soft and fragile. Measuring its mechanical properties without destroying it is not straight forward and therefore the initial evolution of the equilibrium modulus $G_e$ is represented with a dashed line. As the reaction progresses, more crosslinks within the network are formed (Figure II-8 from (c) to (d)), further increasing the mechanical properties, represented in Figure II-9 by the increase of the modulus $G_e$. How to measure and model the viscosity evolution and the development of the mechanical properties as function of the extent of reaction will be discussed in section 0.

1.2.2 Glass transition, vitrification and diffusion control

Vitrification is the transformation from a liquid or rubbery state to a glassy structure. Reacting molecules will form increasingly larger chains (higher $M_w$), which results in increasing the glass transition temperature. An empirical relation between the extent of reaction and the glass transition temperature is given by the DiBenedetto equation:

$$T_g(x) = \frac{\lambda x}{1 - (1 - \lambda)x} (T_{g1} - T_{g0}) + T_{g0} \quad (eq. \ II-28)$$

Where $T_{g0}$ and $T_{g1}$ corresponds with the glass transition temperature of the uncured polymer and the fully cured system respectively and $\lambda$ is a fitting factor. Figure II-10 shows experimental results of the $T_g$ evolution as function of the extent of reaction for an amine-cured epoxy and the best fit of (eq. II-28) to the data.

When as a result of the progressing reaction the $T_g$ is increased to the level of the curing temperature, the polymer will start to vitrifying, reducing the segmental mobility. However, for the reaction to proceed, the functional groups on the polymer chains need to diffuse towards one another. As vitrification restricts the mobility of the chain segments, the diffusion of the reactive functional groups slows down, and the reaction rate lowers. This vitrification process is not a single transition point. First the higher molar mass species will be impacted by the vitrification and at a later point the lower molar mass species, up until the reaction is completely halted due to diffusion limitations. By bringing the vitrified polymer above the full cure glass transition temperature, full cure can be obtained.
1.2.3 Phase separation

During curing, functional groups react and transform into new links. As a consequence, the chemical environment changes as the curing progresses. A monomer mixture at the start of the reaction that was homogenous might, due to the changing chemical environment, be prone to phase separation. Phase separation caused by curing is called reaction-induced phase separation (RIPS). When RIPS occurs, the different phases will likely have different concentrations of the functional group and therefore the reaction kinetics will differ between these phases. The mechanical properties of the phases are also often different, leading for example to a more ductile phase in a thermoset, which toughens it compared to the homogenous thermoset. Controlling the phase separation and sizes of the phases can be of critical importance for improving material properties.

1.2.4 Time-temperature-transformation (TTT) diagram

The different transitions in the network formation can be summarized in a single diagram called a time-temperature-transformation diagram. An illustration of such a diagram is shown in Figure II-11. This diagram is valid for isothermal conditions. The x-axis of the diagram a logarithmic time, while the y-axis is the temperature. The diagram consists of several lines, which mark the time needed at each temperature to reach a certain transformation.
A first line is the gelation line. Before the gelation line the polymer is liquid, above the line gelation has occurred and the infinite network has formed. The gelation line is typically an iso-conversion line, describing the time to reach the gel conversion as function of temperature. A second iso-conversional line is the full cure line, which runs approximately parallel to the gelation line. Between the gelation line and the full cure line the material is a not fully cured gel and thus has a sol fraction. After the full cure line, the material is fully cured, meaning that the sol fraction has been completely incorporated into the network and al dangling groups have reacted (within topological restrictions). The next important line is the vitrification line: it starts from the glass transition temperature of the uncured material $T_{g0}$, has an S-like shape, and ends at the glass transition temperature of the fully cured material $T_{g1}$. The line divides the diagram in a clear and a shaded area. In the clear area, the material is in a liquid/rubbery state, while in the shaded area, the material is in a vitrified glassy state. A final line is the char line, which marks when the degradation (or charring) of the polymer starts. As the lines mark the different transitions, in the areas in between them the polymer will be in a certain state. There are 7 states: liquid, sol-gel rubber, gel rubber, sol glass, sol-gel glass, gel glass, and char.

2 Polymerization mechanism and structure formation

Together with the functionality of the monomers, the polymerization mechanism and its kinetics has a huge influence on the build-up of the molecular architecture of polymers, as mentioned in section 1. There are two main types of polymerization mechanisms: step-growth, chain-growth. In the chain growth mechanism, there is a special case of polymerization called
living polymerizations. These types will be briefly discussed, with a focus on step-growth as this is the type of mechanism polyurethane formation is considered to follow.

2.1 Step-growth polymerization

The step-growth mechanism essentially comes down to the reaction of a $n$-mer and a $m$-mer to form a $(n+m)$-mer.

\[
\text{n-mer} + \text{m-mer} \rightarrow (n+m)\text{-mer}
\]

The overall reaction rate at any time is the sum of the rate of formations of mers of all different lengths (dimer, trimer, ...). This will lead to a complex kinetic analysis as each $(n+m)$-mer formation reaction has its own reaction rate. By assuming that each functional group has the same reactivity regardless of the length of the molecule it is attached to, the kinetic mechanism can be simplified. This approach was first proposed by Flory and seems to hold for a variety of polymer systems. Using this principle, the polymerization kinetics can be studied using small molecules, which can omit some difficulties typical for polymerizations, like diffusion-controlled reactions and reaction-induced phase separation (see section 1.2.2 and 1.2.3). When using bifunctional monomers, a linear polymer chain will form. The polymer chain grows by combining two smaller polymer or oligomer chains. Therefore the longest polymer chain will be formed when the extent of the polymerization goes towards full cure. Another consequence of this mechanism is that small differences in stoichiometry will have a large influence on the average length of the polymer chain, as will be mathematically shown in section 2.4. In polycondensation reactions, a special case of step growth polymerization, low molar mass molecules (like water) are created during the reaction, thus slightly reducing the molecular weight, while in polyaddition reactions the product is exclusively polymer.

2.2 Chain-growth polymerization

The chain-growth mechanism is mostly observed in free radical polymerization. In order to discuss the molar mass evolution, the kinetics behind the polymerization must be discussed. A free radical polymerization mechanism consists of at least three types of reaction steps: initiation, propagation and termination. In the initiation step, radicals are formed, usually by decomposition of a radical initiator:

\[I \underset{k_i}{\longrightarrow} nR^-\]  \hspace{1cm} (eq. II-29)

Where $I$ is the initiator and $R^-$ is the radical, $n$ is a stoichiometric coefficient and $k_i$ is the reaction rate constant of the initiation. In the first propagation step, the radical from the initiator will react with a monomer, forming a radical chain of one monomer unit long having a radical end group (eq. II-30). This step is also called the chain initiation step. A radical chain of any length can react with another monomer unit, extending the chain by one unit (eq. II-31) (chain propagation). Hence the name chain-growth polymerization:
Where $M$ is a monomer unit, $M_1$ is a radical chain of one monomer unit long, $M_i$ is a chain of length $i$ and $k_{pi}$ is the rate constant of the propagation reaction of a radical chain of length $i$.

In the simplest termination step, two radical chains will meet and combine to form the one polymer chain.

$$M_i + M_j \xrightarrow{k_t} P_{i+j} \quad (eq. II-32)$$

The reaction rate of the propagation and termination reaction are slow compared to the reaction rate of the propagation. As a consequence, once the radical chain is initiated, the chain will grow rapidly before being terminated. After only a small amount of conversion long polymer chains will have been formed, while at high conversion monomer is still present. This is in stark contrast with the step growth polymerization for which only at the end of the reaction the long polymer chains are formed, while at that time hardly any monomer is left.

### 2.3 Living polymerization

The polymerization mechanism behind living polymerization is similar to the chain-growth mechanism, but the kinetics are different. A first difference is that in living polymerization there is no termination step. A second difference is that the reaction rate of the propagation step is much lower compared to the chain-growth polymerization. The combination of these two factors causes all chain initiation reactions to happen at about the same time, the molar mass growing steadily, and all units growing at the same rate. The growing entities are kept ‘alive’ during the whole polymerization process, hence the name living polymerization. These living polymerizations can be achieved by stabilizing the radical or through ionic polymerizations. The molar mass evolutions of step-growth, chain-growth and living polymerizations is summarized in Figure II-12.
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Figure II-12 The molar mass as a function of the extent of reaction for linear step-growth, chain-growth and living polymerizations Taken from 2

2.4 Calculating molar mass evolution in step-growth polymerizations

During step growth polymerization, the average molar mass of the molecules will gradually increase. As there is an important link between the molar mass of a polymer and its properties, a sufficiently accurate prediction of the molar mass evolution can lead to a good prediction of the final properties of the polymer, without the need for (expensive) tests. This is why several models and approaches have been developed to predict average molar mass and molar mass distributions. First the derivation for an idealized case for linear step growth polymerizations will be discussed, followed by a discussion on other methods to describe branched and network polymerizations.

2.4.1 Carothers Theory

Flory 30 and Carothers 31 developed a mathematical derivation for estimating the average molar mass for a bimolecular polymerization. In their model an A functional group will react with a B functional group. The model is valid is using monomers of the type A-A, B-B and A-B. 4 The number-average degree of polymerization ($DP_n$) is defined as follows:

$$DP_n = \frac{N_0}{N} \quad (eq. \ II-33)$$

Where the $N_0$ is the initial number of molecules and $N$ is the number of molecules after a certain time in the reaction. The extent of reaction $x$ can be linked to the number-average degree of polymerization by noting that the extent of reaction is the ratio of the number of functional groups which have reacted to the initial functional groups present, leading to following equation:
This formula is valid for stoichiometric mixtures. The formula can be generalized for off-stoichiometric mixtures by introducing the stoichiometric imbalance factor $r$, defined by the ratio of number of $A$ functional groups ($N_A$) over the number of $B$ functional groups ($N_B$):

\[ r = \frac{N_A}{N_B} \]  

(eq. II-35)

In (eq. II-35), the $B$ functional groups are always in excess, meaning that $r$ is always between 0 and 1. The formula for the average degree of polymerization correcting for stoichiometric imbalance is then given by (eq. II-36). By multiplying the average molar mass of the monomer units ($M_0$) by the number-average degree of polymerization, the number-average molar mass can be calculated (eq. II-37).

\[ DP_n = \frac{1 + r}{1 + r - rx} \]  

(eq. II-36)

\[ M_n = M_0 DP_n \]  

(eq. II-37)

The influence of $r$ and $x$ are on the average degree of polymerization is illustrated in Table II-1. What can be observed in this table is that a small stoichiometric imbalance or incomplete reaction, will have a major influence on the degree of polymerization and thus on the properties of the polymer. To make a linear polymer of high molar mass using a step-growth mechanism, it is essential to have very pure starting bifunctional monomers and to mix them in perfect stoichiometric ratio. Obtaining molar masses of about 10-100 kg mol$^{-1}$ is possible, but more often the lengths in the order of 15-30 kg mol$^{-1}$ are achieved. These masses are much lower than the masses that can be obtained via chain-growth polymerizations, which are in the order of 50-10000 kg mol$^{-1}$.\cite{Footnote 4}

Table II-1 Degree of polymerization $DP_n$ in linear polymers by varying the extent of reaction $x$ and the stoichiometric imbalance $r$ according to (eq. II-36). One molar unit would typically have a molar mass of about 100 g.mol$^{-1}$.\cite{Footnote 4}

<table>
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<th>$r$</th>
<th>$x$</th>
<th>0.900</th>
<th>0.950</th>
<th>0.990</th>
<th>0.999</th>
<th>1.000</th>
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<td>18.7</td>
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<tr>
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<td>13.4</td>
<td>28.3</td>
<td>37.6</td>
<td>39.0</td>
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<tr>
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<td>9.6</td>
<td>18.3</td>
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<td>166.1</td>
<td>199.0</td>
<td></td>
</tr>
<tr>
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<td>666.8</td>
<td>1999.0</td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td>10.0</td>
<td>20.0</td>
<td>100.0</td>
<td>1000.0</td>
<td>$\infty$</td>
<td></td>
</tr>
</tbody>
</table>
2.4.2 Statistical theory for the formation of linear polymers

While Carothers’ theory is only applicable to derive number-average quantities, a method to calculate weight average-based quantities was developed by Flory. Assumptions that are used (often implied) for these calculations are 1) the functional groups have the same reactivity independently of the molecule they are part of. This means that the length of the molecule will not change the reactivity of the functional groups. 2) The functional groups react independently from one another. 3) Cyclization does not happen: a functional group of a molecule will not react with another functional group of the same molecule. Flory could derive the probability that a randomly chosen molecule contains exactly $m$ monomer units:

$$P(m) = (1 - x)x^{m-1} \quad (eq. \, II-38)$$

If $N$ is the total amount of molecules at a time $t$, then number of molecules with $m$ monomer units or the number of $m$-mers, $N_m$, is given by:

$$N_m = NP(m) = N(1 - x)x^{m-1} \quad (eq. \, II-39)$$

The total number of molecules $N$ can often not be measured, but by substituting (eq. II-33) and using (eq. II-34), the following formula can be obtained.

$$N_m = N_0(1 - x)^2x^{m-1} \quad (eq. \, II-40)$$

The weight fraction of $m$-mers, $w_m$, is equal to the ratio of number of $m$-mers times their weight ($mM_0$) and divided the total mass of all molecules, resulting in:

$$w_m = \frac{(mM_0)N_m}{N_0M_0} = \frac{mN_m}{N_0} \quad (eq. \, II-41)$$

Substitution of (eq. II-40) in (eq. II-41) leads to:

$$w_m = m(1 - x)^2x^{m-1} \quad (eq. \, II-42)$$

Equations (eq. II-38) and (eq. II-42) are also known as the Flory distribution, giving the mol-fraction and weight-fraction distribution, respectively. Using the definition of the number-average molar mass (eq. II-1) and substituting (eq. II-39), the molar mass at any conversion can be calculated.

$$M_n(x) = \sum_{m=1}^{\infty} mM_0N_m / N = M_0(1 - x)\sum_{m=1}^{\infty} mx^{m-1} \quad (eq. \, II-43)$$

Using a mathematical relation (eq. II-43) can be simplified to:

$$M_n(x) = M_0(1 - x)\frac{1}{(1 - x)^2} = \frac{M_0}{1 - x} \quad (eq. \, II-44)$$

In a similar way, the evolution of the mass-average molar mass can be calculated (eq. II-45) and by taking the ratio of the weight and the number-average molar mass, the polydispersity of linear step growth polymerization can be predicted (eq. II-46). In stoichiometric conditions and
at full cure, a polydispersity of 2 is obtained (eq. II-46). In well-controlled radical chain-growth and living polymerizations much narrower distribution can be obtained.

\[ M_w = M_0 \frac{1 + x}{1 - x} \quad \text{(eq. II-45)} \]

\[ PDI = \frac{M_w}{M_n} = 1 + x \quad \text{(eq. II-46)} \]

2.4.3 Branching and network forming polymers

In 1944 a formula for calculating the molar mass distribution for a mixture of monomer units of type \( A_f \) containing \( f \) \( A \)-functional groups up to a maximum of \( k \) functional groups, which homopolymerize was presented by Stockmayer:

\[
n(u_1, u_2, \ldots, u_f, \ldots, u_k) = \frac{f_{\text{tot}} \lambda_1!}{x \lambda_2!} (1 - x)^{\lambda_2} \prod_{f=1}^{k} \frac{(a_f x)^{u_f}}{u_f!} \]

\[
\lambda_1 = \left( \sum_{f=1}^{k} (f - 1) u_f \right) \quad \text{(eq. II-47)}
\]

\[
\lambda_2 = \left( 2 + \sum_{f=1}^{k} (f - 2) u_f \right)
\]

Where \( n \) is the molar number of polymeric molecules composed of \( (u_1, u_2, \ldots, u_f, \ldots, u_k) \) monomer units. A \( u_1 \) monomer unit is defined as \( A_1 \), thus having one functional group, similarly a \( u_2 \) monomer unit has 2 functional groups etc., up to a maximum of \( k \) for \( u_k \). The variable \( f_{\text{tot}} \) is the total number of functional groups in the system. Similar formulas calculating copolymerizations were developed in a later stage. In principle the molar mass distribution can be calculated as a function of the extent of reaction \( x \) and the mixture of the monomer units using (eq. II-47). When calculating larger entities and/or using an extensive number of different monomer units, the calculation become prohibitively more computationally expensive to calculate. To circumvent this problem, different approximations for calculating the molar mass distribution and molar mass averages have been developed.

Using the recursive nature of step growth polymerization, Gordon could calculate the average molar mass, gel point and sol fraction using the stochastic theory of cascade processes and probability generating functions (pgf). An expression for the distribution is not needed to calculate the statistics. The use of pgf is today still a topic of research for calculating molar mass distributions for both step-growth and chain-growth polymerizations.

In 1976, Macosko and Miller used the same stochastic cascade principle, but instead of transforming these formulas, they applied them directly using expected values and probabilities. A similar approach was used in 1979 by Durand and Bruneau leading to the same equations.
Using the recursive structure, formulas for the mass-average molar mass and higher order mass-averages could be obtained.\textsuperscript{51} The advantage of this approach is that the formulas are relatively simple. In case of network forming polymers, gelation and post-gel properties could be calculated, like the sol- and gel fraction. This gel fraction can be further divided into an elastic effective and pending fraction.\textsuperscript{51,52} In turn, these fractions can be used to calculate the crosslink density and equilibrium modulus in the rubbery state.\textsuperscript{52–56} Using this idea extensions to the original method have been made, including the relaxing of the Flory approximations.\textsuperscript{55,57–62} In Chapter VIII, this approach will be extended to consider the difficulties that can arise in polyurethane polymerizations. The disadvantage of this approach is that not the whole distribution is obtained, but by calculating the different average molar masses, the higher order moments of the distribution are calculated and an idea of the shape of the distribution can be obtained.

A totally different approach is using Monte-Carlo simulations. In this numerical method the reaction products are predicted using repeated random sampling.\textsuperscript{63} The simulation starts from a mix of monomers. A random monomer is chosen at each timestep and the probability that a monomer chosen is directly proportional to the mole fraction of the monomer in the mixture. In the next step, the likelihood that the chosen monomer will react is calculated using a Metropolis criterion.\textsuperscript{64} The site remains unreacted if the step was rejected. Otherwise the monomer is extended and the reaction mixture is updated. It is important to note that the equilibrium polymerization products are simulated for a certain extent of reaction and not the reaction kinetics.\textsuperscript{63} Calculating the high molar mass spectrum of the molar mass distribution is inaccurate due to the stochastic nature of the Monte-Carlo simulation.\textsuperscript{38,65} By using a large population of monomers, the whole molar mass distribution can be predicted with a more accurate result but this has large calculation times as a disadvantage.\textsuperscript{38} For process simulations like for example a finite elements method, the Monte-Carlo simulations are less suited.

3  Measuring and modeling polymerization kinetics

3.1  Measuring reaction kinetics in calorimetry

In calorimetric techniques the heat flow is measured as function of time and temperature as a result of an applied temperature program. As all polymerization reactions are exothermic, their reaction enthalpy can be measured. Using the total reaction heat ($\Delta H_{\text{tot}}$) and the assumption that the degree of conversion of a reactant or the extent of reaction ($\chi$) is proportional to the heat generated, following formula is obtained:

$$\chi(t) = \frac{\Delta H(t)}{\Delta H_{\text{tot}}} \quad \text{(eq. II-48)}$$

With $\Delta H(t)$ the reaction heat generated from the start to time $t$. Calorimetric techniques are among the best techniques to study polymerization reactions and their complexities, like vitrification and diffusion-controlled reactions. The more commonly used device is a
(modulated temperature) differential scanning calorimeter ((MT)DSC), while a less common one is an isothermal micro-calorimeter. In calorimetric experiments the measured heat flow \( \frac{dQ}{dt} \) can arise from different contributions:

\[
\frac{dQ}{dt} = C_\text{p} \frac{dT}{dt} + f(t, T) + \text{instr} \tag{eq. II-49}
\]

The first term of (eq. II-49) finds its origin in the heat capacity \( C_\text{p} \) of the material, which is scaled by the heating rate. The polymerization reaction is included in the second term \( f(t, T) \), but this term can also represent other contribution, like melting and crystallization. The last term is a heat flow contribution due to the instrument itself. By careful calibration and instrument design, this contribution can be minimized.

When performing calorimetric measurements, there are two major types of temperature programs: non-isothermal and isothermal experiments.

3.1.1 Non-isothermal experiments (DSC)

![Figure II-13 DSC measurements of the cure of an epoxy-amine network measured in non-isothermal conditions using different scanning rates. Taken from 66](image)

A non-isothermal DSC experiment is performed at a constant heating rate. Typically, higher scanning rates will give higher peaks, shifting towards higher temperatures, as can be seen in Figure II-13, for the cure of an epoxy resin with an amine hardener. These experiments give information about the reaction in a broad temperature range, typically reaching temperatures and conditions that cannot be employed (reliably) in isothermal conditions. In non-isothermal
measurements the start and end of the reaction can clearly be observed. By determining the area under the curve, $\Delta H_{\text{tot}}$ is obtained. This can be used to determine the progress of the extent of reaction, using (eq. II-48), and is needed for analyzing isothermal experiments, in which the $\Delta H_{\text{tot}}$ is not readily measured.

Because the reaction rate constants of all elementary reactions are changing during the experiment, except in case it has an activation energy equal to zero, it is much harder to observe kinetic effects like autocatalysis or inhibition in these measurements, and thus non-isothermal experiments should be combined with isothermal experiments for a more efficient kinetic analysis.

3.1.2 Isothermal experiments (DSC, microcalorimetry and modulated temperature DSC)

An isothermal program consists of two steps: a first is the initial scan to the required isothermal temperature, in the second the temperature is kept constant. By applying a constant temperature, the reaction rate constants remain constant throughout the progress of the reaction. This helps identifying aspects like inhibition or autocatalysis, which are not always easy to determine in non-isothermal experiments. Isothermal measurements can be done both in DSC and in microcalorimetry. The typical DSC equipment is useful for faster measurements, taking several minutes up to hours, of samples of a few milligram, while a microcalorimeter is designed to measure samples of the order of grams for hours up to weeks.

As an example, Figure II-14 shows the heat flow and heat capacity measurement of the cure of an epoxy resin with an anhydride hardener in isothermal conditions, measured using MTDSC. The heat flow, proportional to the reaction rate, initially increases and then decreases. The increase in reaction rate is due to autocatalysis, meaning that the formed products catalyze the reaction. The subsequent decrease in heat flow is due to the consumption of reactive groups. This autocatalytic aspect of the polymerization mechanism is easily observed in isothermal condition, while in non-isothermal conditions this would be hard to identify.

The signals resulting from a MTDSC experiment are the non-reversing heat flow and the reversing heat capacity. How these signals are obtained will be discussed in more detail in chapter III. When a polymer vitrifies, a drop in the reversing heat capacity is measured, as observed in Figure II-14. As mentioned in section 1.2.2, vitrification occurs if the $T_g$, which increase due to polymerization, becomes equal or higher than the cure temperature, leading to diffusion-controlled reactions and a lowering of the reaction rate. This makes MTSD highly suitable for studying the cure and vitrification of thermosetting polymers.
3.2 Reaction kinetics and modeling approaches

3.2.1 Reaction rates and reaction orders

In this section, abstract notations will be used in combination with an example of urethane formation, in order to help the reader understand how the formal equations are applied. An in-depth analysis of the kinetics of the polyurethane formation is given in section 4. The formation of a urethane group (UR) can be simply represented by the reaction of an alcohol group (OH) and an isocyanate group (NCO). As the reactivity of a primary and secondary alcohol is different, a subscript p and s will be used to distinguish them.

\[
\text{OH}_p + \text{NCO} \rightarrow k_1 \rightarrow \text{UR} \quad \text{(eq. II-50)}
\]

\[
\text{OH}_s + \text{NCO} \rightarrow k_2 \rightarrow \text{UR} \quad \text{(eq. II-51)}
\]

In general, when \(n\) species react, their reaction rate can be described by following empirical rate equation:

\[
v = k \prod_{i=1}^{n} C_i^{\alpha_i} \quad \text{(eq. II-52)}
\]

Where \(C_i\) is the concentration of species \(i\), also written as \([i]\), with a partial reaction order \(\alpha_i\). The sum of the partial reaction orders \(\alpha_{\text{tot}}\) gives the total reaction order of the reaction. The reaction rate \(v\) has units of mol.l\(^{-1}\).s\(^{-1}\) and the units of the reaction rate constant \(k\) will depend on the reaction order of the reaction: (mol/l)\(^{1-\alpha_{\text{tot}}}\).s\(^{-1}\). For the urethane formation using a primary alcohol, this would come down to (eq. II-53).
Where $\alpha$ is the partial reaction order of OH\textsubscript{p} groups and $\beta$ is the partial reaction order of NCO groups. In elementary reactions, the reaction orders of the species correspond with the stoichiometric coefficients. So, if reaction (eq. II-50) is an elementary reaction than $\alpha$ and $\beta$ would both be equal to one.

The reaction rate constant is temperature dependent and follows an Arrhenius behavior:

$$k(T) = A \exp \left( -\frac{E}{RT} \right)$$  \hspace{1cm} (eq. II-54)

Where $A$ is the pre-exponential factor and has the same units as $k$, $E$ is the activation energy given in J.mol\textsuperscript{-1} and $R$ is the universal gas constant.

Figure II-15 Graphical representation of the Arrhenius law: (left) typical Arrhenius plot showing $\ln(k)$ versus the reciprocal temperature, $T^{-1}$, (right) $k$ versus the temperature. Curves calculated for $\ln(A)=14.6$ and $E=50$ kJ.mol\textsuperscript{-1}.

The temperature dependence of the reaction rate is often given graphically in an Arrhenius plot in which the natural logarithm of the reaction rate constant is plotted versus the reciprocal temperature (Figure II-15(left)). By using this graphical representation, the Arrhenius parameters can directly by determined: the extrapolated intercept of rate constant with the y-axis will give the $\ln(A)$, while the slope is given by $-E/R$.

3.2.2 Initial reaction rates

Determining the partial reaction orders of a (polymerization) reaction is not always straightforward. The concentrations of the different species will vary as the time progresses due to the reaction and thus determining the concentrations at an intermediate time may be difficult. The concentration of all species is best known at the start of the reaction. By using reaction mixtures with a range of well-chosen initial concentrations and measuring the initial (overall) reaction rate, the partial reaction orders can be determined. This is done by linearizing (eq. II-52), taking the logarithm, leading to (eq. II-55). To indicate that the initial rate and concentrations are used, a 0 subscript is added. For the urethane example, the formula becomes (eq. II-56).
\[
\ln(v_0) = \ln(k) + \sum_{i=1}^{n} \alpha_i \ln(C_{i0})
\]
(eq. II-55)

\[
\ln(v_0) = \ln(k) + \alpha[OH]_0 + \beta[NCO]_0
\]
(eq. II-56)

If for the urethane formation, the partial orders \(\alpha\) and/or \(\beta\) are found to differ from one, then the urethane formation is more complex than just the commonly assumed reaction (eq. II-50).

3.2.3 Isoconversional methods or Model-free-kinetics (MFK)

For the analysis of the reaction kinetics over the (full) progress of the reaction, different numerical methods are used. The idea behind these methods starts from the single-step kinetic equation\(^67\):

\[
\frac{dx}{dt} = k(T)f(x)g(P) = A \exp\left(-\frac{E}{RT}\right)f(x)g(P)
\]
(eq. II-57)

Where \(x\) represents the extent of reaction or conversion, \(dx/dt\) the conversion rate, \(f(x)\) is an undetermined conversion dependent function, \(g(P)\) is a pressure dependent function and \(k(T)\) is defined as in (eq. II-54). When working in atmospheric conditions, there is no pressure change and thus \(g\) is constant and incorporated into the pre-exponential factor \(A\). If one assumes that the isoconversional principle, which states that at a constant extent of reaction the reaction rate is only a function of temperature, is valid, than (eq. II-57) can be rewritten in following form, by taking the derivative of the logarithm of the conversion rate with respect to the inverse temperature.

\[
\left[\frac{d\ln\left(\frac{dx}{dt}\right)}{d(T^{-1})}\right]_x = -\frac{E(x)}{R}
\]
(eq. II-58)

By evaluating (eq. II-58) at different extents of conversion, the activation energy can be determined at each extent of reaction without prior knowledge of the reaction model. Because of this, approaches using this are also often referred to as ‘Model-Free’ kinetic methods. This method has also been applied for the polymerization kinetics of polyurethanes\(^68\textendash}^70\) and will be discussed in Chapter IV. The assumption that the reaction rate can be split up a product of a temperature dependent rate constant and conversion dependent factor does not always hold true. An example of this, is when there are parallel processes involving the same reagents. In these cases, it may be more beneficial to do empirical modeling.

3.2.4 (Semi-) empirical kinetic modeling

Out of calorimetric measurement, it is relatively easy to obtain the conversion as well as the conversion rate as function of the time and temperature. In empirical kinetic modeling, the conversion rate is modelled by a selected function, which is dependent on time, temperature and conversion.
\[
\frac{dx}{dt} = f(t, T, x) \quad (eq. \text{II-59})
\]

Using this approach, it is often feasible to fit the reaction rate curves, without knowing the true reaction mechanism and kinetic model behind it. In isothermal conditions, there are three types of kinetic behavior: decelerating, autocatalytic and accelerating (Table II-2 and Figure II-16). The autocatalytic models have known quite some success for predicting thermoset curing, for example in epoxy-amine\[^{22,71}\], epoxy-anhydride\[^{18,23}\] and polyurethanes\[^{72}\]. The kinetic mechanism behind the epoxy-amine reaction has been studied extensively\[^{22,71}\]. By making some approximations, the rate equations derived from the reaction mechanism can be reduced to the autocatalytic formula, hence why this equation is considered to be semi-empirical. A major disadvantage of this approach is that the model and the corresponding parameter values are usually only valid for a single composition. In order to include the effect of the composition of the reaction mixture, a mechanistic kinetic model is required.

<table>
<thead>
<tr>
<th>mechanism</th>
<th>( f(t, T, x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decelerating or Catalytic ((n^\text{th}}) order reaction)</td>
<td>( k(T)(1 - x)^n )</td>
</tr>
<tr>
<td>Accelerating</td>
<td>( k(T)x^n )</td>
</tr>
<tr>
<td>Autocatalytic</td>
<td>((k_1(T) + k_2(T)x^m)(1 - x)^n)</td>
</tr>
</tbody>
</table>

Figure II-16 Different reaction profiles: (1) acceleration, (2) decelerating, and (3) autocatalytic. Taken from \[^{73}\]

3.2.5 Vitrification and diffusion-controlled cure

To incorporate the effect of vitrification on the reaction kinetics, (eq. II-59) can be adjusted by introducing a diffusion factor \( DF(x, T) \):\[^{18,23}\]
The value of the diffusion factor ranges from 1 to 0, respectively corresponding with a $T_g$ well below the cure temperature, and a $T_g$ well above the cure temperature. Its origin can be understood from the following reasoning. The characteristic effective reaction time, $t_{\text{eff}}$, of a reaction in a condensed state can be described as the time needed for the diffusion of the functional groups towards each other, $t_{\text{diff}}$, plus the time for these groups to react, $t_{\text{chem}}$:

$$t_{\text{eff}} = t_{\text{diff}} + t_{\text{chem}}$$ (eq. II-61)

Or equivalently in the form of rate constants, (eq. II-61) can be transformed into:

$$1/k_{\text{eff}} = 1/k_{\text{diff}} + 1/k_{\text{chem}}$$ (eq. II-62)

With $k_{\text{eff}}$ the effective rate constant, $k_{\text{diff}}$ the rate constant representing diffusion, and $k_{\text{chem}}$ the chemical rate constant. From (eq. II-62) and assuming $k_{\text{eff}}$ can be written as $k_{\text{chem}}$ $DF$, the following expression for $DF$ is obtained:

$$DF = \frac{k_{\text{diff}}}{k_{\text{diff}} + k_{\text{chem}}}$$ (eq. II-63)

The diffusion rate of molecules in a liquid is closely related to the viscosity of the polymer. By combining (eq. II-21) and (eq. II-22), which describe the evolution of viscosity with the temperature and $T_g$, the diffusion rate constant has been successfully modeled using (eq. II-64). In this case, the evolution of the $T_g$ was modelled using the DiBenedetto equation (eq. II-28).

$$\ln(k_{\text{diff}}) = \ln(A_{\text{diff}}) - \frac{E_{\text{diff}}}{RT} + \frac{C_1(T - T_g(x))}{C_2 + T - T_g(x)}$$ (eq. II-64)

### 3.2.6 Mechanistic modeling

A reaction mechanism is a set of $m$ elementary reactions that describe the formation and consumption of the different species involved. In chemical kinetics, the reaction mechanism results in a set of ordinary differential equations, describing the production and consumption of all species (reactants, products, catalysts and intermediates):

$$\frac{dC_i}{dt} = \sum_{j=1}^{m} v_{ij} v_j$$ (eq. II-65)

Where $v_{ij}$ is the stoichiometric coefficient of species $i$ in elementary reaction $j$, and $v_j$ is the reaction rate (eq. II-53) of elementary reaction $j$. The stoichiometric coefficient is positive if the species is formed and thus on the right-hand side of the elementary reaction step, and it is negative if the species is consumed and therefore on the left-hand side of the reaction step. Assuming that the urethane formation is given by elementary reactions (eq. II-50) and (eq. II-51), the formation rate of the all species involved is given by (eq. II-66):
Similar to (eq. II-60), the effects of diffusion control due to vitrification could be taken into account by a diffusion factor. If the reaction rate of all steps is affected in a similar way by diffusion limitations, the same diffusion factor could be used for all of them. In case for the reaction between isocyanate groups and primary or secondary alcohol groups, this is an acceptable hypothesis. If the diffusion limitations do not affect the reaction rates of the different steps in a similar way, each reaction step would need its own diffusion factor.

The formation rates of the different species can be linked to the heat flow that would result from them. In thermodynamics, the molar reaction enthalpy of a reaction is defined as (eq. II-67).

$$\Delta_r H = \sum_{i=1}^{n} v_i \Delta_f H_i$$ (eq. II-67)

Where $\Delta_r H$ is the molar enthalpy of the reaction (in J.mol$^{-1}$), $\Delta_f H_i$ is the molar enthalpy of formation of species $i$ (in J.mol$^{-1}$) and $v_i$ is the stoichiometric coefficient of species $i$ in the reaction. Using the formation rates of all species (eq. II-65), the heat flow generated by all reactions is given by the following formula, where $\frac{dH}{dt}$ is the heat flow (in W.g$^{-1}$) and $\frac{dC_i}{dt}$ is the formation rate of species $i$ (in mol.g$^{-1}$.s$^{-1}$): 

$$\frac{dH}{dt} = \sum_{i=1}^{n} v_i \Delta_f H_i \frac{dC_i}{dt}$$ (eq. II-68)

Due to the way it is set up, in mechanistic modeling the concentrations of all species are explicitly calculated. The advantage of this approach is that once a reaction mechanism and its kinetic parameters are known, the reaction progress can be predicted for different mixtures of species and for different reaction conditions (temperature profiles), without doing additional experiments. This makes this approach very useful for modelling industrial processes, where often only the initial concentration of the species and the reactor temperature are known with a good precision. Often the more difficult part of mechanistic modelling is, first, knowing whether the reaction mechanism is correct, and, second, finding the kinetic parameters with a sufficiently high accuracy.
4 Polyurethanes and their formation kinetics

4.1 Isocyanate and its reactions

4.1.1 Isocyanate

The isocyanate functional group is highly reactive and multiple reactions with this functional group are known, its high reactivity often leading to undesired side reactions. The high reactivity of isocyanate can be explained by the resonance structures of the functional group. There is still debate among researchers about the electron density distribution within the functional group (Figure II-17). What is however agreed upon is that the lowest electron density is around the carbon atom in the isocyanate group. The reactivity of the isocyanate group can be modified by binding the isocyanate group on either electron accepting or electron giving functional groups. An aromatic ring has an electron accepting effect and will increase the isocyanate reactivity. Industrially used examples of such compounds are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). On the other hand, have isocyanate groups on aliphatic units, like hexamethylene diisocyanate HDI, have a lower reactivity (Figure II-17).

Figure II-17. (top) Schematic representation of the electron density of an isocyanate group in π and p orbitals. Taken from 76. (bottom left) 4,4’ methylene diphenyl diisocyanate (MDI) (bottom middle) 2,4 toluene diisocyanate (TDI) (bottom right) hexamethylene diisocyanate (HDI)

4.1.2 Important reactions in polyurethane

In general, during the reaction of an isocyanate involves a nucleophilic reaction of an X atom on the isocyanate carbon, while a hydrogen atom is added on the nitrogen atom of the isocyanate group. Examples of active hydrogen functional groups that react with isocyanates are alcohols, amines and water, where the X atom is an oxygen or a nitrogen. The reaction with an alcohol will lead to a urethane group (Figure II-18 I), while the reaction with a primary amine will lead to a urea group (Figure II-18 VI). The reaction of primary alcohols is about three times faster than the reaction with secondary alcohols at ambient temperatures. The reaction rate of aliphatic
alcohols is three orders of magnitude higher than for aromatic alcohols. The formation of urea is about a thousand-fold faster when comparing the reaction rate of primary aliphatic amines with isocyanates to the urethane formation resulting from primary aliphatic alcohols. A water molecule will react in a similar way as a primary alcohol with an isocyanate group, forming a carbamate functional group. This functional group is unstable, however, and will fall apart in a primary amine group and carbon dioxide (Figure II-18 V). Due to the formation of (gaseous) carbon dioxide this reaction is also called the foaming reaction. In a subsequent step, the formed amine can react further to urea.

Urethane and urea functional groups also have an active hydrogen. Thus, in a second step isocyanate can react with urethane and urea functional groups, forming allophanate and biuret (Figure II-18 IV & VII).\textsuperscript{77,78} These functional groups are only formed at a reasonable rate at elevated temperatures.

Another type of reactions with isocyanate are the homo-polymerizations. The isocyanate group can homopolymerize in different ways. Two isocyanates can react together forming a uretidione (Figure II-18 III). A more stable entity is formed if three isocyanates react, forming a six-membered isocyanurate ring (Figure II-18 II). To form isocyanurate at a reasonable rate, catalyst must be added. These catalysts can be ternary amines or organic salts.\textsuperscript{79–81}

\textit{Figure II-18. Scheme on the possible reactions of isocyanate with different functional groups, with the urethane reaction highlighted.}\textsuperscript{82}
4.2 Reaction mechanism and kinetics

Although the formation of polyurethane is known for quite some time, as it was discovered in 1937,\textsuperscript{83} the kinetic mechanism behind this formation is still up for debate. When alcohols and isocyanates are mixed, in the absence or presence of catalysts, urethane groups are formed spontaneously. First the unaided urethane formation will be discussed, the pathway when introducing a catalyst is analyzed.

4.2.1 Uncatalyzed mechanisms

In a first proposed mechanism urethane is formed in a concerted reaction and is formed in one elementary reaction step (Figure II-19 (top)). In an alternative pathway, urethane is formed via an enol intermediate, followed by a 1,3-H shift resulting in a urethane (Figure II-19 (bottom)).\textsuperscript{84} Both mechanisms lead to a second order reaction kinetics following (eq. II-69), were studied by molecular modeling,\textsuperscript{85,86} and were applied successfully for different systems.\textsuperscript{78,87–93}

\[
\frac{d[UR]}{dt} = k[NCO][OH]
\]

\textit{(eq. II-69)}

**Concerted pathway**

![Concerted pathway diagram](image)

**Stepwise mechanism**

![Stepwise mechanism diagram](image)

Figure II-19. Uncatalyzed urethane formation via concerted pathway (top) and via a stepwise mechanism (bottom). Taken from\textsuperscript{84}

4.2.2 Alcohol-catalyzed and urethane-catalyzed mechanism

The second order reaction kinetics resulting from an uncatalyzed reaction was not observed by other researchers. A different mechanism was proposed, in which the OH group acts as catalyst (Figure II-20). In a first step, OH and NCO groups form an intermediate complex. In a second
step, another OH group is added on the complex, forming a different intermediate, which in a
final step leads to the formation of a urethane bond and the recovery of an OH group. The
signature of this mechanism was observed in NMR. Using the quasi steady state approximation (QSSA), the expression of the reaction rate deduced for this mechanism is given by (eq. II-70). Assuming $k_1$ is much higher than $k_2[OH]$, (eq. II-70) can be simplified to (eq. II-71). The reaction order of the urethane formation then becomes 3 with the partial reaction order for isocyanate and alcohol being 1 and 2, respectively.

**Figure II-20. Stepwise OH-catalyzed urethane formation.**

Similar to the OH-catalysis, researchers have reported that the urethane bonds formed also have a catalyzing effect on the reaction (Figure II-21). Combining the OH-catalysis and Ur-catalysis and assuming QSSA, the rate expression for the urethane formation is given by (eq. II-72). Assuming that $k_1$ and $k_3$ are much higher than $k_2[OH]$ and $k_4[OH]$, respectively, (eq. II-72) can be reduced to (eq. II-73). This third order reaction behavior was found for a para tolyl isocyanate and a polycarbonate diol.

\[
\frac{d[UR]}{dt} = \frac{k_1k_2}{k_{-1} + k_2[OH]}[NCO][OH]^2 - \frac{k_3k_4k_2}{k_{-3} + k_4[OH]}[NCO][OH][UR] + \frac{k_3k_4}{k_{-3} + k_4[OH]}[NCO][UR] \\
\frac{d[UR]}{dt} = k'[NCO][OH]^2 + k''[NCO][OH][UR]
\]

With $k' \approx \frac{k_1k_2}{k_{-1}}$ and $k'' \approx \frac{k_3k_4}{k_{-3}}$
4.2.3 Organometallic-catalyzed mechanism

Organometallic catalysts catalyze the isocyanate-hydroxyl reaction and are most effective when aliphatic isocyanates are used. The most commonly used organometallic catalysts are tin based. A catalytic cycle is proposed as mechanism for the urethane formation. This mechanism is shown for a tin alcoholate catalyst in Figure II-22. In a first step, a coordination of an isocyanate group by the alcoholate occurs, forming the N-stannylcarmamate intermediate. In a second step, in the presence of an alcohol, a urethane group is formed and the stannylalcoholate is regenerated.

4.2.4 Organic base-catalyzed mechanism

Tertiary amines are the most commonly used organic base catalysts used in urethane formation. Both the isocyanate-hydroxyl and isocyanate-water reactions are catalyzed by these catalysts. The isocyanurate reaction is catalyzed as well, albeit to a lesser extent. Parameters that
influence the effectivity of the catalyst are the basicity and steric hinderance near the amino nitrogen atom. The idea behind the catalysis is that in a first step Figure II-23 (a), the base (B) will abstract a proton from the alcohol (HX), which is followed by the nucleophilic addition of the alkoxide to the isocyanate, forming a ion. In the next step (Figure II-23 (b)), the formation of the urethane occurs by exchanging a hydrogen with HB⁺, recovering the base B.

![Figure II-23. Base catalyzed urethane formation. Taken from 96](image)

The formation step of the complex (a) will change as the reaction environment changes. Three pathways are given in Figure II-24. Pathway (I) happens in a polar environment, when the alcohol is relatively acidic. In this case, first the proton of the alcohol is abstracted, followed in the next step by the ion formation. When the alcohol has a low acidity, pathway (III) is preferred. In this pathway the alcohol will first form an ion with the isocyanate and in the next step a proton will be abstracted by the base. A reaction via pathway (II) happens if the acidity is in between the values for pathway (I) and (III). These different mechanism lead to different reaction rate equations. These mechanisms were evaluated for different alcohols, base catalysts and solvents. It was found that mechanisms II and III are susceptible to steric hinderance of the alcohol and the catalyst while this was not the case for mechanism I.  

![Figure II-24. Three pathways to form the reactive ion. Taken from 96](image)
5 Chemorheology

5.1 Measuring chemorheology

As discussed in section 1.2, curing polymers exhibit typically a change from a viscous to an energy- or entropy-elastic behavior, depending on the environmental conditions and the extent of cure. In order to cope with these behaviors, dynamic rheometry can be used. In dynamic rheometry, a sinusoidal small angle shear displacement is applied and its stress response is measured, forgoing the need for extensive deformation, which would make it impossible to study (glassy) energy-elastic materials. If the material behaves linearly, the response is also a sinusoidal. When the stress and strain are in phase with one another, meaning that the phase angle $\delta$, also called the loss angle, is zero, the material behaves as a Hookean elastic solid (Figure II-25 top). In contrast, when the stress and strain are out of phase and thus having a phase angle of 90° or $\pi/2$ rad, Newtonian liquid behavior is observed (Figure II-25 middle). When the phase angle is in between those extreme values, the materials behaves a viscoelastic material (Figure II-25 bottom).

The behavior of the oscillating stress $\sigma_{osc}$ and strain $\gamma_{osc}$ can be described mathematically using a complex notation:

$$\gamma_{osc}(t) = \gamma_0 e^{i\omega t} \quad \text{(eq. II-74)}$$
$$\sigma_{osc}(t) = \sigma_0 e^{i(\omega t + \delta)} \quad \text{(eq. II-75)}$$

Where $\gamma_0$ and $\sigma_0$ are the amplitude of the sinusoidal perturbation of the strain and stress, respectively, and $\omega$ is the angular frequency. Using (eq. II-76) the oscillating strain rate can be calculated. The formula implies that the oscillating shear rate is 90° displaced with respect to the shear strain.

$$\frac{d}{dt} \gamma_{osc}(t) = \dot{\gamma}_{osc}(t) = i\omega \gamma_0 e^{i\omega t} = i\omega \gamma_{osc}(t) \quad \text{(eq. II-76)}$$

Using Hooke’s law (eq. II-16), the modulus of an elastic material can be calculated by taking the ratio of stress over strain. For a viscoelastic material, the same principle can be used, resulting in a complex modulus $G^*$. The complex modulus is frequency dependent and the transfer function between the input and output signal:

$$G^*(\omega) = \frac{\tilde{F}[\sigma_{osc}(t)]}{\tilde{F}[\gamma_{osc}(t)]} = \frac{\int_{-\infty}^{\infty} \sigma_{osc}(t). e^{-i\omega t}. dt}{\int_{-\infty}^{\infty} \gamma_{osc}(t). e^{-i\omega t}. dt}$$
$$= \frac{\int_{-\infty}^{\infty} \sigma_0 e^{i(\omega t + \delta)}. e^{-i\omega t}. dt}{\int_{-\infty}^{\infty} \gamma_0 e^{i\omega t}. e^{-i\omega t}. dt} = \frac{\sigma_0 e^{i\delta} 2\pi \delta (\omega' - \omega)}{\gamma_0 2\pi \delta (\omega' - \omega)} \quad \text{(eq. II-77)}$$

$$= \frac{\sigma_0}{\gamma_0} (\cos \delta + i \sin \delta) = G' + G''i$$
With $\delta$ the delta function which is equal to one only if $\omega'$ is $\omega$, the frequency of the input signal. The complex modulus can be split up in a real component $G'$, called the storage modulus, and an imaginary component $G''$, called the loss modulus. The storage modulus describes the elastic behavior of the material and is in phase with the strain. The loss modulus is in phase with the strain rate and thus describes the viscous behavior. The loss angle determines to what degree a material is viscous or elastic, with an angle of 90° corresponding with fully viscous and an angle of 0° with fully elastic. In a similar way, now using the formula

$$\tau(t) = G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)$$

Figure II-25 An oscillation stress $\tau$ and the corresponding strain $\gamma$ for an elastic solid (top), a viscous fluid (middle) and a viscoelastic fluid (bottom). Adapted from \cite{14}
for Newtonian fluids (eq. II-15), a complex viscosity $\eta^*$ can be determined, by taking the ration of the oscillating stress over the oscillating strain rate:

$$\eta^* = \frac{\sigma_0}{i\omega\gamma_0} (\cos \delta + i \sin \delta) = \eta' + \eta''i$$  \hspace{1cm} (eq. II-78)

In analogously to the complex modulus, the complex viscosity can be split into its real component $\eta'$ and its imaginary component $\eta''$.

During the curing reaction of a polymer network, the monomers grow from small molecules to oligomers to finally a network. During the gradual change of the material structure and with it the relaxation modes of the material changes. The relaxation modes of the polymer correspond with the motion on different scales, with short relaxation modes being characteristic for small structures and long relaxation modes characteristic for entire molecules or large structures.\(^9\) At gel point the infinite network is formed which will correspond with the longest relaxation times. The relaxation spectrum at gelation becomes independent of the time and frequency because the relaxation of the material is coupled a range of time scales.\(^9\)–\(^10\) The gelation point is the instance at which the loss angle becomes independent of the frequency and is called the Winter-Chambon criterion.\(^10\) When measuring a curing system in a multi-frequency rheological measurement, the moment when loss angle are the same for all frequency is the moment when the gelation occurs.

5.2 Chemorheological models

Models that can incorporate the effect of the changing chemistry, resulting from the reactions, on the rheology of the material are called chemorheological models. Aspects that need to be considered are chemical on the one hand, like the cure conversion and cure kinetics, and physical on the other hand, like gelation and vitrification, and finally, there are environmental aspects, like the temperature and shear rates.

5.2.1 Simple empirical and Arrhenius models

A first, simple model empirically describing the viscosity evolution in an epoxy resin was developed by Malkin and Kulichikin.\(^10\) During the reaction the mixture remained homogenous and there was no gelation or vitrification.

$$\eta = Kt^a$$  \hspace{1cm} (eq. II-79)

Splitting the evolution up in 3 time zones marked by two characteristic times $t_c$ and $t_p$. The $K$ and $a$ are fitting parameters with $a$ changing from one zone to another: $a=a_1$ for $t < t_c$, $a=a_2$ for $t_c < t < t_p$ and $a=a_3$ for $t_p < t$. To include gelation effects in a polyurethane system, (eq. II-79) was adapted:
\[ \frac{\eta}{\eta_0} = \left[ \frac{1 + kt}{1 - \frac{t}{t_\star}} \right]^\alpha \]  
\text{(eq. II-80)}

With \( t_\star \) the gel time, \( k \) a constant and \( \eta_0 \) the initial viscosity. At the gel time, the viscosity tends to zero. A limitation of this equation is that the gel time needs to be known in advance. In (eq. II-79) and (eq. II-80) only limited information about the kinetics of the reactive system is used and applying these models in different reaction conditions (like different temperatures) is limited. Therefore, other models were developed to incorporate kinetic information. The viscosity evolution as function of the extent of reaction, including gelation, for a general thermoset was presented by Castro and Macosko \(^{103,104} \):

\[ \frac{\eta}{\eta_0} = \frac{x^\star}{(x^\star - x)^{A+Bx}} \]  
\text{(eq. II-81)}

Where \( x \) is the extent of reaction, \( x^\star \) is the gel conversion and \( A \) and \( B \) are constants. A kinetic model is needed to predict how \( x \) evolves over time at the temperature of interest. This model assumes the conversion at gelation is constant but depending on the used monomer building blocks which can have different functionalities and by using different stoichiometries the gel conversion will change. These effects cannot be accounted for in this model. This model was applied to model reactive injection molding of polyurethanes. \(^{103} \)

The chemoviscosity profiles of epoxy resins could be described using first order kinetics in both isothermal and non-isothermal conditions. \(^{105} \)

\[ \eta = \eta(T) \exp (\phi kt) \]  
\text{(eq. II-82)}

Where \( \eta(T) \) is the viscosity evolution as function of temperature, \( \phi \) is a constant and \( k \) is the reaction rate constant. Using (eq. II-82) can be used to describe the viscosity evolution at the initial stages of cure and does not include gelation effects. Another limitation of the model is that first order reaction kinetics are assumed.

To explicitly take the reaction kinetics into account, the Arrhenius equations are introduced to predict the chemorheological evolutions. Assuming the reaction kinetics follow a first order reaction, the viscosity evolution can be described by the following model: \(^{106-109} \)

\[ \ln \left( \frac{\eta(t, T)}{\eta_0} \right) = \ln(\eta_0) + \frac{E_v}{RT} + K_k \int_0^t \exp \left( \frac{-E_k}{Rf(T)} \right) dt \]  
\text{(eq. II-83)}

Where \( \eta_0 \) is the zero-shear viscosity, \( E_v \) and \( E_k \) are the viscous and kinetic activation energies respectively, \( K_k \) is a pre-exponential factor and \( f(T) \) is the temperature history of the resin. The viscosity evolution of an epoxy-resin could be described by this model. \(^{108} \)

5.2.2 Structural based models

Another way to approach the problem is by looking at the molar mass evolution and the branching theory. By linking the polymerization kinetics to the molar mass evolution and the
structure build-up, the viscosity can be predicted. Using (eq. II-19) and noting that the mass-average molar mass and the g-factor are conversion dependent, following relation can be obtained:\(^{110}\):

\[
\eta(x) \sim \left(g(x)M_w(x)\right)^\alpha
\]  
(eq. II-84)

The evolution of the average molar mass can be obtained using the recursive method of Macosko and Miller\(^ {48,49}\) (see section 2.4.3), while the g-factor is calculated using the formulas developed by Zimm\(^ {6}\) (see section 1.1.2). To describe the viscosity evolution of a reactive polyurethane, the following relation was used:\(^ {111}\)

\[
\eta(t, T, x) = A \exp\left(-\frac{E_v}{RT}\right) \left(\frac{M_w(x)}{M_{w0}}\right)^\frac{C}{RT+S}
\]  
(eq. II-85)

Where \(M_{w0}\) is the initial mass-average molar mass and \(C\) and \(S\) are constants. The investigated materials where MDI and ε-caprolactone based triol with primary alcohol groups in the presence of a tin catalyst. The viscosity was studied in isothermal and adiabatic conditions. The maximum error observed of the model compared to the experiments was 33%. Alternatively, taking into account the increasing glass transition temperature, the WLF equation (eq. II-21) and the molar mass evolution can be combined:\(^ {112-114}\)

\[
\eta(t, T, x) = A \exp\left(\frac{C_1 \left(T - T_g(x)\right)}{C_2 + T - T_g(x)}\right) \left(g(x)\frac{M_w(x)}{M_{w0}}\right)^\alpha
\]  
(eq. II-86)

Where the evolution of the glass transition temperature is described by the DiBenedetto equation (eq. II-28). This model was applied to describe the viscosity evolution for network forming epoxy – amine systems before gelation.

5.2.3 Mechanical models – calculation of the elastic contribution

There are two classical models to describe the rubber elasticity of polymer networks: the phantom network and affine deformation. The assumption in both theories is that a network is a collection of Gaussian chains, meaning that the spatial position of the chains is independent of the location of the neighboring chains.\(^ {115}\) The inputs for these models are the crosslink density \(\mu\) and the concentration of elastic effective junctions \(\nu\). These can be calculated using the recursive algorithm of Macosko and Miller.\(^ {48,49}\) The assumption made in the phantom network model is that chain ends may fluctuate unhindered about their equilibrium position.

\[
G_e = (\nu - \mu)\rho RT
\]  
(eq. II-87)

Where \(\rho\) is the density and \(R\) is the universal gas constant. This model is good for describing the mechanical properties of loosely crosslinked systems and soft rubbers. When chains end cannot fluctuate unhindered and are thus constrained by the neighboring crosslinks, the affine deformation will describe the rubber modulus:
Chapter II

\[ G_e = \nu \rho RT \]  \hspace{1cm} (eq. II-88)

This model is more suited for densely crosslinked systems and hard rubbers. The phantom network and affine deformation formula can be combined in a single formula by using a fitting parameter \( h \) and adding the effects of trapped entanglement.\(^{52,53,116,117}\)

\[ G_e = (\nu - h\mu)\rho RT + G_N^0 T_e \]  \hspace{1cm} (eq. II-89)

Where \( G_N^0 \) is the rubbery plateau modulus of a linear polymer of high molecular weight and \( T_e \) is the fraction of trapped entanglements in the network.\(^{117}\) The amount of trapped entanglements can also be estimated with the recursive algorithm.\(^{49,52}\) This model was successfully applied on reacting polydimethylsiloxane networks, applying the recursive algorithm.

6 Conclusion

Although the polyurethane reaction has been known for quite some time, the detailed kinetic mechanism behind the urethane formation is still up for debate. In order to improve processing techniques, a good knowledge of the reaction kinetics and the chemorheology of such a system is needed. However, there is a knowledge gap for linking the urethane kinetics to the rheological evolutions. The aim of this work to use a systematic approach to link the cure conditions and kinetics to the rheological behavior. The approach taken in this work was to first investigate the polyurethane reaction kinetics in depth. A reliable kinetic model is required for the subsequent steps. Using the monomer structure and the reaction conditions, the concentration profiles can be calculated. These are the inputs for a recursive algorithm to calculate the average molar mass evolutions. These in turn can be used to calculate viscosity evolutions. The approach is applied for polyurethanes, but can be used for other curing systems, following a step-growth mechanism, such as amine-cured epoxy resins and Diels-Alder self-healing networks.
7 References

Chapter II


60. Miller, D. R. & Macosko, C. W. Substitution Effects in Property Relations for Stepwise...


CHAPTER III
MATERIALS, TECHNIQUES, AND SOFTWARE

1 Materials

In this work the reaction kinetics of the urethane formation between an aromatic isocyanate and aliphatic alcohol will be studied due to their industrial relevance.

1.1 Isocyanates

The isocyanate selected for the investigation is a bifunctional isocyanate called methylene diphenyl diisocyanate (MDI). In 2014 MDI based polyurethanes were responsible for almost 55% of annual polyurethane demand. Two isomers of MDI, MDI24 and MDI44, are commercially available (Table III-1). In industrial applications, usually MDI44 is used, while MDI24 is produced as a side product in the synthesis of MDI44. MDI44 has a melting temperature of 38 °C and thus is solid at room temperature. Additionally, solid MDI44 and MDI24 are both reactive around room temperature, forming dimers. This dimerization reaction rate is slower in the liquid phase. To prevent dimer formation in MDI, the material in the solid phase is stored in a freezer at -20 °C, or alternatively the MDI is stored in an oven at 50 °C in the liquid phase. To facilitate the preparation of reactive mixtures at room temperature using liquid MDI, a (near-) eutectic mixture of MDI24 and MDI44 is used (see Figure III-1), with a mixing ratio of 37 w% MDI24 and 63 w% MDI44. This mixture of MDI24 and MDI44 will be used throughout this work, and will be abbreviated as MDI. If another composition is used, this will be specifically mentioned.

Health and Safety: MDI is a suspected carcinogenic material when inhaled. All manipulations with MDI should be done in a well-ventilated fume hood.

Table III-1 Isocyanates

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name / Formula</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI44</td>
<td>4,4’-methylene diphenyl diisocyanate</td>
<td>Supplied by Huntsman in mixing ratio of 37% MDI24 and 63% MDI44</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="MDI44 structure" /></td>
<td>Long term storage: -20°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Storage before use: 50°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molar weight: 250.25 g.mol⁻¹</td>
</tr>
<tr>
<td>MDI24</td>
<td>2,4’-methylene diphenyl diisocyanate</td>
<td><img src="image" alt="MDI24 structure" /></td>
</tr>
</tbody>
</table>

53
1.2 Alcohols and polyols

A list of aliphatic mono alcohols and poly alcohols (or polyols) selected for the investigation of the reaction kinetics is given Table III-2. All these reagents are liquid and non-reactive at room temperature. They were selected based on their length, functional groups, miscibility and processability when mixed with MDI.

As the polyurethane reaction is moisture sensitive and the polyols hygroscopic, all polyols were dried before use. This was done by adding dried molecular sieves (about 10w%) to the polyols and waiting for at least 24 hours before using the polyols with the molecular sieves filtered off. The molecular sieves were dried in an oven at 200 °C for at least 3 hours, after which they were cooled down to a temperature of about 80 °C. Additionally, PPG-425 and PPG-1000 were first put in a vacuum oven at 80 °C overnight before the molecular sieves were added. This was not done for the other polyols as they are too volatile to be dried under vacuum.
### Table III-2 Polyols and monofunctional alcohols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name / Formula</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexanol</td>
<td>Hexan-1-ol</td>
<td>Aldrich; $M_w = 102.16 \text{ g.mol}^{-1}$ purity=99%</td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>Cyclohexanol</td>
<td>Aldrich; $M_w = 100.16 \text{ g.mol}^{-1}$ purity=99%</td>
</tr>
<tr>
<td>DEGME</td>
<td>Di(ethylene glycol) methyl ether</td>
<td>Aldrich; $M_w = 120.15 \text{ g.mol}^{-1}$ purity=99%</td>
</tr>
<tr>
<td>DPG</td>
<td>Dipropylene glycol</td>
<td>Huntsman; $M_w =134.17 \text{ g.mol}^{-1}$ Purity=99% Mixture of isomers</td>
</tr>
<tr>
<td>DPGDME</td>
<td>Di(propylene glycol) dimethyl ether</td>
<td>Aldrich; $M_w =162.23 \text{ g.mol}^{-1}$ Purity=99% Mixture of isomers</td>
</tr>
<tr>
<td>PPG-425</td>
<td>Polypropylene glycol</td>
<td>Aldrich; $M_w(PPG-425) = 422 \text{ g.mol}^{-1}$ $M_w(PPG-1000) \sim 1000 \text{ g.mol}^{-1}$ $M_w(PPG-4000) \sim 4000 \text{ g.mol}^{-1}$</td>
</tr>
<tr>
<td>PPG-1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPG-4000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 1.3 Ternary amine catalysts

The effect of added ternary amine catalyst on the urethane reaction kinetics is studied in Chapter VII. The catalyst used, DABCO or 1,4-diazabicyclo[2.2.2]octane (Table III-3), is a solid material and is introduced in the reactive mixture by first dissolving it in a polyol. To study the effect of the catalyst on the reaction kinetics, while still being able to handle it at room temperature, only a low amount of catalyst can be added, around $2.24 \mu\text{mol.kg}^{-1}$. This corresponds to 0.04 w% of DABCO dissolved in PPG-425 when a stoichiometric mixture of PPG-425 and MDI is prepared. To accurately dissolve this amount of catalyst in PPG-425, an initial solution of 2 w% of DABCO in PPG-425 is made. To do this first a small amount of the solid DABCO is put in a glass vial. Next, the correct amount of PPG-425 is added to the vial in order to have a 2 w% solution. Because the catalyst does not dissolve easily into the polyol, the
mixture is put in an oven at about 50 °C for about one hour. After this period, the DABCO crystals are visibly dissolved. Before continuing, the mixture is mixed using a mechanical mixer at about 2000 rpm for at least two minutes. In the subsequent dilution step, a small amount of the 2 w% mixture is put in a glass vial. Next, the amount of pure PPG-425 needed to obtain 0.04 w% mixture is added. Finally, the glass vial is closed with a septum to prevent moisture from contaminating the mixture. Catalytic mixtures with 0.01 w%, 0.02 w% and 0.08 w% of catalyst were made starting from the same 2 w% mixture using the same approach.

**Table III-3 Catalyst**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name / Formula</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>DABCO</td>
<td>1,4-diazabicyclo[2.2.2]octane</td>
<td>Huntsman; $M_w = 112.17 \text{ g.mol}^{-1}$</td>
</tr>
</tbody>
</table>

### 1.4 Preparation of reactive mixtures

The polyurethane formation is quite fast at room temperature, even without catalyst. It is thus important for studies of the urethane formation and its kinetics, that the time to make a reactive mixture is kept as short as possible and no time is wasted setting up the measuring devices.

Typically, a reactive mixture of about 1 - 2 g was prepared. To start a bottle of MDI is taken out of the oven and left to cool to room temperature. A 4 ml glass vial is used as sample container and is tarred on a balance. MDI is the more viscous reagent of the two and thus harder to dose in an accurate way and therefore will be dosed first. Cooled down MDI is put in the vial using a plastic pipette. Based on the actual amount of MDI, the amount of polyol or polyol catalyst mixture to be inserted is calculated. Using a 2 ml syringe with needle, an as close as possible mass is injected into the glass vial. Both the masses of the MDI and the added polyol are noted down. The reactive mixture is mixed vigorously (around 2000 rpm) for 30 seconds with a mechanical mixer that is setup next to the balance. Right before the mixing is initiated, a timer is started. In that way, the time the mixture spent at ambient temperature can be accounted for in the evaluation.
2 Techniques

2.1 Differential scanning calorimetry (DSC)

2.1.1 Principle

In DSC the heat flow is measured as a function of time and temperature. This can be expressed mathematically in the following equation:

\[ \dot{Q} = \frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T) + instr(T) \quad (eq. III-1) \]

With \( \dot{Q} \) representing the heat flow rate or heat flow in W.g\(^{-1}\) (throughout this work the convention of plotting the DSC curves with exothermal down will be maintained); \( C_p \) is the heat capacity of the sample in J.g\(^{-1}\).K\(^{-1}\), which is multiplied by the heating rate \( dT/dt \) in K.s\(^{-1}\) or K.min\(^{-1}\); \( f(t, T) \) is the heat flow resulting from thermal transformations (phase changes, reactions, ...), which in this thesis will mainly consist out of the exothermic urethane formation; and \( instr(T) \) is an instrument baseline contribution that is assumed to be only temperature dependent.

The DSC cell has a symmetric design between the sample and reference. Via thermocouples the temperature difference between sample and reference sensor can be measured, which can be translated into the heat flow to or from the sample via a calibration.

2.1.2 Instrument and calibration

The DSC used is a TA Instruments Discovery DSC. This instrument is a heat flux DSC, meaning that the difference in temperature between the sample and the reference sensor is measured in a common thermal environment, the DSC cell, which is purged by nitrogen (50 mL.min\(^{-1}\)). The crucibles used are regular and perforated 40 µl aluminum Tzero hermetic pans supplied by TA Instruments (Figure III-4).

The DSC was calibrated using the Tzero\(^{TM}\) approach, a trademark of TA instruments (T4p). In the design of the Tzero\(^{TM}\) DSC, an extra so-called \( T_0 \) thermocouple is placed in between the sample and the reference sensor (Figure III-2 left). Using this additional thermocouple, effects of asymmetry between sample and reference side, as well as the effect of the contact are measured and corrected for, reducing the instruments contribution in (eq. III-1). The Tzero\(^{TM}\) approach can be schematically represented by an equivalent electrical model of the DSC (Figure III-2 right). The model consists of out thermal resistances for the heat flow to the sample \( R_s \) and reference \( R_r \) sensor, and the heat capacity of the sample \( C_s \) and reference \( C_r \) sensor (note that this includes the DSC crucibles and the sample, when relevant). The equivalent electrical model translates into following equation for deriving the heat flow to the sample:

\[
\frac{dQ}{dt} = -\frac{\Delta T}{R_r} + \Delta T_0 \left( \frac{1}{R_s} - \frac{1}{R_r} \right) + \left( C_r - C_s \right) \frac{dT_s}{dt} - C_r \frac{d\Delta T}{dt} \quad (eq. III-2)
\]
With $T_s$, $T_r$ and $T_0$ the temperature measured at the sample sensor, the reference sensor and the $T_0$ thermocouple in between them, $\Delta T$ the difference between $T_s$ and $T_r$, and $\Delta T_0$ the temperature difference between $T_0$ and $T_s$. In a conventional heat flux DSC (without $T_0$ thermocouple), only the first term in (eq. III-2) is used, representing the so-called T1 measurement. In the second and third term, the imbalances between the thermal resistances and heat capacities of the sample and the reference sensors are incorporated. In the fourth term, the difference in heating rate between the sample and reference is accounted for. Because (eq. III-2) consists of four terms, the name T4 was chosen. The model can be extended by incorporating the asymmetry caused by the sample and reference crucibles in an equivalent way, by including the thermal resistance for heat flow to the crucibles and the heat capacity of the crucibles. A calibration including this pan correction is called a T4P calibration. The thermal resistances and heat capacities are measured by first performing a temperature scan of an empty DSC cell, followed by a similar temperature scan with a sapphire disk put on the sample and reference sensors each. In case of the Discovery DSC, the temperature range is from -90°C to 400°C, the heating rate is 20 K.min$^{-1}$, and the sapphire disks have a mass of about 110 mg. The (T4P) heat flow signal of the DSC was calibrated by measuring a sample of about 2 mg indium at scanning rate of 10 K.min$^{-1}$. The temperature was calibrated using a 4-point calibration by determining the extrapolated onset of the melting peaks of adamantane, gallium, indium and lead.

Figure III-2 (left) Schematic of TA instrument Discovery DSC Cell with $T_0$ capabilities (taken from 3), (right) electrical equivalent model of a DSC using the Tzero$^{TM}$ principle (taken from 4)

2.1.3 Modulated temperature differential scanning calorimetry (MTDSC)

In modulated temperature DSC, a periodic modulation is superimposed upon a linear heating or cooling rate (the underlying rate), with devices of TA Instruments, the company that invented modulated DSC$^{TM}$, using a sinusoidal modulation (Figure III-3). The advantage of using MTDSC is that overlapping thermal transitions can be separated in certain cases. A major example is the glass transition, which can coincide with number of other processes, like irreversible reactions or enthalpy recovery processes. Additionally, an increased sensitivity for heat capacity changes is observed in MTDSC, due to a decrease of the noise level resulting
from the Fourier deconvolution that is used to obtain the amplitude and phase angle of the first harmonic of the periodic signals. In MTDSC, the total heat flow ($\dot{Q}_T$), which is calculated by averaging the value of the modulated heat flow over more than one period, is split up in a reversing ($\dot{Q}_R$) and a non-reversing heat flow ($\dot{Q}_{NR}$). The reversing heat flow is obtained as follows: first, the reversing heat capacity is calculated by taking the ratio of the amplitude of the modulated heat flow ($A_{HF}$) over the amplitude of modulated heating rate ($A_{HR}$):

$$C_{p,rev} = \frac{A_{HF}}{A_{HR}} = \frac{A_{HF}}{A_T\omega} \quad \text{(eq. III-3)}$$

The amplitudes $A_{HF}$ and $A_{HR}$ are the amplitudes of the first harmonic, obtained by Fourier transformation. Then, the reversing heat flow is calculated by multiplying the reversing heat capacity with the underlying heating rate ($dT_{und}/dT$), with $T_{und}$ the linear temperature program:

$$\dot{Q}_R = C_{p,rev} \frac{dT_{und}}{dt} \quad \text{(eq. III-4)}$$

By subtracting the reversing heat flow from the total heat flow, the non-reversing heat flow is calculated:

$$\dot{Q}_{NR} = \dot{Q}_T - \dot{Q}_R \quad \text{(eq. III-5)}$$

MTDSC is exceptionally useful when studying the reaction kinetics of vitrifying thermosets. In this PhD, the monomers and reaction conditions were chosen in a way so vitrification would not take place during curing reactions, as this complicates the kinetic study.

Figure III-3 Implementation of a modulated temperature profile superimposed upon a linear heating for a heat-only program.
Chapter III

2.1.4 Performing a urethane reaction experiment in (MT)DSC

Before starting to make the reactive mixture, some preparations should be made. First, the empty sample crucible (pan and lid) is weighed. When performing an experiment with a perforated crucible, a needle is used to make two holes into the hermetic lid of the crucible. In the next step, the pan is put in the holder of the DSC pan press, to be ready to close it. A glass Pasteur pipet that will be used to insert the sample is placed in close proximity.

Next, the DSC instrument is setup. In case of an isothermal measurement below 100 °C, the standby temperature of the cell is set to be the isothermal temperature. In case of a non-isothermal measurement, the isothermal temperature is set to the start temperature of the measurement. Knowing the mass of the sample pan, an appropriate reference pan is selected (preferably having a weight similar to the one of the sample pan) and is loaded on the reference sensor of the DSC cell.

Now everything is ready to make the reactive mixture, following the mixing procedure described above (section 1.4). A sample of 5 to 20 mg is inserted into the crucible using the glass Pasteur pipet. Then the crucible is closed using the Tzero sample encapsulation press, setup for hermetic Tzero DSC pans. The sample is taken to the DSC, the DSC cell is opened, and the sample is manually placed onto the sample sensor. Next, the DSC cell is closed, the measurement is started, and the timer is stopped. Using this procedure, the time between mixing and starting the measurement, is consistently below 3 minutes, after some practice.

After the measurement, the total mass of the sample crucible is weighed and, knowing the mass of pan and lid, the sample mass can be deduced. The sample mass is saved in the experimental data file and the normalized heat flows are calculated.

*Figure III-4 A perforated Tzero hermetic DSC crucible (left); TAMIII 4 ml glass ampoule (right)*
2.2 Microcalorimetry or TAM

2.2.1 Design and principle

The microcalorimeter used in this work is the TAM-III microcalorimeter of Thermometric (later commercialized by TA Instruments) with 12 microcalorimetry channels (called minicalorimeters) of which 9 use 4 ml crimp seal disposable glass ampoules and 3 use 4 ml heat-sealable disposable ampoules. These calorimeters are placed in thermostatic oil bath with an accuracy of < 1 µK (Figure III-5). The measuring principle of a microcalorimeter and a DSC is the same as they are both calorimeters, in which the difference in heat flow from a sample and from a reference ampoule is measured by measuring temperature differences (Figure III-6). The differentiated temperature is amplified about 100 times, after which it is filtered to reduce the noise generated by the amplifier. The analogous signal is then converted to a digital signal using a 24-bit A/D converter. This results in a dynamic range of the calorimetric signal between -20 and 20 mV with a resolution of 7 nW. The calibration for the conversion from the A/D converter signal towards a measured heat flow is done for each minicalorimeter (each channel) during the manufacturing of the minicalorimeters. This manufacturer calibration cannot be changed, but a relative deviation on this calibration factor, called the gain factor can be measured and adjusted in the TAM. For performing these gain calibrations, internal electrical heaters are positioned close to the sample and reference ampoules. An amount of heat generated by sending a controlled current through the heaters mimics the heat generated in the calorimeter. How the calibration is performed is discussed in sections 2.2.2 and 2.2.3.

An important difference between DSC and TAM is the sample size. A typical sample size for DSC ranges from 1 mg up to 25 mg, while in the TAM samples of 0.1 g up to 4 g are used (Figure III-4). A second difference is the temperature stability and heat flow detection limit: for the Discovery DSC, this limit is <10 mW, while the limit in the TAM-III is <100 µW. The combination of sample masses that are a 100 times larger with the 100 times lower heat flow detection limit makes the microcalorimeter 10000 times more sensitive in specific heat flow, which makes it an excellent device to measure small heat flow over long time periods, ranging from hours to weeks or longer. The major disadvantage of the TAM is that, to accurately measure the heat flow, it requires at least one hour of stabilization after sample insertion.
Gain calibration

Before starting the calibration, one needs to make sure that the calorimeters are empty and that the heat flow signals are all stable. To perform a gain calibration, first a 10-minute baseline is recorded for all minicalorimeters. Next, using the internal heaters of the minicalorimeters, a heat flow of selected magnitude is generated for one hour, after which the heaters are switched off again. The calorimeter is now returning to the steady baseline and a period of one hour is waited to make sure is does. Next, a final baseline of 5 minutes is recorded. The TAM software, based on this measurement, calculates the gain factor (by integrating the heat flow pulse) and an offset value (using the baseline levels). After calibration, if there is no thermal activity in the minicalorimeter, the measured heat flow should be zero. The offset value describes how the steady state signal deviates from the instrument zero level. This type of heat flow calibration was generally used in this work.
Figure III-6 Design of single minicalorimeters (left) and the cell of a minicalorimeter (right). The calibration heaters are positioned between the heat flow detectors and the sample and reference ampoules. Taken from 7

2.2.3 Dynamic calibration

The heat flow generated by a sample in a minicalorimeter is measured by the heat flow detectors, but due to the heat exchange coefficient and the heat capacity of the sample, its ampoule, and the instrument addenda, the heat flow measured by the heat flow detector will be different from the rate of heat production of the sample. This is insignificant for processes in which the heat flow changes slowly, however, for rapid processes, the measured heat flow should be corrected (desmeared) using the time constants of the minicalorimeter. This correction can be made by the so-called Tian correction:6

\[
P_C = P_R + (\tau_1 + \tau_2) \frac{dP_R}{dt} + \tau_1 \tau_2 \frac{d^2P_R}{dt^2}
\]  

(eq. III-6)

Where \( P_C \) is the corrected heat flow data, \( P_R \) is the raw measured heat flow at the detector, and \( \tau_1 \) and \( \tau_2 \) are time constants of the calorimeter. The magnitude of \( \tau_1 \) and \( \tau_2 \) are in the order of
0.5 hours and 100 hours respectively. These time constants can be measured by performing a so-called dynamic calibration. In this calibration measurement, the calibration heater will turn on in two consecutive steps (Figure III-7). The measured heat flow response will exhibit an multi-exponential decay. Knowing the heat flow input \( (P_C) \) and the measured response \( (P_R) \), the time constants \( \tau_1 \) and \( \tau_2 \) are optimized using a least square minimization algorithm, so that the difference between the input and the corrected (desmeared) response are minimized. The time constants have no direct physical interpretation as they are the result of a Taylor series expansion to better fit the data.

2.2.4 Performing a polyurethane experiment in the TAM

To setup a TAM measurement, first the temperature of the TAM is set to the desired isothermal temperature. Once the temperature in the TAM is stable, which may take up to 12 hours depending on the temperature change, an initial baseline measurement is started. The instrument will first check whether the heat flow of the empty calorimeters is stable enough to measure the baseline. In this check the measured heat flow of the last 30 min is evaluated. A first parameter that is checked, is whether the slope of this heat flow is lower than a given threshold, \(< 250 \text{ nW.h}^{-1}\) for these measurements (for the moderate signal stability setting). The second parameter that is checked is whether the variation of the heat flow around the running average is below a threshold of 200 nW (for the moderate signal stability setting). Once both conditions are met, the minicalorimeter is considered stable. Now an initial baseline measurement can be started by recording the heat flow for 30 min (this should be increased if heat flows of less than 100 µW need to be measured). The average heat flow over this period is

![Figure III-7 Dynamic calibration: the power delivered by the calibration heater (red), measured heat flow (blue) (Taken from 6)](image-url)
considered the zero-heat flow level of the empty minicalorimeter. Once the initial baseline has been measured, the calorimeter is ready to start an experiment. The initial baseline procedure must be performed for each individual minicalorimeter.

Next, a reactive sample is prepared following the procedure described in section 1.4. Between 0.2 g and 1 g of reactive sample is put into a tarred disposable ampoule. Then the ampoule is sealed with a crimp seal and a dedicated eyelet is screwed into the metal cover of the crimp seal. The sample ampoule is now ready for the TAM. The measuring procedure used is based on the TAM-III user manual. The ampoule is attached to the hook of the ampoule lifting tool and lowered into the selected minicalorimeter, into the equilibration position (inside the thermostat). The sample remains in this position for 15 minutes to ensure that the sample has the same temperature as the calorimeter, after which it is lowered into the measuring position. If the sample would immediately be lowered into the measuring position, the temperature inside calorimeter would be excessively disturbed, lead to a strongly disturbed heat flow signal, and take longer to stabilize to the true reaction heat flow. From the moment the sample is lowered into the measuring position, the heat flow is recorded. Due to thermal lag between the sample and the cell, the heat flow signal will be still distorted. After 45 minutes this effect has dampened down and from this time onwards the heat flow is accurately recorded.

During a chosen time interval, the reaction exotherm is measured. After this period, the sample is removed and a final baseline needs to be recorded. Because the sample is removed, the heat flow signal of the calorimeter will be distorted once more. It will take some time, usually about 3 to 5 hours, for the heat flow signal to be stable again on the level of the noise (< 1 µW). The instrument will check when it is ready to measure the baseline, using the same parameters as for the initial baseline measurement. The final baseline level is measured by taking the average heat flow of the calorimeter over a 30 min time period. Using both the initial and final baseline levels measures, a linear baseline can be calculated using the initial and finale time and the initial and final baseline level. Through this approach, baseline drift, which might be important for longer experiments (in the order of weeks), can be compensated for. Usually this drift is negligible at the scale of the reaction heat flows measured in this work. This baseline is subtracted from the raw measured heat flow. In a final step, this heat flow is divided by the sample mass to normalize it.

2.3 Dynamic rheometry

The rheometer used is a Discovery HR-2 with an Environmental Test Chamber (a purged electrical oven) from TA Instruments. Two types of geometry setups are available for the rheometer, a cone and plate and a parallel plate system (Figure III-8). The cone and plate setup is designed in such a way that throughout the sample the same stress and strain is applied, except at the truncated cone tip. For this setup, the following relations link the stress and strain to the measured torque and displacement:
Where \( M \) is the torque, \( R \) is the radius of geometry, \( \phi \) shear angle (the displacement) and \( \beta \) is the cone angle. The cone and plate configuration is designed for a specific gap, which must be respected in order to get correct measurements. In the parallel plate setup, two circular plates are mounted on the instrument. In this setup, the stress and strain vary across the radius of the plate, due to the changing shear rate, which the zero in the center of the plate and linearly increases with the radius towards the edge. Meaning the material at the outer rim of the parallel plate setup contributes most to the total signal. This must be considered when performing an experiment, making sure that the outer layer is correctly trimmed. The stress and strain for the parallel plate setup is calculated using the following formulas:

\[
\sigma = \frac{3M}{2\pi R^3} \tag{eq. III-7}
\]

\[
\gamma = \frac{\phi}{\beta} \tag{eq. III-8}
\]

\[
\sigma = \frac{3M}{2\pi R^3} \left[ 3 + \frac{\ln M}{\ln \dot{\gamma}_R} \right] \tag{eq. III-9}
\]

\[
\gamma = \frac{\phi}{h} r \tag{eq. III-10}
\]

With \( \dot{\gamma}_R = R \omega / h \)

Where \( h \) is the gap between the two parallel plates. The parallel plate setup has disposable aluminum plates, which is not the case for the cone and plate (stainless steel). Working with polyurethanes, which can be seen as two component glues, this is an advantage and the reason why only parallel plates with diameter of the 25 mm were used in this PhD.

Figure III-8 Rheometer geometries adapted from\(^8\): cone and plate (left) and parallel plate (right)
Prior to the start of a measurement perform an experiment, two calibrations are performed. First the *inertia calibration*, which compensates for the inertia of the rotor to the torque measured and takes about two minutes. Next comes a *rotational mapping*, in which the resistance from the bearing is measured, taking about 15 minutes. In the following step, the temperature of the oven of the rheometer is set to the initial temperature of the measurement. After thermal equilibrium is reached, the zero-gap calibration is done. The top plate is moved to about 2 cm above the bottom plate and the oven is closed. After programming the measurement, the rheometer is ready to begin a reactive polyurethane measurement.

A reactive mixture is prepared by following the procedure described in section 1.4. The oven is opened and with a Pasteur pipet about 1 ml of reactive material is put in the center of the bottom plate. The top plate is lowered gradually till the top plate touches the liquid. Subsequently the top plate is lowered in small steps, while slowly spinning the rotor. This is done to fill the gap evenly. Once the liquid fills the uniformly gap, the lowering is stopped. Potential spilling of the polyurethane is cleaned before closing the oven. The measurement is started and the timer, which was started during the mixing procedure is stopped.
3 Software for kinetic and structural evolution

During this PhD, software was developed for building, solving and optimizing kinetic mechanisms, and for calculating structure evolutions of polymers that follow a step-growth polymerization mechanism (Figure III-9). The software was written in Matlab® version 2016a. A graphical user interface was constructed around the code, making it accessible for a broader audience. In this section the algorithms and options of the software will be briefly discussed.

![Flowchart giving the general structure of the software with the green arrows given the iterative optimization loop](image)

3.1 Reaction mechanism

A reaction mechanism, consisting of a set of elementary reactions, can be translated in a set of ordinary differential equations (ODEs) (Chapter II section 3.2.6). Most of these ODEs do not have an analytical solution and must be solved numerically. An appropriate solving algorithm needs to be used to integrate the ODEs in an efficient way for given initial conditions (initial concentrations) and accompanying conditions (temperature programmes). A general expression for a set of ODE representing a kinetic mechanism is given by (eq. III-11). The vectorial variables and parameters are represented in bold.
\[
\frac{dC}{dt} = f(t, T, C, p) \quad (eq. \text{III-11})
\]
\[
C(t = 0) = C_0 \quad (eq. \text{III-12})
\]

In these equations, \(C\) is the (time-dependent) n-dimensional vector of the concentrations of the species, \(C_0\) is a vector holding the initial concentrations of the species, \(f\) is a function describing the reaction mechanism (eq. II-64) and \(p\) is a vector containing the parameters of the mechanism. These parameters are, for example, the Arrhenius parameters, but they can also include the initial conditions.

\[
J = \frac{\partial f(t, T, C, p)}{\partial C} \quad (eq. \text{III-13})
\]

Sets of ODEs based on reaction mechanisms are often ‘stiff’. Matlab has many stiff ODE solvers (ode15s, ode23s, ode23t, ode23tb and ode15i). Ode15s was chosen as solver as it was found to be both fast and stable. Like many stiff ode solvers, ode15s requires a Jacobian matrix (eq. III-13). If no Jacobian matrix is supplied to the solver, a numerical approximation is calculated. In the software, the analytical solution of the Jacobian matrix of the reaction mechanism function was derived and supplied to the solver, improving the stability and the speed of the integration. The analytical solution is given by (eq. III-14) and is derived by applying (eq. III-13) on (eq. II-64).

\[
\frac{\partial f_i(t, T, C, p)}{\partial C_\lambda} = \frac{\partial}{\partial C_\lambda} \sum_{j=1}^{m} v_{ij} v_j(t, T, C, p) = \sum_{j=1}^{m} v_{ij} \frac{\partial}{\partial C_\lambda} v_j(t, T, C, p) \quad (eq. \text{III-14})
\]

Where \(f_i\) is the function giving the reaction rate change for a species \(i\), \(v_j\) is the reaction rate corresponding with the \(j^{th}\) reaction in the reaction mechanism, \(v_{ij}\) is the stoichiometric coefficient corresponding with the \(j^{th}\) species in the \(j^{th}\) reaction, and \(m\) is the number of reactions in the reaction mechanism. Using (eq. II-51), the last term in (eq. III-14) can be further expanded to (eq. III-15):

\[
\frac{\partial}{\partial C_\lambda} v_j(t, T, C, p) = k_j v_{\lambda j} C_\lambda^{v_{\lambda j}-1} \prod_{i=1}^{n} C_i^{v_{ij}} \quad (eq. \text{III-15})
\]

Where \(k_j\) is the reaction rate constant of the \(j^{th}\) reaction. This assumes the rate constants are independent of the concentrations, which is not necessarily the case, as the rate constants may depend on the viscosity (diffusion-controlled reactions) or on the dielectric constant of the medium, both of which may be composition dependent.
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3.2  Kinetic parameters

3.2.1  Arrhenius parameters

Next to the initial concentrations, the kinetic parameters must be supplied to the ODE solver. There are several ways to define and parameterize the rate constants, each having advantages and disadvantages. The default representation of the Arrhenius law in the software is given by (eq. III-16).

\[ k = 10^{(\log k_{T_r})} \exp \left( -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right) \]  

(eq. III-16)

Where the parameters are a reference temperature \( T_r \) and the 10-based logarithm of the rate constant at the reference temperature, \( \log k_{T_r} \). The pre-exponential factor \( A \) of the Arrhenius law (eq. II-53) can be calculated based on these parameters using (eq. III-17).

\[ A = 10^{(\log k_{T_r})} \exp \left( \frac{E}{RT_r} \right) \]  

(eq. III-17)

![Figure III-10 The evolution of 3 rate constant as function of temperature as defined by (eq. III-16) with a constant \( \log k_{T_r} = -2 \) at a \( T_r = 40 \) °C and changing the \( E \) to 40, 50, and 60 kJ.mol\(^{-1}\).](image)

The reason for selecting (eq. III-16) rather than the Arrhenius equation is that it improves the decoupling of the effects of changes to these parameters. Often the rate constant of a reaction is best known within a certain temperature range. As an example, three rate constants are defined with the rate constant of \( 10^{-2} \) at a \( T_r = 40 \) °C and with activation energies of 40, 50, and 60 kJ.mol\(^{-1}\) (Figure III-10). The pre-exponential factors corresponding with these parameters are given in Table III-4. Within a useful temperature range of 0 °C to 200 °C, the different reaction rate constant curves are quite close together, while the pre-
exponential factors $A$ changes more than three orders of magnitude. Defining the rate constant using (eq. III-16), the influence of the temperature on the rate constant (in a temperature range around the reference temperature) and the average value of the rate constant at the reference temperature can decoupled. This is especially useful for the parameter optimization and will be further discussed in section 3.4.2.

Table III-4 The pre-exponential factors corresponding with the curves for different activation energies of Figure III-10, where $\log k_{Tr} = -2$ and $T_r = 40 \, ^\circ C$.

<table>
<thead>
<tr>
<th>$E$ [kJ.mol$^{-1}$]</th>
<th>log($A$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>4.68</td>
</tr>
<tr>
<td>50</td>
<td>6.34</td>
</tr>
<tr>
<td>60</td>
<td>8.01</td>
</tr>
</tbody>
</table>

In case of an equilibrium reaction, there is a second way of defining the parameters based on the equilibrium constant $K_c$.

$$K_c = \frac{k_f}{k_b} C_0^{-\sum v_i} \quad (eq. \, III-18)$$

Where $k_f$ and $k_b$ are the forward and backward reaction rate constants of the equilibrium, $C_0$ is the standard concentration of 1 mol.l$^{-1}$, and $v_i$ are the stoichiometric coefficients as defined in (eq. II-64). The equilibrium constant can also be described based on the reaction thermodynamics via the van’t Hoff equation.

$$\ln(K) = -\frac{\Delta_r G^\circ}{RT} = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \quad (eq. \, III-19)$$

Where $\Delta_r G^\circ$ is the standard reaction Gibbs energy, $\Delta_r H^\circ$ is the standard reaction enthalpy, and $\Delta_r S^\circ$ is the standard reaction entropy. Using (eq. III-18) and (eq. III-19), the Arrhenius parameters can be linked to the thermodynamic constants.

$$\Delta_r H^\circ = E_f - E_b \quad (eq. \, III-20)$$

$$\frac{\Delta_r S^\circ}{R} = \ln \left( \frac{A_f}{A_b} C_0^{-\sum v_i} \right) \quad (eq. \, III-21)$$

If the reaction rates of the equilibrium are fast compared to the other reactions involving the same species, then the species involved in the equilibrium will be at equilibrium ratios throughout the reaction. To implement this in the software, (eq. III-16) is used for both forward and backward reaction. One of the $\log k_{Tr}$, usually the one from the reverse reaction, is kept constant, and a high rate, compared to the normal reaction rates, is chosen within reason. When a too low reaction rate constant is chosen, the equilibrium will not be established to a sufficient degree, while a too high reaction rate constant will lead to a slower numerical ODE integration.
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The second reaction rate constant \( \log k_{T_2} \) is chosen so that the equilibrium constant is followed, using (eq. III-20) and (eq. III-21).

A third way to define the (rate) parameters is in relation to other parameters. This is useful for example to define the reaction rate for similar reactions involving closely related species. An example is the reaction rate of the urethane formation between an isocyanate group and a primary or secondary alcohol (see (eq. II-65)). The reaction rate constant of a secondary alcohol reaction is linked to the one of the primary alcohol by a difference between their reaction rate constant parameters, \( \Delta \log k_{T_r} \) and \( \Delta E \) ((eq. III-22) and (eq. III-23)). These parameters can be used to calculate the parameters of (eq. III-16). This facilitates keeping the difference within reasonable limits.

\[
\log k_{T_2} = \log k_{T_1} + \Delta \log k_{T_r} \quad \text{(eq. III-22)}
\]
\[
E_2 = E_1 + \Delta E \quad \text{(eq. III-23)}
\]

3.2.2 Diffusion control of reaction rates

As discussed in Chapter II, the rise in glass transition temperature can induce vitrification during cure, leading to a lowering of the reaction rate due to strongly reduced diffusion rates. In that case, the effective reaction rate constant \( k_{\text{eff}} \) can be written as a combination of the diffusion rate constant \( k_{\text{diff}} \) and the chemical rate constant \( k_{\text{chem}} \). Using (eq. II-61), the following formula can be derived:

\[
k_{\text{eff}} = \left( \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{chem}}} \right)^{-1} \quad \text{(eq. III-24)}
\]

For the chemical rate constant, the Arrhenius law as given by (eq. III-17) is used. For the diffusion rate constant, a combination of the viscosity evolution and the WLF law is used (eq. II-63). The WLF law requires a function for the concentration dependent glass transition temperature, where often the DiBenedetto equation is used (eq. II-27). The DiBenedetto equation gives the glass transition temperature for a single composition, while using the mechanistic modelling, often different (off-stoichiometric) compositions are used. In case of polymerizations forming linear chains, the Flory-Fox relationship\(^{11}\), which relates the structure development to the glass transition temperature, can be used instead. The implementation of the structure development in the software will be further discussed in section 3.3.3 and Chapter VIII.
3.3 Calculation of experimental signals and polymer properties.

3.3.1 Concentrations and spectroscopy

By solving the set of coupled ODE, the concentrations and the rates of change of the concentrations of all species are calculated. For an experimental validation of the reaction model, the simulated concentration profiles can be compared directly with experimentally measures concentration profiles. Techniques that measure concentrations directly are quantitative NMR and titration. Concentrations can be measured indirectly as well, e.g., by FTIR and UV-vis spectroscopy, as the absorbance measured at a given wavelength is in fact a weighted sum of concentrations, where the weights are the absorption coefficients of the different species at that given wavelength. This can be expressed using the Beer-Lambert law:

\[ A = \log \left( \frac{I_0}{I} \right) = \sum_{i=1}^{n} \varepsilon_i C_i L \]  

(eq. III-25)

Where \( A \) is the absorbance, \( I_0 \) is the intensity of the incident light, \( I \) is the transmitted intensity, \( \varepsilon_i \) is the molar absorption coefficient of a species \( i \) (all at the experimental wavelength), and \( L \) is the path length the light has traveled through the sample.

3.3.2 Heat flow

The goal of calculating the (reaction) heat flow is to compare it to the heat flows measured by DSC and TAM. The evolution of the heat flow as function of time and temperature can be calculated based on the rate of change of the concentrations of the species, calculated by the ODE solver, and the enthalpies of formation of those species (eq. II-67). The enthalpy of formation of a species can be estimated using literature values or using group contribution methods. In case of an equilibrium reaction, the formation enthalpies can be deduced from the van’t Hoff equation (eq. III-20). As discussed in section 2.1, the heat flow measured in a non-isothermal DSC experiment has a contribution of the reaction as well as arising from the heat capacity. The reaction heat flow can be obtained by subtracting the heat capacity contribution from the total heat flow. The methodology of baseline subtraction will be discussed in Chapter IV.

In some cases, the baseline is hard to establish precisely. This is the case for Diels-alder systems that were modelled using the software package developed in this work.\(^{12}\) (Figure III-11). By adding the reaction heat flow via the enthalpy of formation and accounting for a linear baseline, the heat flow can be calculated and compared to the measured raw heat flow coming out of DSC. Through an iterative parameter optimization, the parameters of the linear baseline can be adjusted within reasonable limits so a good match between the measured and the experimental heat flow can be obtained. Each individual experiment will have a (slightly) different baseline.
Figure III-11 An overlay of DSC heat flow curves measured for the unbinding of a Diels-Alder system prepared under different conditions with an optimized baseline\textsuperscript{12}

The heat flow is calculated starting from (eq. II-67) for a certain data point \( t_j \) and parameters set \( p \). The parameters comprise the thermodynamic \( p_{th} \), the kinetic \( p_{kin} \), the initial conditions \( p_{init} \) and the baseline parameters \( p_{bl} \). In case of equilibrium reactions, the thermodynamic and the kinetic parameters can overlap (see section 3.2.1).

\[
\dot{Q}_{\text{mod}}(t_j, T, p) = \sum_{i=1}^{n} v_i \Delta t H_i(p_{th}) \frac{dC_i(t_j, T, p_{kin}, p_{init})}{dt} + f_{bl}(t_j, T, p_{bl}) \tag{eq. III-26}
\]

Where \( \dot{Q}_{\text{mod}} \) is the modeled heat flow, \( C_i \) is the concentration of a specie \( i \), \( \Delta t H_i \) is the enthalpy of formation of a species \( i \), \( n \) is the number of species, and \( f_{bl} \) is a baseline function. The formation rate of the species is obtained after numerical integration of the kinetic model (section 3.1). The parameters influencing the formation rate are the kinetic parameters (section 0) and the initial concentrations of the species. The formation enthalpies can be directly defined by values or can be derived, like for example in equilibrium reactions (eq. III-20). If the baseline could be properly subtracted from the experimental measurement, there is no need for baseline compensation and \( f_{bl} \) is zero. When this is not the case, \( f_{bl} \) is a straight line.

3.3.3 Structure evolution

By including information about the structure of the monomers, such as their functionality and molar mass, the evolution of the average molar mass and post-gel properties can be calculated based on the concentrations using the recursive algorithm.\textsuperscript{13,14} These can be structural properties can subsequently be linked to the viscosity evolution and the build-up of the mechanical properties. An example of the molar mass and the crosslink density evolution for the formation of an \( A_4 + B_2 \) network as a function of the extent of reaction is given in Figure III-12. The implementation and calculation of these properties will be extensively discussed in Chapter VIII.
Figure III-12 The number average ($M_n$) and mass average molar mass ($M_w$) as function of the extent of reaction for an $A_4 + B_2$ network before gelation; the weight fraction of solubles $w_s$, the fraction of tri-functional crosslinks $X_3$ and tetra-functional $X_4$ crosslinks in the gel. Adapted from 14

3.4 Optimization

3.4.1 Principle, algorithms and implementation

Once a reaction kinetic model is implemented in the software, including the reaction mechanism and all corresponding kinetic model parameters as well as all parameters needed for making the link with the experimental measurements, the simulated profiles, e.g., the reaction heat flow, can be calculated (section 3.3). By direct visual comparison of these model data with the experimentally measured data, an idea is obtained of how well the model describes the experiment. The importance of this visual investigation cannot be underestimated, as it will quickly show whether the model is properly implemented and whether the initial values of model parameters are suitable, albeit maybe just in the order of magnitude. To quantify how well the experiment and model match, or in other words, how well the model fits the experiment, the difference between the experimentally obtained results and the model result is calculated (the residuals):

$$r(t_i, p) = y_i - f_{mod}(t_i, p)$$  \hspace{1cm} (eq. III-27)
Where $y_i$ is the experimental obtained result as measured on time $t_j$, $f_{\text{mod}}$ is the model function describing the experiment, $t_i$ is the time instance of the experimental result and $p$ is a vector containing all the parameters of the model. In essence, a model fits the data perfectly when these differences are less than the experimental error for all experimental data points, after optimizing those parameters that are not known exactly. Determining the error for the kinetic experiments is not straightforward as there are errors in concentrations in the mixing procedure of the reactive components and the measurement errors (see Chapter IV). In general, the square of the differences is minimized rather than the residuals themselves (eq. III-28).

$$g(p) = \min_p \sum_j \left[ r(t_j, p) \right]^2$$  
(eq. III-28)

Algorithms using these least squares as input are called least square curve fitting algorithms. Several optimization solvers are available in Matlab. Two of them are used in the software: \textit{lsqnonlin} and \textit{fmincon}.

The algorithm behind the \textit{lsqnonlin} solver is the trust-region-reflective least squares algorithm.\textsuperscript{15} The function $g$ describes a hyperplane in an $n$-dimensional space, where $n$ is the number of optimizable parameters and thus the length of the $p$ vector. Starting from an initial $p$, the algorithm wants to step towards a lower value $g$. This is done by approximating the function $g$ by a simpler function $q$, which reflects the behavior of the function $g$ reasonably well in the neighborhood $N$ of the point $p$. Now a trial step $s$ is calculated, which is minimizing $g$ in the neighborhood $N$. If a step $s$ can be found such that $g(p + s)$ is smaller than $g(p)$, the step is accepted. If no such a step is found, the neighborhood $N$ is shrunk, and the process is repeated.

There are several algorithms available for the \textit{fmincon} solver, of which the trust-region-reflective algorithm is one.\textsuperscript{16} A difference between the two solvers is that \textit{lsqnonlin} only accepts the boundaries of the parameters between a minimum and a maximum value, while for the \textit{fmincon} solver also linear and nonlinear boundary conditions can be applied. Out of hands on experience, if the parameters are only poorly known, the \textit{fmincon} solver will converge more easily towards a global minimum compared to the \textit{lsqnonlin} solver. If the parameters are better known, then the \textit{lsqnonlin} solver will converge towards a lower least square value compared to the \textit{fmincon} solver. Note that the input for the \textit{lsqnonlin} solver is (eq. III-27), while for the \textit{fmincon} (eq. III-28) is the input.

The implementation of (eq. III-27) for the heat flow will be more closely examined as it will be used throughout this work for kinetic model fitting. During the nonlinear parameter optimization, the parameters are optimized for making the model represent better the heat flow measurements of a series of different experiments at the same time. In this case, the general formula (eq. III-27) translates into (eq. III-29), where $r_{kj}$ is a matrix of the residuals with $k$ being the number of the experiment and $j$ being a measurement point of that experiment. The maximum number of measurement points for an experiment is $m$, if an experiment has fewer measurement point zeros are added to fill the matrix $r_{kj}$. In the software, the data of a whole
experiment is imported, including sections of the experiment for which the heat flow might not be accurately measured, but which are needed to have the full information about the temperature evolution. By introducing a point by point weight factor \( w_j \), the residuals at selected measurement points will be ignored by the optimization algorithm. For experimental data points with no or a low confidence, a weight value of zero is used. Other data points have a positive value for the weight. By increasing the value of the weight factor for certain data points, the optimization can also be forced into a certain direction. In (eq. III-29), the points are also scaled by the total sum of the weight values. This is done to prevent experiments with more data points to be disproportionally favored in the optimization.

\[
\begin{align*}
    r_{kj}(p) &= \left( \frac{\omega_k}{\hat{Q}^\text{max}_k} \right) \left( \frac{w_j}{\sum_{l=1}^{m} w_l} \right) \left( \hat{Q}_{ktj} - \hat{Q}_{\text{mod}}(t_j, T, p) \right) \\
    \text{(eq. III-29)}
\end{align*}
\]

An experiment by experiment weight factor \( \omega_k \) is added to scale the experiment to one another, so experiment with a higher degree of confidence can be given a larger weight. Additionally, the individual experiments are scaled by the most extreme measured data point \( \hat{Q}^\text{max}_k \), which is calculated by (eq. III-30). The maximum scale factor is introduced to help combine experiments measured in different conditions. Take as an example non-isothermal experiments measured at different scanning rates. Lower scanning rates will lead to a lower \( \hat{Q}^\text{max}_k \), while high scanning rate experiments will result in higher \( \hat{Q}^\text{max}_k \), even in case the total amount of heat evolved is the same. This scaling transforms the residual into a relative deviation.

\[
\hat{Q}^\text{max}_k = \max_{t_{j1}} \left| \hat{Q}_{ktj} \right| \\
\text{(eq. III-30)}
\]

3.4.2 Defining optimizable parameters

The way how the optimizable parameters are implemented, will have an influence on the speed, accuracy and confidence of the optimization. This will be illustrated by considering the Arrhenius law. When varying the optimizable parameters of the Arrhenius law, the activation energy \( E \) and the pre-exponential factor \( A \) will have very different effects on the reaction rate. Because the activation energy is in the exponent, small changes will have a large influence on the rate constant, while small changes in the pre-exponential factor will have a (proportional) minor influence on the rate constant. This is shown in Figure III-13, where an Arrhenius plot for an activation energy of 50 kJ. mol\(^{-1}\) and a pre-exponential factor of 1.0 \( 10^5 \), is compared to lines for these parameters individually lowered by 30%. By changing the activation energy, the slope of the curve changes compared to the original curve, but its intercept with the ordinate (corresponding to \( T \rightarrow \infty \)) remains unchanged, having a major effect in the temperature region of 0°C to 200°C that is of interest. Lowering the pre-exponential factor shifts the curve down over the whole temperature range, having only a minor effect. For optimization algorithms, it is better if changing the individual parameters within a certain range results in proportional
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effects on the outcome. To accommodate to this, the Arrhenius law can be written as function of the activation energy and the 10-based logarithm of the pre-exponential factor $\log A$:

$$k = 10^{\log A} \cdot \exp \left( -\frac{E}{RT} \right)$$  \hspace{1cm} (eq. III-31)

The effect of this implementation is shown in Figure III-13, where the $\log A$ is lowered by 30% from the initial value of 5. This results in a significant downward shift compared to the reference curve. Comparing the effect of changing the $\log A$ and $E$ with 30% on the rate constant, the effect is proportional in the interesting temperature region.

![Figure III-13 The effect of changing the parameters of the Arrhenius law on the reaction rate constant. The reference curve is for an activation energy $E$ of 50 kJ. mol$^{-1}$ and a pre-exponential factor $A$ of $1.0 \cdot 10^5$ (kref); curve with a value of $A$ lowered by 30% (kA); curve with a value of $E$ lowered by 30% (kE). Using (eq. III-30) lowering the $\log A$ by 30% (klogA).](image)

The implementation of rate constants and their temperature dependence in the software (eq. III-16) differs from the Arrhenius law, given by (eq. III-31). As discussed in section 3.2.1, by implementation of (eq. III-16) the effect of the activation energy and the second parameter (the rate constant at the reference temperature) will be decoupled. Often the reaction rate constant should be within a range of acceptable values at a certain temperature, while similarly there is the range of acceptable activation energies for a particular chemistry of the elementary reaction step considered. To illustrate the usefulness of (eq. III-16), assume that the logarithm of the rate constant $\log k_{Tr}$ at the reference temperature of 40°C is $-2 \pm 0.5$ and the activation energy $E$ is $50 \pm 10$ kJ. mol$^{-1}$, giving a range of acceptable reaction rate constants illustrated by the red area in Figure III-14 (top). To cover all the acceptable values in the temperature range of interest using the Arrhenius law (eq. III-31), using lower and upper bounds as needed for lsqnonlin (see section 3.4.1), while allowing for the same range of activation energies ($\pm 10$ kJ. mol$^{-1}$), the logarithm of the pre-exponential factor $\log A$ must be permitted to range by more than $\pm 2$ (4.34
and 8.51). Combined with the full range of possible activation energies, the area covered by (eq. III-31) in the temperature range of interest is much larger than the area covered by (eq. III-16), which is much narrower around the reference temperature of 40°C. This narrow region will aid the optimization algorithm to go towards an optimal solution. A narrower region can be obtained using (eq. III-31) when a linearly changing boundary condition is used. This is incompatible with the *lsqnonlin*, but achievable with the *fmincon* solver. Here the highest log$A$ and the lowest activation energy vary gradually to the lowest log$A$ and the highest activation energy. The area covered in this way is shown in Figure III-14 (bottom). Although the difference between the two implementations is smaller in the latter case, the area covered by implementation with (eq. III-16) is still narrower than the other implementation, while being compatible with all optimization solvers, and is hence the approach taken in this work.

In the software, the boundary limits between which the parameters can vary must be supplied to prevent the optimization algorithm from changing the parameters into physically unrealistic values. The parameters supplied to the optimization algorithm $p'$ are normalized parameters using these bounds:

$$p' = \frac{p - p_{lb}}{p_{ub} - p_{lb}} \quad (eq. \ III-32)$$

Where $p$ are the parameters accessed by the user and $p_{lb}$ and $p_{ub}$ are the lower and upper bounds of this parameter, respectively.
Figure III-14 (top) Optimization region for the reaction rate constant covered by using (eq. III-16) with $\log k_{T_r} = -2 \pm 0.5$ and $E = 50 \pm 10$ kJ mol$^{-1}$ at the reference temperature of 40 °C in red and using (eq. III-31) $\log A = 6.35 \pm 2.16$ and $E = 50 \pm 10$ kJ mol$^{-1}$ in blue; (bottom) Implementation with a varying $\log A$ and activation energy using (eq. III-31) leading to a narrower optimization region in blue; the implementation using (eq. III-16) in red.

3.4.3 Sensitivity analysis

Evaluating the effect of changing a parameter value would have on the concentration profile and the subsequent heat flow is valuable as it gives insight in whether a parameter is important in the optimization. In a sensitivity analysis, the effects of small changes of the parameters on the concentrations of the species is evaluated, represented mathematically by (eq. III-33).
For chemical kinetics, (eq. III-33) is not readily calculated, however it can be approximated using Taylor series:

\[
\frac{\partial C(t)}{\partial p_j} = C(t, p_j) - C'(t, p_j) \Delta p_j + C''(t, p_j) \Delta p_j^2 - C^{(3)}(t, p_j) \frac{\Delta p_j^3}{6} \quad (\text{eq. III-34})
\]

\[
C(t, p_j + \Delta p_j) = C(t, p_j) + C'(t, p_j) \Delta p_j + C''(t, p_j) \Delta p_j^2 + C^{(3)}(t, p_j) \frac{\Delta p_j^3}{6} \quad (\text{eq. III-35})
\]

Where \( p_j \) is the \( j \)th parameter in the parameter vector \( p \) and \( \Delta p_j \) is the small variation on parameter \( p_j \). All other parameters in (eq. III-34) and (eq. III-35) are fixed. By subtracting (eq. III-34) from (eq. III-35) and some rearrangements (eq. III-36) is obtained:

\[
C'(t, p_j) = \frac{C(t, p_j + \Delta p_j) - C(t, p_j - \Delta p_j)}{2 \Delta p_j} - \left( C^{(3)}(t, p_j) - C^{(3)}(t, p_j) \right) \frac{\Delta p_j^2}{6} \quad (\text{eq. III-36})
\]

\[
C'(t, p_j) \approx \frac{C(t, p_j + \Delta p_j) - C(t, p_j - \Delta p_j)}{2 \Delta p_j}
\]

Selecting a suitable \( \Delta p_j \) can be done knowing the order of the error on the approximation is \( O(\Delta p_j^2) \) and the precision of the calculation of \( C(t) \). For example, if \( C(t) \) is known up to 6 significant numbers than a variation of \( 10^{-3} \) on \( p_j \) is required.

Another way of solving (eq. III-33) is by numerical differentiation versus time:

\[
\frac{d}{dt} \frac{\partial C(t)}{\partial p_j} = f(t) \frac{\partial C(t)}{\partial p_j} + \frac{\partial f(t, T, C, p)}{\partial p_j} \quad (\text{eq. III-37})
\]

Or equivalently replacing \( \frac{\partial C(t)}{\partial p_j} \) by \( U(t) \)

\[
\frac{dU(t)}{dt} = f(t) U(t) + \frac{\partial f(t, T, C, p)}{\partial p_j} \quad (\text{eq. III-38})
\]

Where \( J \) is the Jacobian matrix as defined by (eq. III-13) and \( f \) is given by (eq. III-11). The initial conditions of \( U(t = 0) \) is the zero vector \( 0 \) if the parameter is not an initial condition (like an initial concentration) and is a vector \((0, \ldots, 0, 1, 0, \ldots, 0)^T \) where the one is on the \( i \)th position if the parameter \( p_i \) is an initial condition for species \( i \). The stability of the numerical integration of (eq. III-38) should be similar to (eq. III-11) as they have the same Jacobian matrix \( J \). When doing a sensitivity analysis in the software, (eq. III-11) and (eq. III-38) are integrated simultaneously.

The effect on the heat flow evolution can be calculated as well. Starting from (eq. III-26) and assuming that the baseline function is zero, the following formula can be derived.
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\[ \frac{\partial}{\partial p_j} \dot{Q}_{\text{mod}}(t_j, T, \mathbf{p}) = \]

\[ \sum_{i=1}^{n} \nu_i \frac{dC_i(t_j, T, \mathbf{p}_{\text{kin}}, \mathbf{p}_{\text{init}})}{dt} \frac{\partial}{\partial p_j} [\Delta f H_i(\mathbf{p}_{\text{th}})] \]

\[ + \sum_{i=1}^{n} \nu_i \Delta f H_i(\mathbf{p}_{\text{th}}) \frac{\partial}{\partial p_j} \left[ \frac{dC_i(t_j, T, \mathbf{p}_{\text{kin}}, \mathbf{p}_{\text{init}})}{dt} \right] \]  

(eq. III-39)

Where the second term in (eq. III-39) is calculated using the solution of (eq. III-37) and (eq. III-38). In most cases, either the first term or the second term of (eq. III-39) will be zero as the thermodynamic parameters are independent of the kinetic and the initial conditions parameters. An exception is when they are defined by an equilibrium (eq. III-20).

The calculation of (eq. III-39) can also aid the optimization algorithm \textit{lsqnonlin} as this solver needs to calculate a Jacobian. The Jacobian is given by (eq. III-40) using (eq. III-27)

\[ \frac{\partial}{\partial p_j} r(t_j, \mathbf{p}) = -\frac{\partial}{\partial p_j} f_{\text{mod}}(t_j, \mathbf{p}) \]

(eq. III-40)

In case for the heat flow, implementation of (eq. III-40) with an \( f_{\text{mod}} \) as defined by (eq. III-29) leads to (eq. III-41).

\[ \frac{\partial}{\partial p_j} r(t_j, \mathbf{p}) = -\frac{\partial}{\partial p_j} \dot{Q}_{\text{mod}}(t_j, T, \mathbf{p}) \]

(eq. III-41)
4 References

CHAPTER IV
CALORIMETRIC METHOD DEVELOPMENT FOR ANALYZING
POLYURETHANE REACTION KINETICS

1 Introduction

In this chapter, the methodology and approaches for measuring, correcting and analyzing the polyurethane reaction kinetics over the full conversion using calorimetry will be discussed. The two calorimetric techniques used are differential scanning calorimetry (DSC) and microcalorimetry, the latter abbreviated as TAM (Thermal Activity Monitor) after the TAM-III measuring device from Thermometric (currently TA Instruments). In calorimetry, two major types of measurements can be distinguished: non-isothermal and isothermal. Isothermal measurements were performed using DSC and TAM, while only DSC was used for the non-isothermal measurements. This chapter is focused on the methodology, the polyurethane reaction kinetics and the reaction mechanisms will be discussed in Chapters V, VI and VII.

In non-isothermal DSC measurements, the contribution of baseline on the heat flow measurement is important. To obtain the heat and heat flow generated by the polymerization reaction, needed for studying its kinetics, the baseline contribution must be removed. Several methods for obtaining a baseline can be used with varying degrees of accuracy, which can change in function of the reaction conditions, like the scan rate and the sample composition. These methods will be discussed and evaluated in this chapter.

For isothermal measurements, TAM and DSC each have their strengths and weaknesses. DSC has short time constant (of the order of seconds) making it ideal for measuring fast processes over short time periods (of the order of minutes to hours). The baseline of the DSC is not absolute, however, and will vary from experiment to experiment, making a good interpretation of the kinetics dependent on its selection. In contrast, TAM has a much longer time constant (of the order of several minutes) but a nearly absolute baseline. Due to the design and operation of the TAM (see Chapter III), the first 45-60 minutes of a heat flow measurement are not reliable (influenced by the insertion of the sample), but once one hour is past, the heat flow can be measured with a high precision over periods that can extend up to months. By combining the two techniques, the fast response time of the DSC can be combined with the baseline precision of the TAM, making the combined isothermal method suitable for fast changing initial reactions with a slow changing end of the reaction. The impact of combining both techniques on the isothermal kinetics derived will be evaluated.

With the obtained results, the conversion and conversion rates can be calculated. There are next analyzed with model free kinetics (MFK) (see Chapter II section 3.2.3). Several MFK methods have been developed, which are applicable under different conditions.1-3
2 Thermal stability of polyurethane

The Friedman method\(^4\) will be used throughout this work. How this method works is illustrated with a thermal degradation of the polyurethanes. The thermal stability of polyurethanes is an important factor when doing kinetic measurements in calorimetry, because, firstly, thermal degradation will have a heat effect that can obscure the polymerization kinetics, and secondly, because the degradation products may influence the polymerization kinetics. So, a safe temperature region to do calorimetric measurements is determined using thermogravimetric analysis. With this technique the mass loss caused to degradation and decomposition of the polyurethane sample is measured as function of temperature and scan rate. The start of mass loss is not necessarily in a one on one relation with the start of degradation, as network fragmentation may result in segments too heavy to evaporate, but will lead to a good indication of the absolute maximum temperature above which no reliable kinetic data can be obtained. These TGA results will also be used to illustrate the use of model free kinetics (MFK) to analyze kinetic data.

First the thermal stability of the fully cured polyurethane was investigated. This fully cured material was made by mixing DPG and MDI in stoichiometric conditions and curing it in an oven at 120 °C for a day. Next, small samples of 1-2 mg were put in tarred platinum TGA pans. The used temperature program in TGA is shown in Figure IV-1.

![Figure IV-1](image)

*Figure IV-1. A schematic representation of the non-isothermal temperature program to investigate the thermal stability of fully cured polyurethane samples using TGA.*

The stability of the polyurethane was investigated in an inert N\(_2\) atmosphere. The first step in the program consist of an isothermal step at 40 °C of 5 minutes. During this period the oxygen gas remaining in the TGA oven is purged away. After this period the sample is heated at 5 K.min\(^{-1}\) to 120 °C and kept there isothermal for 5 minutes. During the heating and isothermal period water potentially adsorbed on the sample is evaporated: typically about 0.5 w% of moisture was lost. Next the sample is heated from 120 °C to 600 °C to investigate the thermal stability. Several scanning rates were used in order to get basic kinetic insight in the degradation of the polyurethane samples. When the temperature reaches 600 °C, it is kept isothermal for 10 minutes in order to fully degrade the polyurethane and obtain the residue.
The result of the degradation of the polyurethane at heating rates of 2, 5, 10 and 20 K.min\(^{-1}\) are given in Figure IV-2. The degradation happens in two steps. For experiment at a heating rate of 5 K.min\(^{-1}\), the first degradation step starts around 200 °C, after which a plateau is reached, followed by a second degradation step that starts around 450 °C. After reaching 600 °C and the subsequent isothermal period of 5 minutes, the polymer was fully degraded: less then 1 w% was observed, independent of the scanning rate. By increasing the scanning rate, the first degradation step is observed at higher temperatures (Figure IV-2 (left black arrow)) and the degradation rate is increased, as observed from the higher peak in the derivative. This behavior is typical for kinetic processes with high activation energies, which degradations often are. The onset temperature of this degradation, however, remains approximately constant at 200 °C (Figure IV-2 (right)). Like for the first degradation step, the second degradation step is observed at higher temperatures for the higher scanning rates. The weight plateau reached after the first degradation is lower for the experiments performed at higher scanning rates.

Using model free kinetics (MFK) (see Chapter II section 3.2.3), a rough estimate of the degradation kinetics of the first degradation step can be made using the extent of degradation \( x \) and the degradation rate:

\[
x = \frac{w_0 - w_t}{w_0}
\]  

\[(\text{eq. IV-1})\]

Where \( w_0 \) is the measured mass of the sample after the drying step and \( w_t \) is the mass measured at time \( t \). The degradation rate is defined as:

\[
\frac{dx}{dt} = -\frac{1}{w_0} \frac{dw_t}{dt}
\]  

\[(\text{eq. IV-2})\]

To investigate these non-isothermal degradation kinetics, Friedman’s method\(^4\) is used. In this method, a certain extent of reaction or degradation is selected and the corresponding
temperature $T_x$ and rate are looked up. Using (eq. II-54) and knowing that the pressure is constant throughout the experiment, the following formula can be derived:

$$\ln \left( \frac{dx}{dt} \right) = \ln(Af(x)) - \frac{E_x}{RT_x}$$

(eq. IV-3)

By plotting the logarithm of the rate $\ln \left( \frac{dx}{dt} \right)$ versus the reciprocal temperature $1/T_x$ using date points from the experiments having different scanning rates, the activation energy $E_x$ at that extent of reaction can be determined by multiplying the slope (obtained by linear regression) by $-R$ (Figure IV-3). As only the start of the degradation is of interest and as degradation kinetics can be quite complex, a low extent of degradation of 0.01 (or 1% of weight loss) was chosen for the Friedman analysis. An activation energy of 169.4 kJ.mol$^{-1}$ was obtained. This is a high value compared to the values one typically finds for the activation energy of step growth polymerization kinetics, which have values between 40 and 100 kJ.mol$^{-1}$. As a result of the high activation energy, the degradation kinetics are strongly temperature dependent. To illustrate this: the reaction rate at 210 °C is 2.4 times faster than the rate at 200 °C. To conclude, the safe maximum temperature for a DSC experiment to avoid the degradation as much as possible is 200 °C.

![Figure IV-3](image_url)

*Figure IV-3. Arrhenius plot showing the natural logarithm of the degradation rate at an extent of degradation of 0.01 versus the reciprocal temperature at that extent, using data from the TGA experiments of Figure IV-2.*

### 3 Non-isothermal polyurethane cure in DSC

#### 3.1 The heat-cool-heat cycle

Non-isothermal experiments for studying the cure kinetics are performed in DSC using a so-called heat-cool-heat (HCH) cycle. The results for a non-isothermal experiment performed at a heating rate of 2 K.min$^{-1}$ is shown in Figure IV-4, together with the temperature program. The measurement starts with a cooling at 20 K.min$^{-1}$ to -70 °C, in order to freeze in all possible reactions, followed by a 5 minute isothermal period to ensure that the DSC reaches a stable state at -70 °C. Next the heating is performed at a selected heating rate, 2 K.min$^{-1}$ in this case.
During this first heating, the initial glass transition temperature $T_{g0}$ of the uncured material, insofar no reactions occurred before the low temperature was reached, is measured. For this material, the $T_{g0}$ is around -70 °C, so immediately upon heating the material devitrifies and an enthalpy relaxation is observed. Around -20 °C, a small exothermic peak (I) is observed, which is explained by a cold crystallization of MDI from the mixture. Upon further heating, an endothermic peak (II) is observed near 20 °C, ending around 40°C, which is attributed to the melting of the (eutectic) MDI crystals. These cold crystallization and melting peaks are not observed in all non-isothermal experiments, and they have no measurable effects on the reaction kinetics in the temperature region of interest (between 20 °C and 200 °C). Off-stoichiometric experiments with an excess of isocyanate groups have a higher weight fraction of MDI present compared to the stoichiometric mixtures, and as a result, the cold crystallization and melting peaks will be more prevalent in this case (see section 3.2.2).

The effect of the cold crystallization is more pronounced for the low scanning rate experiments, as more time is given during the heating for crystal growth originating from nuclei formed at lower temperatures. The cold crystallization and melting peaks are superimposed upon a large exothermic peak (III) corresponding with the urethane formation, showing a maximum rate at 95 °C. Even though the temperature continues to increase, the reaction rate subsequently slows down because of the advanced consumption of the alcohol and isocyanate groups, reaching a minimum at the highest temperature of 200 °C. Next, the temperature is kept for one minute at 200 °C before cooling down. In the second heating from -70 °C to 200 °C at the same scanning rate of 2 K.min$^{-1}$, the full cure glass transition temperature $T_{g1}$ of 20 °C is observed. After the devitrification, no residual reaction is observed, confirming that full cure was achieved during the heating and the subsequent cooling. At 200 °C (IV), the heat flow of the first and second heating do not coincide, indicating that during the first heating some reaction is still occurring.
at these high temperatures. If the scanning rate is increased, this effect is more pronounced, as will be discussed later (see section 3.2.2 and Figure IV-9). To ensure full cure is achieved, a longer than one-minute period isothermal at 200 °C could be programmed. However, the formed polyurethane is not thermally stable at 200 °C for longer times (see section 2). To avoid inducing a too extensive degradation, an intermediate isothermal cure at 150 °C for 30 minutes is programmed after the initial heating (Figure IV-4 (left)).

3.2 Analyzing non-isothermal experiments and baseline construction

3.2.1 Baseline construction

The heat flow measured in a non-isothermal DSC experiment of a curing system, is the combination of the reaction heat flow, a heat capacity contribution and an instrument contribution (eq. II-48). To obtain only the heat flow generated by the reaction, the heat capacity and instrument contributions need to be subtracted from the total measured heat flow. The line which is the result of the combination of these two contributions is called the baseline. This results in:

\[
\dot{H}(t, x, T) = \dot{Q}(t, x, T) - f_{bl}(t, x, T) \tag{eq. IV-4}
\]

Where \(\dot{H}\) is the reaction heat flow, \(\dot{Q}\) is the measured heat flow, and \(f_{bl}\) the baseline curve.

In literature, a linear baseline is often constructed by drawing a straight line between a point on the curve before the reaction exotherm starts and a point on the curve after the reaction peak (Figure IV-5). In case of the investigated polyurethanes, this approach is not suitable because the cold crystallization is obscuring the initial straight piece before the reaction exotherm, and because full cure is not achieved during the heating, even at the lower scan rates. Thus, another approach needs to be taken to construct the baseline and obtain the reaction heat flow.

The heat capacity based baseline approach, accounts for the fact that the heat capacity of the reacting sample changes linearly as the reaction progresses. The heat capacity and instrument contribution of the fully cured material \(C_{p1}\) is measured during the second heating of the HCH cycle (see Figure IV-4). A linear fit through the second heating in the temperature interval of between 30 to 170 °C can be used as an approximation of the baseline for the fully cured sample. This temperature range is above the glass transition temperature of 20 °C and remains 30 K below the maximum temperature of 200 °C, to prevent potential interference of degradation (see section 2). The heat capacity evolution of the uncured sample \(C_{p0}\) can be obtained from the cooling at 20 K.min\(^{-1}\) to the starting temperature of the HCH cycle (Figure IV-4). Note that \(C_{p0}\) is an approximation of the heat capacity of the uncured material, as during the sample preparation some reaction takes place.
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Figure IV-5. Non-isothermal experiment of an epoxy-amine curing system with linear baseline constructed by taking parts before and after the reaction peak. Adapted from\textsuperscript{5}

As the heat capacity change in a limited temperature interval can be approximated with a straight line, the heat capacities for both the uncured and fully cured material can be described by following formula:

\begin{equation}
C_{pi}(T) = C_{pi}(T_R) + \beta_i(T - T_R) \quad \text{(eq. IV-5)}
\end{equation}

Where \( C_{pi}(T) \) is the heat capacity for a uncured material when \( i \) equals zero and the fully cured material when \( i \) equals one, \( C_{pi}(T_R) \) is the heat capacity at a reference temperature \( T_R \) of the uncured and fully cured material when \( i \) equals zero and one, respectively, and \( \beta_i \) is the slope of the \( C_{pi} \) evolution in the neighborhood of the reference temperature \( T_R \).

The best way to calculate the baseline function is to use the extent of reaction as a weighting between the uncured and cured heat capacities. The heat capacity is converted to a heat flow by multiplying by the heating rate \( \frac{dT}{dt} \).

\begin{equation}
f_{bl}(t, T, x) = \left[ (1 - x(t))C_{p0}(T) + x(t)C_{p1}(T) \right] \frac{dT}{dt} \quad \text{(eq. IV-6)}
\end{equation}

The extent of reaction \( x \) at time \( t \) can be calculated using the reaction heat released up until that point in time, \( \Delta H(t) \), and dividing it by the total reaction heat \( \Delta H_{tot} \) (eq. II-47). However, \( \Delta H(t) \) depends on the baseline function and must therefore be calculated iteratively. Because of cold crystallization and melting of the MDI at temperatures below 40°C, calculating the \( x \) evolution in this temperature region is unreliable.
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The sigmoidal baseline method is using a temperature dependent sigmoidal function $f_{\text{sig}}(T)$ to approximate $x(t)$ and calculate the baseline function. The advantage of using this function is that it is independent of the $x$ evolution and thus not affected by the cold crystallization and melting. Substituting $x(T)$ for $f_{\text{sig}}(T)$ in (eq. IV-6) leads to:

$$f_{\text{bl}}(t, T, x) = \left[(1 - f_{\text{sig}}(a, b, T)) C_p(T) + f_{\text{sig}}(a, b, T)C_{p1}(T)\right] \frac{dT}{dt} \quad \text{(eq. IV-7)}$$

For the sigmoidal function, an adapted logistic function was chosen (eq. IV-8) with two parameters $a$ and $b$. If $a$ is equal to one and $b$ is equal to zero, the value of the sigmoidal function is 0.5 in the middle of the interval (Figure IV-6). Increasing the $b$ parameter will shift the midpoint to the value $b$ on the $x$-axis, while increasing $a$ will make the transition narrower.

$$f_{\text{sig}}(T) = \frac{1}{1 + \exp(-a(T - b))} \quad \text{(eq. IV-8)}$$

The parameters $a$ and $b$ need to be calculated so that $f_{\text{sig}}(T)$ can be used to approximate $x(T)$. However, the extent of conversion can only be approximated once an initial baseline is proposed. Hence, an initial value of $a$ and $b$ must be proposed and then updated iteratively till convergence has been reached. As $a$ and $b$ will heavily influence $x(T)$, suitable initial conditions are needed.

For the baseline of the reaction exotherm, the mid-point for the sigmoidal baseline should correspond with the extent of conversion equal to 0.5. This point can be approximated by using the temperature at the peak maximum $T_{\text{peak}}$, providing the initial value of $b$. The parameter $a$ is calculated using the width of the reaction peak, estimated using the two temperatures for which the heat flow is half of the peak maximum, one before the peak, $T_{\text{hw1}}$, and one after, $T_{\text{hw2}}$ (Figure IV-7). The peak half width is about one third of the width of the full reaction peak. Thus, an initial value of three was used for the $a^\prime$ parameter in the following formula:

$$a = a^\prime (T_{\text{hw2}} - T_{\text{hw1}})^{-1} \quad \text{(eq. IV-9)}$$
Calorimetric method development for analyzing polyurethane reaction kinetics

The result of the baseline construction for a stoichiometric mixture of MDI and PPG-425 can be found in Figure IV-7. At temperatures below 0 °C, the \( C_p^0 \) curve and the baseline curve \( f_{bl} \) coincide. At temperatures above 150 °C, the baseline curve is coinciding with the second heating. This is consistent with (eq. IV-6), because at lower temperatures, no significant reaction has happened, meaning the extent of conversion is low, thus \( C_p(x) \) is close to \( C_p^0 \). At high temperatures, most of the reaction has taken place, leading to a high extent of conversion and a \( C_p(x) \) close to \( C_p^1 \). In the intermediate temperatures, between 0 and 150 °C, most of the reaction is occurring and a transition of the baseline curve between the initial and final values is observed.

![Figure IV-7. Baseline construction for the curing of a stoichiometric mixture of MDI - PPG-425 at a heating rate of 2 K.min\(^{-1}\), showing the first heating, the second heating, the heat flow due to the capacity of the unreacted sample \( C_p^0 \) (eq. IV-5), the heat flow due to the heat capacity of the fully reacted sample \( C_p^1 \), and the constructed sigmoidal baseline (dashed black). The peak maximum is indicated by (+) and the points at \( T_{hw1} \) and \( T_{hw2} \) by (x). The inset is a zoom on the baseline.](image)

Once the baseline is constructed, the heat flow solely resulting from the reaction can be calculated using (eq. IV-4), resulting in Figure IV-8 (left). Note that at room temperature, the reaction rate is already significant. Thus, during the preparation of the mixture and the starting of the measurement the polymerization reaction already proceeds. The preparation time should therefore be minimized in order to measure the reaction heat flow accurately and as completely as feasible. The way this was achieved is discussed in Chapter III section 2.1.4.
The reaction heat generated up to a time \( t \) is calculated by integrating the reaction heat flow with respect to the zero level and is highlighted by a shading in Figure IV-8 (left):

\[
\Delta H(t) = \int_0^t \dot{H}(t) \, dt
\]

(eq. IV-10)

As can be observed, the highlighted area includes heat effects attributed to the cold crystallization and melting, which is obviously not part of the reaction heat. However, as it can be assumed that the cold crystallization exotherm and the melting endotherm are compensating one another, a correct measurement of the reaction heat is obtained once these events have concluded. This is a reasonable approximation as crystallization and melting are reversible processes, and as long as no significant amount of crystallization occurs during the cooling (this could lead to a small underestimation of the reaction heat). The reaction heat released during the scan is -221 J.g\(^{-1}\). As some urethane formation occurred during the preparation step, this value underestimates the reaction heat for 100% conversion.

Using the reaction heat \( \Delta H(t) \), the extent of reaction \( x(t) \) can be calculated (eq. II-47). To confirm that the sigmoidal curve \( f_{\text{sig}}(T) \) is a reasonable approximation for \( x(t) \), the two are compared in Figure IV-8 (right). Over the whole temperature interval, \( x \) and \( f_{\text{sig}} \) coincide nicely. This is the case for experiments where the cold crystallization and melting is quite limited and nearly full cure is achieved within the heating. It is not the case for experiments done at high scanning rates and where an excess of MDI is present. In these cases, the baseline needs to be adjusted to take into account incomplete reaction and the side reactions at high temperatures (see next section).

![Figure IV-8. Analysis of the curing of a stoichiometric mixture of MDI - PPG425 at 2 K.min\(^{-1}\). (left) Reaction heat flow after baseline subtraction (eq. IV-4). The shaded blue area represents the partial integration of the reaction heat (eq. IV-10). (right) Evolution of the extent of reaction \( x(t) \) (solid) and the sigmoidal curve \( f_{\text{sig}}(T) \) (dashed) plotted as a function of the temperature.](image-url)
3.2.2 Baseline construction for higher scanning rates

The heat flow of the first and second heating for the reaction of a stoichiometric mixture of MDI – PPG425 at different scanning rates is displayed in Figure IV-9 (left). In the experiments performed at 5 and 10 K.min\(^{-1}\) the reaction was incomplete at the end of the first heating: the heat flow at 200 °C for the first heating is clearly deviating in exothermic direction from the heat flow in the second heating (to a lesser extent this is also the case at 2 K.min\(^{-1}\)).

The comparison of the extent of conversion \(x(t)\) and \(f_{\text{sig}}(T)\) for the different scanning rates is shown in Figure IV-9 (right). When \(x\) is below 0.5, the two coincide quite well, while at higher conversions, the two deviate from one another at the scanning rates of 5 and 10 K.min\(^{-1}\). To have a good baseline for the whole experiment, both \(x(t)\) and \(f_{\text{sig}}(T)\) are combined as follows:

\[
 f_{bl}(t,T,x) = \left[(1 - g(t,T))C_{p0}(T) + g(t,T)C_{p1}(T)\right] \frac{dT}{dt} \\
 \text{where } g(t,T) = f_{\text{sig}}(T) \text{ if } x < 0.5 \\
 \text{and } g(t,T) = x(t) \text{ if } x > 0.5 
\]  

(eq. IV-11)

\[
 H_{C} = \dot{H}(t,x,T) \left(\frac{dT}{dt}\right)^{-1} 
\]  

(eq. IV-12)
As the heating rate increases, the reaction starts at a higher temperature and the reaction peak and its maximum are shifted towards higher temperatures. As a result, only for the experiment performed at 1 K.min\(^{-1}\) full cure was attained during the first heating. Low heating rate experiments spent more time at low temperatures, resulting in higher amounts of crystals being formed and more distinct crystallization and melting peaks.

**Figure IV-10.** Results for the curing of a stoichiometric mixture of MDI – PPG425 measured at heating rates of 1, 2, 5 and 10 K.min\(^{-1}\). (left) Reaction heat flows \(\dot{H}\) (colored and solid) and zero heat flow level (black and dashed). (right) The reaction heat flow in heat capacity units \(\dot{H}_C\) for the same experiments.

### Baseline construction for excess isocyanate experiments

The results of a HCH experiment for an off-stoichiometric MDI – PPG425 mixture with a concentration of isocyanate groups double the concentration of alcohol groups at a heating rate of 2 K.min\(^{-1}\) is given in Figure IV-11. In the temperature range between -20 °C and 40 °C, the cold crystallization and melting of MDI is clearly visible and more pronounced than for stoichiometric conditions (see Figure IV-11). As in excess isocyanate conditions the weight fraction of MDI is higher than for stoichiometric conditions, 54.1 w% instead of 37.0 w%, the crystallizable fraction is higher.

The peak maximum of the reaction exotherm is found at 90 °C after which the reaction slows down a minimum at 151 °C after which a second peak is observed. This phenomenon can be explained as a reversible reaction of isocyanate with urethane resulting in allophanate. When all alcohol functional groups are reacted to urethane groups, isocyanate groups and urethane groups are present in equal amounts, which are stoichiometric conditions for the allophanate formation. The allophanate formation is an equilibrium reaction, where the exothermic allophanate formation is promoted at low temperatures and the endothermic decomposition happens as higher temperatures. During the first heating, when the urethane reaction is nearly complete, allophanate formation occurs and accelerates with increasing temperature, as observed from the small exothermic peak at 172 °C. At temperatures higher than 172 °C, the decomposition reaction becomes increasingly favored, resulting in an endothermic peak. In the second heating, these exothermic and endothermic peaks are also observed, confirming the
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reversibility of the allophanate reaction. In the second heating, the midpoint of the glass transition is observed at 0 °C. This is 20 K lower than the full cure glass transition temperature of the stoichiometric ratio. Polymerizations in off-stoichiometric conditions lead to lower molar masses and thus lower glass transition temperatures (see Chapter II section 1.1.3).6

The reaction heat flow obtained after baseline subtraction is plotted in Figure IV-12 (left), while the corresponding extent of conversion is plotted in Figure IV-12 (right). The extent of reaction is overestimated at first due to the crystallization, which is compensated by the subsequent melting. At high temperatures, the extent of conversion is overestimated due to the allophanate formation. The baseline, as displayed in Figure IV-11, is constructed with \( f_{\text{sig}}(T) \), which is quite a good approximation for \( x(T) \) over the whole temperature range and which is unaffected by cold crystallization, melting, allophanate formation and decomposition.

Figure IV-11 Baseline construction for the curing of an off-stoichiometric 2-1 mixture of MDI - PPG-425 at a heating rate of 2 K.min\(^{-1}\), with the first and second heating and the constructed sigmoidal baseline.

Figure IV-12 Analysis of the curing of an off-stoichiometric 2-1 mixture of MDI - PPG-425 at 2 K.min\(^{-1}\). (left) Reaction heat flow after baseline subtraction (eq. IV-4). The shaded blue area represents the partial integration of the reaction heat (eq. IV-10). (right) Evolution of the extent of reaction \( x \) (solid) and the sigmoidal curve \( f_{\text{sig}}(T) \) (dashed) versus the temperature.
4 Isothermal calorimetric measurements

4.1 DSC

In isothermal calorimetric measurements, the heat flow is measured at a certain temperature for a given time. Like for the non-isothermal measurements, keeping the preparation time to a minimum is essential to measure most of the reaction. The way this is achieved is described in Chapter III section 2.1.4.

The heat flow measured in DSC for the reaction of a stoichiometric MDI – PPG-425 mixture with 0.04 w% catalyst at 40 °C is shown in Figure IV-13. The exothermic heat flow is high at the beginning of the reaction, decreases rapidly as the reaction progresses, and has a long reaction tail. This is typical for chemical reactions of a high reaction order. Such information is not readily derived from non-isothermal measurements. To study reaction kinetics in depth a combination of non-isothermal and isothermal measurements is needed.

Like in non-isothermal measurements, the isothermal DSC heat flow signal must be corrected with a baseline. In contrast with non-isothermal measurements, the baseline in isothermal experiments is only the result of the instrument: there is no heat capacity contribution as the temperature is constant. Thus, starting from (eq. II-48) the following equation can be derived:

\[ \dot{H}(t, x, T_{iso}) = \dot{Q}(t, x, T_{iso}) - f_{bl}(T_{iso}) \]  \hspace{1cm} (eq. IV-13)

Where \( \dot{Q}(t, x, T_{iso}) \) is the heat flow measured as a function of time at the isothermal temperature, \( f_{bl}(T_{iso}) \) is the instrument contribution to the heat flow, which is assumed to be constant, and \( \dot{H}(t, x, T_{iso}) \) is the reaction heat flow of the polyurethane reaction. The instrument contribution is measured when the reaction heat flow becomes zero, however, as the polyurethane reaction has a long reaction tail, it is hard to determine when this contribution has become really zero. Typically, it is assumed that the reaction is finished once the heat flow becomes constant as a function of time, at which point only the instrument contribution would be measured. The baseline level determined from the average heat flow of the final hour of the DSC experiment is shown as a dashed line in Figure IV-13.
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Figure IV-13. DSC heat flow signal for the reaction of a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst system measured at 40 °C (solid line) and a suggested baseline (dotted). The inset is a zoom on the baseline.

4.2 Microcalorimetry

Isothermal microcalorimetry can be used as a more sensitive alternative for isothermal DSC measurements. The result for a microcalorimetry experiment of a stoichiometric MDI – PPG-425 mixture with 0.04 w% catalyst at 40 °C, the same conditions as for DSC in Figure IV-13, is given in Figure IV-14. The measurement was performed in a minicalorimeter of the TAM-III, a multi-channel microcalorimeter of TA Instruments. Performing a measurement in TAM is more elaborate than doing a measurement in DSC. Like a DSC, the TAM has an instrument contribution, however, in the TAM the baseline is explicitly measured. The description of how to perform a measurement in TAM and how to measure the baseline is given in Chapter III section 2.3.4.

A zoom on the first two hours of the reaction is displayed in Figure IV-14 (bottom left). The graph is separated into three zones. The first zone (I – Temperature equilibration) is when the ampoule is in the equilibration position. During this period the ampoule is heated to the isothermal temperature of the TAM over at least 15 minutes. The second zone (II – Signal stabilization) is started when the sample is lowered into the measuring position and takes 45 minutes. During this period a heat flow is measured but is smeared due to the slowness of the instrument (see also Chapter II section 2.2.3). In the last zone (III - Measurement) the heat flow is measured accurately.

As in the isothermal DSC experiment, the heat flow starts at a high exothermal level, reducing as the reaction progresses. Looking at the last couple of hours of the experiment in the zoom (Figure IV-14 (bottom right)), still a heat flow is measured. Clearly, 20 hours after the start of
the reaction at 40 °C, the reaction is not finished yet. Also note that the noise on the heat flow cannot be clearly seen, implying that the reaction heat flow is still being recorded accurately (the absolute heat flow measured after 20 hours, 66 µW, is still well above the noise level of less than 1 µW). In the analysis of the isothermal DSC measurement of Figure IV-13, the reaction was assumed to be over after about 5 hours, while in TAM the reaction is clearly still ongoing, slowing down about a 10-fold in the next 15 hours. Although this is an important advantage of the TAM, it should be noted that it took one hour for the TAM to measure the heat flow accurately, therefore missing a significant amount of information, which was measured in DSC. There is thus a need for a method that can measure both the fast, initial reaction and the slow-changing tail of the reaction.

Figure IV-14. TAM-III heat flow signal for the reaction of a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst measured at 40 °C. (top) heat flow signal (solid) and baseline (dashed). (bottom left) A zoom of on the first two hours of the measurement. The different zones are separated by a dash dotted line. Zone I is the first 15 min when the ampoule is in the equilibration position, zone II is the next 45 min period for temperature stabilization, zone III gives the stable heat flow measurement. (bottom right) A zoom at the baseline level.
4.3 Combination of TAM and DSC

As established in the previous section, DSC is more suited for measuring faster processes taking a minutes to a few hours, but has the disadvantage that the baseline is not absolute, while TAM is suited for measuring slow processes taking a couple of hours up to several days, having a nearly absolute baseline when comparing it to the reaction heat flow. In this section, an approach will be described that uses both techniques to accurately measure the polyurethane reaction in its full complexity, exploiting the fast response of the DSC and the near absolute heat flow measurement of the TAM.

As the baseline level in TAM is known to a near-absolute level, compared to the reaction heat flows, the DSC heat flow curve is shifted up or down, so that it matches the heat flow curve measured in TAM (baseline level subtracted). This provides a near absolute baseline compensation for the DSC result. As the start of the measurement in DSC and TAM are not exactly the same, also a shift in time is needed. Because the preparation and temperature equilibration for an isothermal DSC experiment is much shorter than for one in TAM, the DSC time scale is used as a reference, adjusting the TAM time scale. Finally, there will be an additional time correction to compensate for the mixing procedure.

To automate this process, a numerical procedure was developed. The procedure starts by fitting a third order polynomial (eq. IV-14) through the heat flow measured in DSC over a time period starting from 50 minutes to 120 minutes after the start of reaction using a least square curve fitting algorithm.

$$\dot{Q}_{poly}^{DSC}(t) = a_1 + a_2 t + a_3 t^2 + a_4 t^3$$  \hspace{1cm} (eq. IV-14)

The fitting parameters $a_2$, $a_3$ and $a_4$ will describe the shape of the heat flow curve, while parameter $a_1$ determines the vertical position, which includes the contribution of the baseline. An example of a fit is given in Figure IV-15.

![Figure IV-15. The raw DSC and the third order polynomial fit of the measurements of a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst at 40 °C. The shaded red area is the fit region for the polynomial.](image-url)
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In a second step, a polynomial (eq. IV-15) is fitted through the heat flow of the TAM over a period starting from 60 minutes to 120 minutes after the measurements was started. The fitting parameters are $b_1$ resulting in vertical shift, and $t_c$ resulting in a horizontal shift, while the parameters $a_2, a_3$ and $a_4$ are the same as for the DSC polynomial, therefore keeping the shape identical to the DSC heat flow.

$$Q_{pol}^{TAM}(t) = b_1 + a_2(t - t_c) + a_3(t - t_c)^2 + a_4(t - t_c)^3 \quad (eq. \ IV-15)$$

By subtracting $b_1$ from $a_1$, the baseline contribution in DSC is calculated, which can be subsequently be subtracted from the measured DSC heat flow.

The time correction in TAM can be done by subtracting $t_c$ from the time signal. Note that $t_c$ is also measured externally, as during the mixing procedure the time needed to insert the sample in the DSC and TAM is recorded. However, this time might not be exactly the same. A reason for this, is that the samples used in DSC, having a size of a couple of milligrams, and TAM, being a few tenths of a gram, will not experience exactly the same temperature changes when being inserted into the devices. The DSC crucible will reach the device temperature within 10 seconds, while the TAM ampoule takes minutes to reach the device temperature. In case of a reaction temperature higher than ambient temperature, this will lead to a slower start-up of the reaction in TAM and thus a shift to later times, and vice versa. This effect is more pronounced for a larger temperature difference between the isothermal temperature and ambient temperature, and for larger TAM sample sizes.

The results of the DSC heat flow shift and TAM time shift manipulations can be seen in Figure IV-16. The heat flow measured in DSC at the start is much higher compared to the one measured in TAM, as a result of the much faster characteristic time scale of the DSC. After one hour both heat flows measured in DSC and TAM coincide for the next hours, meaning that both techniques are compatible. After four hours, the TAM result becomes much more reliable, as the DSC signal becomes smaller than its noise level.
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Figure IV-16. The raw DSC, vertically shifted DSC, the raw TAM and horizontally shifted TAM measurements of a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst at 40 °C. (top) The overall result. (bottom left) A zoom on the first two hours of the TAM heat flow, split up into three zones as in Figure IV-14. (bottom right) A zoom on the baseline level.

4.4 Calculating the reaction heat and its impact on the kinetics evaluation

4.4.1 Reaction during the sample preparation

With the combined calorimetry curve from DSC and TAM and knowing that the baseline of this curve is nearly zero, the reaction heat released during the reaction can be calculated by integrating the reaction heat flow (eq. IV-10). As the reaction rate is the highest at the start of the reaction and as the reaction is occurring at ambient temperature, it is important to note that the reaction heat \( \Delta H_{\text{prep}} \) released during the preparation of the reaction mixture, which takes about 3 minutes, is not measured. However, \( \Delta H_{\text{prep}} \) can be approximated by extrapolating the reaction heat flow measured for a combined calorimetry experiment at 25 °C backward over the time of preparation (Figure IV-17) (left). The extrapolation is done by fitting a second order polynomial function to the heat flow recorded from one to ten minutes, and extrapolating the curve backward to –3 minutes, thus incorporating the sample preparation time. The one-to-ten
minute interval is chosen because the heat flow signal in DSC is only stable one minute after starting the measurement. By integrating the extrapolated curve over the three minutes of preparation time, \( \Delta H_{\text{prep}} \) is estimated to be about -14 J.g\(^{-1}\). The reaction heat measured during a non-isothermal experiment for a stoichiometric MDI - PPG-425 mixture in which full cure was reached during the first heating was -221 J.g\(^{-1}\) (see section 3.2.1). The total reaction heat of the urethane formation is the sum of the preparation reaction heat and measured reaction heat of the non-isothermal experiment and is equal to -235 J.g\(^{-1}\), corresponding with a molar reaction enthalpy \( \Delta_r H \) of -80 kJ.mol\(^{-1}\). The extent of reaction during the preparation, \( x_{\text{prep}} \), is estimated to be 6.0 %. This is a significant contribution and therefore the preparation time had to be reduced to a minimum.

Due to the longer preparation time and the 15 minute equilibration period in TAM, an even higher amount of reaction heat is missed (Figure IV-17) (right). For the experiment done at 25 °C, the reaction heat missed corresponds with -58 J.g\(^{-1}\) and an extent of conversion of 25 %. Although it takes about one more hour for the transient TAM heat flow to stabilize to its real value, all heat evolved is measured after the insertion in the measurement position.

\[
\begin{align*}
\text{Figure IV-17. (left) The combined (DSC and TAM) reaction heat flow for a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst measured at 25 °C (solid), showing the extrapolated curve (dashed) and the reaction heat released during the preparation of the reaction mixture } \Delta H_{\text{prep}} \text{ (green shaded area). (right) TAM and combined and extrapolated reaction heat flows and missed reaction heat in TAM (blue shaded area).}
\end{align*}
\]

4.4.2 Effect of defining the correct baseline for DSC

A zoom on the baseline of the combined experiment is shown in Figure IV-18, including also the shifted DSC curve. From four hours onwards, the DSC heat flow deviates from the heat flow measured in TAM, because the DSC is not designed to measure heat flow on this scale. For a 10 mg sample, which is a reasonable sample mass for a long isothermal measurement, the absolute heat flow measured in DSC four hours after the start of the reaction is -15.4 µW. The heat flow accuracy of the Discovery DSC that was employed is ± 10 µW, which is in the same order of magnitude as the absolute measured heat flow.\(^7\) The noise on the DSC heat flow starts to become noticeable at this heat flow level, which is justified as the noise according to the
specifications is below 0.08 µW. For comparison: the absolute heat flow measured in TAM for a sample of 0.5 g is -0.768 mW where the accuracy in TAM is better than 1 µW, which is far below the measured heat flow.

If only DSC was used, the baseline would be estimated using the average heat flow over last hour of the measurement, implying some of the reaction heat would not be accounted for. Using the shifted DSC heat flow and the correct baseline from TAM, this missed heat can be calculated as the area of the rectangle in Figure IV-18, amounting to -23 J.g\(^{-1}\) and corresponding with 9.8 % missed extent of reaction.

![Figure IV-18. The shifted DSC and combined heat flow for a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst measured at 40 °C, zoomed in on the baseline. Red-shaded area represents the reaction heat missed if the DSC baseline is used.]

4.4.3 Effect of errors when calculating conversion profiles

The effects of improving the baseline selection for DSC and accounting for the reaction during preparation can be illustrated using the conversion profiles for the reaction of a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst at 40 °C, given in Figure IV-19.

When only using a TAM for investigating the polyurethane experiments, about 40% of the reaction heat is missed, comprising 6 % missed during the sample preparation and 34 % during the 15-minute period the sample must thermally equilibrate in the TAM.

The conversion for the DSC measurement initially coincides with the combined experiment and start to deviate visibly from it when a conversion of about 65 % is reached. This is caused by the incorrect estimation of the baseline in DSC, and about 10 % of the reaction conversion is missed due to it in this experiment. The kinetic evaluation of the reaction at high conversion suffers the most from this effect, as will be discussed in the next section.

The effect of estimating and including the preparation is significant as otherwise 6.0 % conversion remains unaccounted for. The conversion reached using the combined DSC and TAM information, including the preparation, is 99.5 %. The remaining reaction could still be measured as the heat flow is still accurately measured in TAM (Figure IV-14 (bottom right)).
Figure IV-19. The conversion profiles calculated for DSC, TAM, combined and combined including preparation for a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst at 40 °C (solid) and their final extent of conversion (dashed).

4.4.4 Influence of the corrections on kinetic evaluation

The conversion rate of the reaction can be calculated by dividing the reaction heat flow by the total reaction heat.

\[
\frac{dx}{dt} = \frac{\dot{H}(t)}{\Delta H_{\text{tot}}} \quad \text{(eq. IV-16)}
\]

The choice of the baseline level and whether to include the preparation or not will influence the calculation of the reaction heat flow \( \dot{H} \), and subsequently the conversion rate. By assuming the urethane reaction is an \( n \)th order reaction, the conversion rate can be written in following forms:

\[
\frac{dx}{dt} = k(1 - x)^n \quad \text{(eq. IV-17)}
\]

\[
\log \left( \frac{dx}{dt} \right) = \log(k) + n \log(1 - x) \quad \text{(eq. IV-18)}
\]

Where \( k \) is the reaction rate constant, expressed in s\(^{-1}\). By plotting the logarithm of the experimental reaction rate as calculated by (eq. IV-16) versus the logarithm of one minus the measured extent of reaction, the overall reaction order \( n \) can be determined from the slope of this curve, while the reaction rate constant is found at the intercept with the y-axis. Such a plot is given in Figure IV-20 based on the results of the isothermal experiments in DSC and TAM.
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from Figure IV-16, applying the different corrections. The analysis of the reaction order and accompanying reaction rate constant is given in Table IV-1. In this chapter, only the impact of the techniques and methodology will be discussed, while a comprehensive analysis of the polyurethane reaction kinetics and reaction orders will be discussed in Chapters V, VI and VII.

Figure IV-20. Kinetic analysis for the reaction of a stoichiometric MDI – PPG-425 system with 0.04 w% catalyst at 40 °C. Double logarithmic plot of the reaction rate $dx/dt$ as a function of their respective $(1-x)$ for (left) DSC, TAM, combined and combined including preparation, and (right) the improved results for DSC including preparation and TAM with the reverse integration. The blue- and the red-shaded area are the conversion ranges between 10% to 30% and 60% to 80% respectively.

The most correct calculation of the extent of reaction and the accompanying reaction rate is obtained for the combined DSC and TAM method with the inclusion of the preparation time (Comb & prep in Figure IV-20). The reaction order, the slope of the curve, changes gradually from 2.70 in the conversion range between 0.10 to 0.30, to 1.88 in the conversion range between 0.60 to 0.80 (see also Table IV-1).

Using the combined curve without including the preparation time (Comb), the curve shifts to the right and curves downwards with increasing conversion (right to left). The reaction order of 2.69 in the low conversion region is very close to the one for the combined curve with preparation, but it deviates increasingly as the reaction progresses. This lower reaction rate could be misinterpreted as a diffusion control effect. The analysis based on the DSC curve only is similar, with a sharp deviation starting at 60 % (DSC). Using the raw data from TAM only is clearly not a reliable approach for kinetic evaluations of fast (polyurethane) reactions (TAM).

The quality of the individual DSC and TAM experiments can be improved upon by introducing corrections based on these individual measurements only. For a DSC experiment, the preparation can be included as described in section 4.4.1., which makes the curve coincide with the combined curve with preparation up to 50% conversion (DSC & Prep). This indicates kinetic analysis based on DSC only could be safely used in a low conversion range.
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Table IV-1 The reaction orders and reaction rates determined by (eq. IV-18) for the different techniques, highlighting the effect of the corrections.

<table>
<thead>
<tr>
<th>Method</th>
<th>( x ) range</th>
<th>( 0.10 - 0.30 )</th>
<th>( 0.60 - 0.80 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>( \log (k) )</td>
<td>( n )</td>
</tr>
<tr>
<td>Comb &amp; prep</td>
<td>2.62</td>
<td>3.11</td>
<td>1.87</td>
</tr>
<tr>
<td>Comb</td>
<td>2.66</td>
<td>3.18</td>
<td>2.33</td>
</tr>
<tr>
<td>DSC</td>
<td>2.72</td>
<td>3.19</td>
<td>-</td>
</tr>
<tr>
<td>DSC &amp; prep</td>
<td>2.66</td>
<td>3.11</td>
<td>2.54</td>
</tr>
<tr>
<td>TAM</td>
<td>4.03</td>
<td>3.61</td>
<td>-</td>
</tr>
<tr>
<td>TAM rev.</td>
<td>-</td>
<td>-</td>
<td>1.87</td>
</tr>
</tbody>
</table>

To correctly estimate the extent of reaction in TAM, (eq. II-47) cannot be used as a large fraction of the reaction heat is missed during preparation and equilibration. Instead of calculating the conversion from the start of the reaction, which is not well known, the reaction heat is calculated starting from the total reaction heat. To calculate the heat released up to time \( t \), the heat released from time \( t \) till the end of the measurement \( t_{\text{end}} \) is subtracted from the total reaction heat. This method is will be called reverse integration. At first one could assume that full cure was achieved during the TAM measurement. However, as can be seen in Figure IV-14 (bottom right), the urethane reaction is still ongoing and some reaction heat is unaccounted for in that case. This reaction heat \( \Delta H_{\text{end}} \) was approximated by the area of a triangle with base \( t_{\text{end}} \) and height \( \dot{H}(t_{\text{end}}) \), resulting in (eq. IV-19). The resulting kinetic analysis can be found as (TAM rev.) in Figure IV-20 (right). The reaction order and rate constant for the higher extents of reaction obtained from the TAM only data using this reverse integration approach are close to the ones obtained using the combined curve with preparation (Table IV-1).

\[
\Delta H(t) = \Delta H_{\text{tot}} - \int_{t}^{t_{\text{end}}} \dot{H}(t) dt + \Delta H_{\text{end}} \quad \text{(eq. IV-19)}
\]

As an extension to the reaction order analysis of Figure IV-20, an evaluation of the reaction rate as a function of the extent of reaction is shown in Figure IV-21 (left) for the different approaches. The reaction rate is the highest a low conversion and the reaction slows down as it progresses. Autocatalysis is not observed in these curves. While the combined DSC and TAM data including preparation (Comb & prep) can be used from the lowest extent of reaction to the highest extent of reaction, the DSC curve can only reliably be used from the lowest extent of reaction up to about 60%, when the heat flow has decreased to -21 µW or about 2 times the noise level (DSC & prep). At lower heat flows, the kinetic analysis becomes too strongly influenced by the noise (this noise level is instrument dependent, of course). For TAM only,
using the reverse integration method, the heat flow is reliable from an extent of reaction of about 50% to the final conversion reached.

Figure IV-21 shows the instantaneous reaction order, determined by differentiating (eq. IV-18) versus log(1-x), as a function of the reaction conversion. The numerical differentiating must be done carefully, using third order Lagrange interpolation, as effects of noise are enhanced in the numerical differentiation. The reaction order starts close to three at a reaction conversion of 15% and gradually lowers to an order of 1.8 at a conversion of 90%. This decrease in the reaction order indicates the reaction is not simply a third order reaction, which could be a self-catalyzed reaction between isocyanate and alcohol, but rather follows a more complex reaction mechanism. The effect of noise on the calculation of the reaction order of the combined curve and the DSC curve can be noticed from an extent of conversion of 50% onwards; it is caused by the noise measured in DSC. From a conversion of 65% onwards, the reaction order can again be determined more reliably with the combined curve, because from this point onwards the reaction heat flow and reaction heat are calculated using the more stable TAM data.

These results illustrate that for a more comprehensive kinetic analysis of the polyurethane polymerization, using a combination of approaches that are suitable to measure the fast initial reactions and others to measure the slow, drawn-out reaction tails is crucial.

5 Kinetic analysis using model free kinetics

Starting from calorimetric measurements of the urethane formation in both isothermal and non-isothermal conditions, the kinetics can be evaluated using the same model free kinetics strategy as was elaborated in section 2 for the TGA analyses. For this end, the conversion and conversion rate are calculated using the reaction heat flow, of course, instead of using the weight lost and its time derivative. For selected extents of conversion, the conversion rate and the corresponding temperature can be derived from the corresponding reaction heat flow. In general, when selecting the range of conversions for an MFK analysis, conversions close to zero and
one are poorly evaluated, as the impact of the baseline selection and related errors in calculating the conversion are more important. For the urethane formation, the significant progress of the reaction during preparation prevents detailed analyses at low conversions. In case of non-isothermal experiments, the incomplete cure at the end of the first heating will also limit the higher end of the range of conversions for which the MFK analysis can be performed.

Using (eq. IV-3), the activation energies can be determined for data derived from sets of isothermal, non-isothermal and combined sets of experiments. For non-isothermal measurements, the temperatures \( T_x \) are the temperatures at the time when a selected conversion \( x \) is reached. For isothermal measurements, \( T_x \) is simply the isothermal temperature itself, remaining constant throughout the experiment. As the reaction peak shifts to higher temperatures with increasing scanning rates, the \( T_x \) for experiments done at higher scanning rates will also be higher than the ones obtained from experiments at lower scanning rate. Combining the conversion rates and temperatures of experiments in isothermal and non-isothermal conditions extends the investigated temperature range, thereby improving, in theory, the temperature region over which the obtained activation energies are valid.

The natural logarithm of the conversion rate as function of the inverse temperature of both the isothermal and the non-isothermal results using the Friedman method is given in Figure IV-22 (left). The plotted line is a line is fitted through the data points of both non-isothermal and isothermal measurements. The using the slope of the line, the activation energy is calculated (eq. IV-3). The activation energy of the urethane reaction calculated with the isothermal only, non-isothermal only and the combined isothermal and non-isothermal data points is given in Figure IV-22 (right). The activation energy evolution of the three curves is quite different, with the activation energy at 15% conversion being 41 kJ.mol\(^{-1}\), 36 kJ.mol\(^{-1}\) and 29 kJ.mol\(^{-1}\) for the non-isothermal, isothermal and combined measurements respectively. The activation energy using the isothermal result only remains approximately constant within the investigated conversion range. While the activation energy of the non-isothermal measurement is approximately constant while the conversion is below 40% and after 40% rapidly decreases. The baseline for the non-isothermal measurements at high temperature is less well known and might be an explanation for the evolution of the energy. A possible reason for the difference in activation energy between the isothermal and non-isothermal measurements is that several competing and/or independent reactions are happening which have a different importance as function of temperature.\(^9\) The allophanate formation is one of these reactions which only becomes important at elevated temperatures (see section 3.2.3). The activation energy using both non-isothermal and isothermal results lead to activation energy lower than both the individual measurements. This approach assumes that the mechanism reaction for both non-isothermal and isothermal measurement remains the same over the whole temperature interval. As this is not the case, it makes using this approach less reliable than the individual measurement in their respective temperature region.
A difference in activation energy between isothermal and non-isothermal experiments for polyurethane have also been observed in literature but for aliphatic isocyanates with aliphatic alcohols in the presence of a tin catalyst making them hard to compare with measured results.

Figure IV-22. (left) The natural logarithm of conversion rates as function of the inverse of the temperature of the non-isothermal (*) and isothermal (x) measurements for conversions of 15%, 25%, 35%, 45%, 55% and 65%. (right) The resulting activation energies as function of the conversion.

6 Conclusions

For a comprehensive analysis of the polyurethane kinetics over a sufficiently large temperature range to be useful for applications, a combination of non-isothermal and isothermal experiments will be needed. Non-isothermal measurements are essential in determining the glass transition temperatures of the polymer of both the initial unreacted and the fully cured polymer. Non-isothermal measurements also give the total reaction heat released during the reaction and provide kinetic information over a broad temperature interval. Difficulties in these measurements arise due to the cold crystallization and melting of the MDI and determining the baseline of the measurement. A baseline is constructed by using the heat capacity of the uncured and the fully cured material, which are joint using the extent of reaction evolution. An approximated sigmoidal curve, an adapted logistic curve, was substituted for the conversion profiles in order to join the heat capacity evolution curves.

Isothermal measurements are very suited to help determine reaction mechanism of reactions. Two isothermal techniques DSC and TAM were used. In the DSC, an isothermal baseline must be subtracted in order to obtain the reaction heat flow. The baseline was constructed by using the average heat flow the last hour of an isothermal measurement, where for the urethane formation this cannot be clearly observed in DSC. In the TAM measurement, during the first 1 hour after inserting the sample in the device, no accurate heat flow can be measured. After this period the reaction heat flow is measured with a nearly zero baseline. The two techniques were combined to cope with the limitations of individual techniques leading to good information at the start of the reaction and an accurate measurement of the reaction at the end of the reaction. Using the combined method, the kinetics can be determined over the whole measured extent of
reaction. The reaction order of the urethane formation with 0.04w% catalyst changes from an order of 3 at the start of the reaction where the extent of reaction is 15% and lowers gradually to an order 1.8 when the conversion reaches a value of 90%.

The results of the MFK for the isothermal, non-isothermal and combined measurements give different results indicating that different reaction mechanism become important at different temperature ranges. The activation energy is more reliable for the non-isothermal measurement at high temperature while for the isothermal measurement more reliable results are obtained at low temperature.
Calorimetric method development for analyzing polyurethane reaction kinetics

7 References


CHAPTER V

POLYURETHANE KINETICS WITH MONOFUNCTIONAL ALCOHOLS

1 Introduction

Knowing the reaction mechanism behind the urethane formation is of vital importance for the further development of the prediction of chemorheological behavior. The goal of this chapter is to obtain a mechanistic model, a plausible reaction mechanism with kinetic parameters, which can describe the kinetics of the urethane formation for a wide range of compositions and temperatures.

Two major types of polyol backbones are used industrially to produce polyurethanes, namely polyether and polyester glycols, and in this work the former type is used. The most frequently used polyether glycols come in the form of polyethylene glycols (PEG) and polypropylene glycols (PPG) or a combination of the two. These multifunctional base components come in the form of linear or branched structures, depending on the starting monomer, catalysts used, and the reaction conditions. In this chapter, the reaction kinetics are first investigated using monofunctional reagents, chemically closely resembling the industrially used polyols. Monofunctional reagents are chosen as they reduce the viscosity increase, reducing the effects of diffusion limitations on the reaction, and as they are often available in higher purity. This makes them more suited as model reagents.

First, the thermochemistry of the urethane reaction is investigated. This is done using the group additivity methods first developed by Benson. In this method, molecular properties of a molecule or a piece of molecule, like the formation enthalpy, heat capacity, entropy,… can be predicted by adding up the properties of the individual structural units or groups present. The group contributions are determined using a large set of molecules for which the properties were accurately measured. By increasing the number of molecules on which the groups are based, the molecular properties of a new molecule are estimated with a higher degree of accuracy. The reaction enthalpy of the urethane bond and the allophanate bond and the formation enthalpies of the different compounds in the reaction mixture will be calculated using this method.

The reactivity of primary and secondary alcohols in the formation of urethane bonds are different, with primary alcohols reacting faster than secondary alcohols, as reported in literature. To be able to investigate the urethane reaction, which has a significant reactivity at room temperature, it was opted to study the urethane formation with slower secondary alcohols first. Cyclohexanol was selected as model component for investigating the reaction of isocyanate with secondary alcohols, while diethylene glycol methyl ether (DEGME) was
selected as model system for investigating the reaction of primary alcohols. MDI, the most commonly used aromatic isocyanate, was used as the isocyanate reagent. The reaction kinetics were investigated experimentally using calorimetric techniques (DSC and TAM). The reaction enthalpy of the urethane formation measured using calorimetry will be confronted with the results obtained for the group additivity method. In a next step, the total and partial reaction orders of the urethane formation are derived. Using a model free kinetic method, the activation energy of the overall reaction can be estimated.

Reaction mechanisms presented in literature are implemented and compared to the measured kinetics. These models proved unsatisfactory for predicting the experimentally obtained kinetics. Therefore, an ionic model inspired by the catalyzed urethane reaction and aided by the experimentally derived (partial) reaction orders, was developed. Starting from initial values predicted by the model free kinetics, the kinetic parameters were adjusted using a least square optimization algorithm comparing the reaction heat flow of the model and the calorimetric experiments.

2 Materials

The MDI isocyanate used in this chapter is a mixture of MDI44 and MDI24 in a mixing ratio of 63 w% and 37 w%, respectively (see Table III-1). The alcohol monomers can be divided into the primary alcohols of diethylene glycol methyl ether (DEGME) and 1-hexanol, and secondary alcohol cyclohexanol. Dipropylene glycol dimethyl ether (DPGDME) is used as a hydroxyl-free source of ether groups.

3 Thermochemistry

3.1 The urethane formation

The reaction thermodynamics of the urethane formation at 298.15 K can be estimated using the group additivity method, which is based on the nearest-neighbor approximation and the liquid phase contributions. The formation enthalpy of a molecule can be calculated by the following formula:

\[ \Delta_f H^\circ(molecule) = \sum_{i=1}^{m} n_i \Delta_f H^\circ_i + C \]

(eq. V-1)

Where \( \Delta_f H^\circ \) is the formation enthalpy of a molecule (or a part of a molecule), \( \Delta_f H^\circ_i \) is the group contribution of group \( i \) to the formation enthalpy, \( n_i \) is the number of those groups building up the molecule, and \( C \) is a correction term that includes, among others, ring corrections, gauche corrections, and ortho and para substitutions.

Using the formation enthalpies of the reacting functional groups of the reagents (primary alcohol OH\(_\text{p}\), secondary alcohol OH\(_\text{s}\), aromatic isocyanate NCO) and of the formed functional
Polyurethane kinetics with monofunctional alcohols

groups in the product (urethane), the reaction enthalpy can be estimated. Depending on whether
the urethane bond was formed out of a primary or a secondary alcohol, a different reaction
enthalpy will be found. To differentiate between these two urethanes, they will be named
primary urethane UR\textsubscript{p} and secondary urethane UR\textsubscript{s}. A schematic with the functional groups and
indicating the groups needed to calculate the reaction enthalpy is given in Figure V-1.

![Figure V-1. Schematic of the urethane formation indicating the groups needed to calculate
the reaction enthalpy. All other groups remain unaffected by the reaction.]

The values for the formation enthalpies in the liquid state $\Delta f H^0$ (liq) of groups I, II, IV, V and
VIII were tabulated by Domalski and Hearing in a huge compilation of group additivity
contributions covering 1512 compounds containing the elements: carbon, hydrogen, oxygen,
nitrogen, sulfur, and halogens in the gas, liquid, and solid phases, and providing about 1000
references for the literature values cited. Group VI is not tabulated and, to the best of our
knowledge, has not been calculated yet in literature, while the formation enthalpy of group III
and VII in the liquid state is not tabulated. The lack of thermochemical information for such an
industrially important and ‘old’ reaction is striking, but is better understood in the context of
the discussion of the difficulties for accurate calorimetric studies in Chapter IV.

The $\Delta f H^0$ (liq) of group III, VI and VII can be estimated by looking up a reference molecule
with a known formation enthalpy in the liquid state containing group in question \( j \) and
subtracting all other groups from the formation enthalpy (using (eq. V-1)):

$$n_j \Delta f H^0_j = \Delta f H^0(molecule) - \sum_{\substack{i=1 \\ i \neq j}}^{m} n_i \Delta f H^0_i - C$$

(\textit{eq. V-2})

Phenyl isocyanate was selected as the reference molecule for group III. For group VI ethyl
carbamate and methyl carbamate were chosen as reference molecules. N-phenyl acetamide can
be used for the calculation of group VII, however a direct measurement of the formation
enthalpy in the liquid state of this molecule is not given. It can be indirectly determined using
the reaction enthalpy of the reaction in Figure V-2, where the formation enthalpy in the liquid
state of all other molecules are known.
Figure V-2. The formation reaction of n-phenyl acetamide with known reaction enthalpy of $-100.9 \pm 0.3$ kJ.mol$^{-1}$, used to estimate the formation enthalpy contribution of group VII.$^{12}$

The calculations and the results for groups III, VI and VII can be found in Table V-1. Even though the chemical structure of ethyl carbamate and methyl carbamate are quite similar, the resulting formation enthalpy of CO-(N)(O), group VII, estimated from their data is $-153.97$ and $-165.17$ kJ.mol$^{-1}$, respectively. The difference between the two is about 11 kJ.mol$^{-1}$, which is quite significant. A possible explanation for the difference between the two, is the high polarity of the urethane group, which in the liquid state lead to strong hydrogen bonding, influencing the formation enthalpy. Note that the nitrogen in CO-(N)(O), group VII, in the ethyl carbamate and methyl carbamate is quite different from the one in the aromatic urethane of Figure V-1, which is attached to an aromatic ring.

Knowing the formation enthalpy of groups I to VIII, the formation enthalpy of the molecular parts given in Figure V-1 can be calculated. Next, the reaction enthalpy of the urethane bond formation can be calculated by subtracting the formation enthalpy of the alcohol and the isocyanate part of the reagents from the formed urethane molecular part. For the primary urethane, this results in $-109$ kJ.mol$^{-1}$. The reaction enthalpy between n-butanol and phenyl isocyanate, leading to a primary urethane, was experimentally measured to be $-83.9 \pm 4$ kJ.mol$^{-1}$. This gives a big difference (25 kJ.mol$^{-1}$) between the predicted reaction enthalpy and the measured reaction enthalpy. A possible explanation for the large difference is the less well estimated value of the CO-(N)(O) group (group VII), where the nitrogen is attached to an aromatic ring and the chemical environment is less polar. Using the experimentally obtained reaction enthalpy for the reaction between n-butanol and phenyl isocyanate, which is considered to be a better model for estimating the group than the ethyl carbamate and methyl carbamate molecules, the formation enthalpy of the CO-(N)(O) group is estimated to be $-134.81$ kJ.mol$^{-1}$.

Figure V-3. The reference molecules for the calculation of groups III, VI and VII (see Table V-1): a) Phenyl isocyanate, b) N-phenyl acetamide, c) Ethyl carbamate, d) Methyl carbamate
Table V-1 Calculations of groups III, VI and VII

<table>
<thead>
<tr>
<th>Phenyl isocyanate</th>
<th>$n_i$</th>
<th>$\Delta h^o_1$ (liq) (\text{kJ.mol}^{-1})</th>
<th>N-phenyl acetamide</th>
<th>$n_i$</th>
<th>$\Delta h^o_1$ (liq) (\text{kJ.mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB-(H)(CB)$_2$</td>
<td>5</td>
<td>8.16</td>
<td>CB-(H)(CB)$_2$</td>
<td>5</td>
<td>8.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CB-(N)(CB)$_2$</td>
<td>1</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO-(N) (C)</td>
<td>1</td>
<td>-185.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-(H)$_3$(CO)</td>
<td>1</td>
<td>-47.61</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>40.8</td>
<td>Total</td>
<td></td>
<td>-190.31</td>
</tr>
<tr>
<td>$\Delta h^o_1$ (liq)</td>
<td>-33.9</td>
<td>$\text{kJ.mol}^{-1}$</td>
<td>$\Delta h^o_1$ (liq)</td>
<td>-211.08</td>
<td></td>
</tr>
</tbody>
</table>

Estimated:

<table>
<thead>
<tr>
<th>Ethyl carbamate</th>
<th>$n_i$</th>
<th>$\Delta h^o_1$ (liq) (\text{kJ.mol}^{-1})</th>
<th>Methyl carbamate</th>
<th>$n_i$</th>
<th>$\Delta h^o_1$ (liq) (\text{kJ.mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-(H)$_2$(CO)</td>
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<td>N-(H)$_2$(CO)</td>
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<td>1</td>
<td>-196.02</td>
<td>O-(C)(CO)</td>
<td>1</td>
<td>-196.02</td>
</tr>
<tr>
<td>C-(H)$_2$(O)(C)</td>
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<td>-35.80</td>
<td>C-(H)$_3$(C)</td>
<td>1</td>
<td>-47.61</td>
</tr>
<tr>
<td>C-(H)$_3$(C)</td>
<td>1</td>
<td>-47.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
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<td>-343.33</td>
<td>Total</td>
<td></td>
<td>-307.53</td>
</tr>
<tr>
<td>$\Delta h^o_1$ (liq)</td>
<td>-497.30</td>
<td>$\text{kJ.mol}^{-1}$</td>
<td>$\Delta h^o_1$ (liq)</td>
<td>-472.70</td>
<td></td>
</tr>
</tbody>
</table>

Estimated:

| CO-(N)(O)         |       | -153.97                         | CO-(N)(O)         |       | -165.17                         |

Ideally, reliable experimental thermochemical data of a larger number of molecules would be used to estimate the contributions for groups for which values are missing. This would make the groups more reliable, and might provide information for corrections that account for the specificity of certain groups, like for distinguishing the contribution for a carbamate and a urethane group.

---

*a* Value for $\Delta h^o_1$ (liq) not given in NIST. $\Delta h^o_1$ (liq) is calculated out of the reaction enthalpy $\Delta h^o$ in the liquid phase between $\text{C}_4\text{H}_6\text{O}_3 + \text{C}_6\text{H}_7\text{N} = \text{C}_8\text{H}_9\text{NO} + \text{C}_2\text{H}_4\text{O}_2$, acetic anhydride + Aniline = N-phenyl acetamide + acetic acid.\textsuperscript{34}
Table V-2 The groups building the primary and secondary alcohol and aromatic isocyanate reagents and the primary and secondary urethane products, with their numbers as indicated in Figure V-1. The group formation enthalpies in the liquid state are taken from, with the exception of groups III, VI and VIII, which are calculated in Table V-1 and are colored.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$\Delta H^\circ_i$ (liq) kJ.mol$^{-1}$</th>
<th>Product</th>
<th>$\Delta H^\circ_i$ (liq) kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary alcohol OH$_p$</strong></td>
<td></td>
<td><strong>Primary urethane UR$_p$</strong></td>
<td></td>
</tr>
<tr>
<td>I C-(H)$_2$(O)(C)</td>
<td>-35.80</td>
<td>IV C-(H)$_2$(O)(C)</td>
<td>-35.80</td>
</tr>
<tr>
<td>II O-(H)(C)</td>
<td>-191.50</td>
<td>V O-(C)(CO)</td>
<td>-196.02</td>
</tr>
<tr>
<td><strong>Phenyl isocyanate NCO</strong></td>
<td></td>
<td>VI CO-(N)(O)</td>
<td>-159.57/-134.81</td>
</tr>
<tr>
<td>III CB-(CNO)(CB)$_2$</td>
<td>-74.70</td>
<td>VII N-(H)(CB)(CO)</td>
<td>-20.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VIII CB-(N)(CB)$_2$</td>
<td>1.50</td>
</tr>
<tr>
<td><strong>Secondary alcohol OH$_s$</strong></td>
<td></td>
<td><strong>Secondary urethane UR$_s$</strong></td>
<td></td>
</tr>
<tr>
<td>I C-(H)(O)(C)$_2$ (alcohol, peroxide)</td>
<td>-27.60</td>
<td>IV C-(H)(O)(C)$_2$ (ether, ester)</td>
<td>-21.00</td>
</tr>
<tr>
<td>II O-(H)(C)</td>
<td>-191.50</td>
<td>V O-(C)(CO)</td>
<td>-196.02</td>
</tr>
<tr>
<td><strong>Phenyl isocyanate NCO</strong></td>
<td></td>
<td>VI CO-(N)(O)</td>
<td>-159.57/-134.81</td>
</tr>
<tr>
<td>III CB-(CNO)(CB)$_2$</td>
<td>-74.70</td>
<td>VII N-(H)(CB)(CO)</td>
<td>-20.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VIII CB-(N)(CB)$_2$</td>
<td>1.50</td>
</tr>
</tbody>
</table>

3.2 The allophanate formation

The reaction enthalpy of the formation of the allophanate group from a urethane and an isocyanate (Figure V-4) can also be determined using the group additivity method. Depending on whether the allophanate is formed out of a primary urethane or a secondary urethane will influence the formation enthalpy and therefore the two allophanates are distinguished as a primary allophanate AL$_p$ and a secondary allophanate AL$_s$. The calculation and the results are given in Table V-3.

Using the formation enthalpies of the primary and secondary urethane and the primary and secondary allophanate, the reaction enthalpy of these reactions (Figure V-1 and Figure V-4) can be calculated (see Table V-4). The difference between the reaction enthalpy of the primary and secondary urethane is 6.6 kJ.mol$^{-1}$, while there is no difference in reaction enthalpy between the formation of primary and secondary allophanate from isocyanate and their respective urethanes. The reaction enthalpy for the allophanate reaction is -58.1 kJ.mol$^{-1}$, which is close to the value of -54.5 kJ.mol$^{-1}$ obtained by ab initio calculations. Determining the formation enthalpy of allophanate experimentally is not straightforward as this is an equilibrium reaction.

The estimated reaction enthalpies for the urethane reaction will be compared with experimentally measured enthalpies in the next section and will be implemented for the calculation of the reaction heat flow in the kinetic modeling in section 5.
Table V-3 The groups building the primary and secondary alcohol and aromatic isocyanate reagents and the primary and secondary urethane products, with their numbers corresponding to the schematic Figure V-1. The formation enthalpy in the liquid state are taken from with the exception of group VI CO-(N)(O)°

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Δ(\Delta H^0(\text{liq}))</th>
<th>Product</th>
<th>Δ(\Delta H^0(\text{liq}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ.mol(^{-1})</td>
<td></td>
<td>kJ.mol(^{-1})</td>
</tr>
<tr>
<td><strong>Primary urethane UR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV  C-(H)(_2)(O)(C)</td>
<td>-35.80</td>
<td>IV  C-(H)(_2)(O)(C)</td>
<td>-35.80</td>
</tr>
<tr>
<td>V   O-(C)(CO)</td>
<td>-196.02</td>
<td>V   O-(C)(CO)</td>
<td>-196.02</td>
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<tr>
<td>VI  CO-(N)(O)</td>
<td>-134.81*</td>
<td>VI  CO-(N)(O)</td>
<td>-134.81*</td>
</tr>
<tr>
<td>VII N-(H)(CB)(CO)</td>
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<td>-20.77*</td>
</tr>
<tr>
<td>VIII CB-(N)(CB)(_2)</td>
<td>1.50</td>
<td>VIII 2 x CB-(N)(CB)(_2)</td>
<td>2 x 1.50</td>
</tr>
<tr>
<td><strong>Phenyl isocyanate NCO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III CB-(CNO)(CB)(_2)</td>
<td>-74.70</td>
<td>IX N-(C)(CO)(_2)</td>
<td>56.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Secondary urethane UR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV  C-(H)(O)(C)(_2) (ether, ester)</td>
<td>-21.00</td>
<td>IV  C-(H)(O)(C)(_2) (ether, ester)</td>
<td>-21.00</td>
</tr>
<tr>
<td>V   O-(C)(CO)</td>
<td>-196.02</td>
<td>V   O-(C)(CO)</td>
<td>-196.02</td>
</tr>
<tr>
<td>VI  CO-(N)(O)</td>
<td>-134.81*</td>
<td>VI  CO-(N)(O)</td>
<td>-134.81*</td>
</tr>
<tr>
<td>VII N-(H)(CB)(CO)</td>
<td>-20.77*</td>
<td>VII N-(H)(CB)(CO)</td>
<td>-20.77*</td>
</tr>
<tr>
<td>VIII CB-(N)(CB)(_2)</td>
<td>1.50</td>
<td>VIII 2 x CB-(N)(CB)(_2)</td>
<td>3.00</td>
</tr>
<tr>
<td><strong>Phenyl isocyanate NCO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III CB-(CNO)(CB)(_2)</td>
<td>-74.70</td>
<td>IX N-(C)(CO)(_2)</td>
<td>56.20</td>
</tr>
</tbody>
</table>

Figure V-4. Schematic of the allophanate formation indicating the groups needed to calculate the reaction enthalpy. All other groups remain unaffected by the reaction.
Table V-4 The calculated reaction enthalpy of the primary and secondary urethane group and the primary and secondary allophanate group using the formation enthalpy calculated in Table V-2 and Table V-3

<table>
<thead>
<tr>
<th>Estimated reaction enthalpy</th>
<th>$\Delta H^0$ (liq) (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^+_p$ + NCO $\rightarrow$ UR$^+_p$</td>
<td>-83.90</td>
</tr>
<tr>
<td>OH$^+_s$ + NCO $\rightarrow$ UR$^+_s$</td>
<td>-77.30</td>
</tr>
<tr>
<td>UR$^+_p$ + NCO $\rightarrow$ AL$^+_p$</td>
<td>-58.10</td>
</tr>
<tr>
<td>UR$^+_s$ + NCO $\rightarrow$ AL$^+_s$</td>
<td>-58.10</td>
</tr>
</tbody>
</table>

4 Experimental evaluation of the reaction kinetics

4.1 Reaction of isocyanate with secondary alcohols

The kinetics of the reaction of isocyanate with the slower secondary alcohols was studied using calorimetry in non-isothermal and isothermal conditions for stoichiometric mixtures, as well as for different stoichiometric ratios.

4.1.1 Effect of temperature

The results of a non-isothermal measurement at a heating rate of 5 K·min$^{-1}$ showing the first and second heating is given in Figure V-5. The reaction peak observed in the first heating starts at -10 °C, reaches a maximum at 58 °C, and slow down afterwards, never to reach full cure during the heating. The area of the observed reaction exotherm amounts to -298 J·g$^{-1}$. In the second heating the full cure glass transition temperature is measured at 45 °C. As a consequence, isothermal experiments performed at temperatures below 45 °C will potentially exhibit diffusion-controlled conditions.

The results of an isothermal MTDSC experiment at 25 °C is given in Figure V-6. The 600-minute isothermal measurement was performed in two segments. The first segment of 10 minutes is measured in standard DSC mode, while the remaining second segment is measured in modulated mode with an amplitude of 0.5 K and a period of 60 s. The data acquisition in conventional mode is faster than in modulated mode, where at least 3 periods must be passed before a measurement point can be determined. As the urethane reaction is the fastest at the start, the fastest experimental method was used. After the fast start, the heat flow slows down more and more gradually as the reaction continues. The reversing heat capacity starts at the highest value and lowers in accordance with the reaction progress. A second drop in the heat capacity, the starting of which is observed after 5 hours of measurement, corresponds with vitrification of the sample. As the reaction rate in the vitrified state is lower than in the mobile state, vitrification should result in a lowered heat flow, however, this effect is not clearly observed. During the 10 hours isothermal cure only partial vitrification was achieved.
Polyurethane kinetics with monofunctional alcohols

Figure V-5. Result of a non-isothermal HCH measurement at 5 K.min$^{-1}$ for a stoichiometric MDI-cyclohexanol mixture, measured in DSC, showing the first heating, second heating and the baseline.

Figure V-6. Result of an isothermal MTDSC experiment at 25 °C for a stoichiometric MDI-cyclohexanol mixture, with the reaction heat flow measured in DSC and MTDSC and reversing heat capacity. (left) first hour of measurement (right) zoom on the heat flow.

After the isothermal cure, an HCH cycle at a heating rate of 2.5 K.min$^{-1}$ was performed (Figure V-7). During the first heating, the sample devitrifies at a temperature of 22 °C, which is followed by a reaction peak that continues to a temperature of 200 °C. In the second heating, a glass transition temperature of 44 °C is observed and no reaction peak, meaning full cure was achieved before the second heating.

The reaction of cyclohexanol with MDI in a stoichiometric ratio was also investigated isothermally at 40 and 60 °C (Figure V-8) in MTDSC. No vitrification was observed during the measurements at these higher temperatures. How the data was treated to obtain the reaction heat flow in isothermal and non-isothermal conditions was discussed in detail in Chapter IV.
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Figure V-7. The result of the residual cure and full cure glass transition for stoichiometric MDI-cyclohexanol mixtures, measured by an HCH cycle after an isothermal cure at 25 °C for 600 minutes (Figure V-6) with the first and second heating at a heating rate of 2.5 K.min\(^{-1}\).

As the isothermal cure temperature is increased, also the reaction heat flow at the start increases (Figure V-8 left), and the evolution of the reaction heat flow towards zero happens faster (Figure V-8 right). Using the results of the isothermal experiment at 25 °C, the reaction heat generated during the preparation time \(\Delta H_{\text{prep}}\) of about three minutes can be estimated by extrapolating the reaction heat flow by 3 minutes to lower times and integrating the heat flow with respect to time (see Chapter IV, section 4.4.1), and corresponds with a \(\Delta H_{\text{prep}}\) of -53 J.g\(^{-1}\).

Figure V-8. Isothermal reaction heat flows for stoichiometric MDI-cyclohexanol mixtures, from DSC measurements at temperatures of 25, 40 and 60 °C (left) the first hour of measurement; (right) zoom on the heat flow in the final stages.

The results for non-isothermal DSC experiments at different scanning rates can be found in Figure V-9. The reaction peak shifts towards higher temperatures as the heating rate increases and the reaction peak broadens as function of temperature. For the experiments done at heating rates of 1 and 2 K.min\(^{-1}\), full cure is achieved during the first heating. For the experiments at heating rates of 5, 10 and 20 K.min\(^{-1}\), the reaction peak is shifted and broadened to the extent that full cure could not be obtained below the maximum temperature of 200 °C, where degradation becomes unavoidable.
By integrating the reaction heat flows as a function of time for the fully cured experiments, the reaction heat $\Delta H_{\text{non-iso}}$ of the cyclohexanol-MDI system can be determined. The reaction heat measured of the experiment performed at 2 K.min$^{-1}$ is -304 J.g$^{-1}$. To obtain the total reaction heat $\Delta H_{\text{tot}}$, the (estimated) heat missed during preparation time needs to be included:

$$\Delta H_{\text{tot}} = \Delta H_{\text{prep}} + \Delta H_{\text{non-iso}} = -357 \text{ J.g}^{-1} \quad (\text{eq. V-3})$$

By dividing the preparation heat by the total heat, the missed conversion due to preparation is estimated to equal 15%. So, in the first 3 minutes of preparation 15% of the total reaction has already occurred, meaning that reducing the preparation time to a minimum is a must. The molar amount of heat generated by the urethane reaction can be calculated by dividing the total reaction heat by the concentration of the isocyanate groups at the start of the reaction $[\text{NCO}]_0$.

$$\Delta_r H^o = \frac{\Delta H_{\text{tot}}}{[\text{NCO}]_0} = -80.4 \text{ kJ.mol}^{-1} \quad (\text{eq. V-4})$$

The obtained reaction enthalpy -80.4 kJ. mol$^{-1}$ is quite close to the reaction enthalpy of -77.3 kJ. mol$^{-1}$ predicted with the additivity method (see Table V-4).

Knowing the total reaction heat, the conversion (eq. II-47) and conversion rate (eq. III-17) can be determined for the isothermal and non-isothermal experiments. Using the model free kinetics method (Friedman) described and applied in Chapter IV section 2, the overall activation energy $E_a(x)$ and the kinetic function $A_f(x)$ can be determined as a function of the reaction conversion (Figure V-10). The activation energy in the investigated conversion interval remains approximately constant, having a value of 49.0 ± 4.8 kJ.mol$^{-1}$ at a conversion of 50%. The obtained activation energy can be used to estimate an initial value for the kinetic parameters of the mechanistic model (section 5).
Figure V-10. (left) Overall activation energy $E_a(x)$ and (right) kinetic function $A.f(x)$ for the cure of a stoichiometric MDI-cyclohexanol mixture as determined by applying the Friedman isoconversional method on the non-isothermal measurements (Figure V-9), with the shaded area giving the 95% confidence interval.

4.1.2 Effect of the reaction stoichiometry

To investigate the effect of alcohol and isocyanate groups on the urethane reaction kinetics, reactions for off-stoichiometric mixtures must be evaluated. In general, the urethane reaction rate can be written as a function of the concentrations of the alcohol and isocyanate groups to their respective partial reaction orders $\alpha$ and $\beta$:

$$\frac{d[\text{UR}]}{dt} = k[\text{OH}]^\alpha[\text{NCO}]^\beta$$

(eq. V-5)

The overall reaction order $n$ being the sum of the partial reaction orders $\alpha$ and $\beta$. Determining these orders can help for finding the reaction mechanism behind the urethane formation, as the same reaction orders must be obtained using a mechanistic model with elementary reaction steps. If the urethane formation was a bimolecular elementary reaction between isocyanate and alcohol, values of one would result for $\alpha$ and $\beta$, and two for $n$.

The concentrations of the functional groups for different molar mixing ratios are given in Table V-5. The results of non-isothermal experiments at 10 K.min$^{-1}$ are given in Figure V-11. The reaction heat flow of the off-stoichiometric ratios is low compared to the stoichiometric ratio and is caused by concentration limitations. In the excess isocyanate experiment ($r = 3$), the cold crystallization and melting of MDI is clearly visible at low temperatures (below 40 °C). For the excess isocyanate experiment, after the first reaction exotherm is completed around 130°C, a second reaction peak with a maximum at 190 °C is observed. This is attributed to allophanate formation, which is the result of the reaction between isocyanate and urethane - excess isocyanate conditions allow for the allophanate formation to happen, as will be further discussed in section 0. By dividing the reaction heat flows for the different mixing ratios by their respective total reaction heat $\Delta H_{\text{tot}}$, the conversion rate can be determined for each of them. The total reaction heat of the different mixing ratios are calculated by multiplying the limiting
Polyurethane kinetics with monofunctional alcohols

concentration by the molar reaction enthalpy of the urethane (eq. V-4) and the results can be found in Table V-5. At the start of the reaction, e.g. around 50 °C, the conversion rates \( \dot{x} \) of the off-stoichiometric ratios are higher than for the stoichiometric ratio, both in case of excess isocyanate and excess alcohol.

*Table V-5 The concentrations of the different stoichiometries of MDI and cyclohexanol with the corresponding reaction heat.\(^x\)*

<table>
<thead>
<tr>
<th>Ratio</th>
<th>([\text{NCO}]_0) mol.kg(^{-1})</th>
<th>([\text{OH}]_0) mol.kg(^{-1})</th>
<th>(\Delta H_{\text{tot}}) J.g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI-Cyclohexanol</td>
<td>6.309</td>
<td>2.103</td>
<td>-162</td>
</tr>
<tr>
<td>r 3 – 1</td>
<td>5.708</td>
<td>2.854</td>
<td>-220</td>
</tr>
<tr>
<td>r 1 – 1</td>
<td>4.439</td>
<td>4.439</td>
<td>-342</td>
</tr>
<tr>
<td>r 1 – 2</td>
<td>3.073</td>
<td>6.146</td>
<td>-237</td>
</tr>
<tr>
<td>r 1 – 3</td>
<td>2.350</td>
<td>7.049</td>
<td>-181</td>
</tr>
</tbody>
</table>

*Figure V-11. Results for non-isothermal experiments at a heating rate of 10 K.min\(^{-1}\) for MDI-cyclohexanol mixtures having isocyanate-alcohol molar ratios of r 3 – 1, r 1 – 1 and r 3 – 1: (left) reaction heat flow and (right) conversion rate \( \dot{x} \) as a function of temperature.*

The results of isothermal experiments at 40 °C for the molar ratios r 2 – 1, r 1 – 1 and r 1 – 2 can be found in Figure V-12. Like for the stoichiometric mixture, both excess isocyanate and excess alcohol mixtures show a catalytic reaction behavior, with a fast reaction rate at the start followed by a long reaction tale (Figure V-12 top left). The reaction heat flow at the start of the excess experiments is comparable to the reaction heat flow of the stoichiometric ratio, but as the reaction progresses the excess experiments’ reaction heat flow goes down more rapidly. By integrating the reaction heat flow as function of time, the extent of reaction can be determined (top right). Due to the fast initial reaction, the reaction during preparation is significant and approximating the missed initial conversion becomes difficult. Therefore the reverse integration method was used to calculate the extent of conversion (see Chapter IV, section 4.4.4). The missed conversion during preparation of the r 2 – 1, r 1 – 1 and r 1 – 2 mixtures are 27%, 30% and 35%, respectively.
Figure V-12. Results for isothermal experiments using the combined DSC and TAM method for MDI-cyclohexanol mixtures having isocyanate-alcohol molar ratios of $r = 2 - 1$, $r = 1 - 1$ and $r = 1 - 2$ at 40 °C: (top left) reaction heat flow and (top right) reaction conversion calculated using reverse integration as a function of time, (bottom left) conversion rate $\dot{x}$ and (bottom right) overall reaction order as a function of conversion $x$.

The conversion rate $\dot{x}$ as function of the conversion is given in Figure V-12 (bottom left). The conversion rate of the off-stoichiometric mixing ratios is faster than for the stoichiometric ratio, with the excess alcohol $r = 1 - 2$ being the fastest. The reaction rate evolution of the excess isocyanate and excess alcohol run nearly parallel from the start of the measurement up to a conversion of 80%, while the evolution for the stoichiometric ratio differs. When two reaction rate evolutions run parallel, the slope is the same, which is the case when the overall reaction order $n$ is the same. The result of the evolution of the overall reaction order $n$ is given in Figure V-12 (bottom right). The order of the stoichiometric ratio starts around 2.7 for a conversion of 30% and lowers to around 2 when the conversion approaches 75%. The reaction orders start at 1.9 and 1.8 for the excess isocyanate and alcohol ratios, respectively. For the excess isocyanate ratio, the reaction order of the remains roughly constant as the reaction progresses, while the reaction order for the excess alcohol ratio lowers to a value of one. The reaction orders of excess isocyanate and alcohol ratios evolutions are close to one another initially, hence the conversion rate evolution running parallel in this conversion region.
4.2 Reaction of isocyanate with primary alcohols

Having made a first characterization of the urethane reaction kinetics using a secondary alcohol, the faster reaction with a primary alcohol will be discussed.

4.2.1 Effect of temperature

The kinetics of urethane formation starting from primary alcohols is investigated using diethylene glycol methyl ether (DEGME), which more closely resembles the molecular structure of PEGs and PPGs than 1-hexanol. The non-isothermal reaction heat flow for stoichiometric ratios of MDI with DEGME is given in Figure V-13. As for the experiments performed with cyclohexanol, the reaction peaks shift towards higher temperature and become broader as the heating rates increases. Full cure is achieved during heating for the experiments at scanning rates of 1, 2 and 5 K.min$^{-1}$, and the reaction heat released during these experiments is $-340 \, \text{J.g}^{-1} \pm 12 \, \text{J.g}^{-1}$.

![Reaction heat flows of measurements for stoichiometric MDI-DEGME mixtures. (top left) Reaction heat flow and (top right) reaction heat flow in heat capacity units for non-isothermal experiments performed at heating rates of 1, 2, 5, 10 and 20 K.min$^{-1}$. (bottom) Reaction heat flow for isothermal cure at temperatures of 25, 40 and 50 °C](image)

Figure V-13. Reaction heat flows of measurements for stoichiometric MDI-DEGME mixtures. (top left) Reaction heat flow and (top right) reaction heat flow in heat capacity units for non-isothermal experiments performed at heating rates of 1, 2, 5, 10 and 20 K.min$^{-1}$. (bottom) Reaction heat flow for isothermal cure at temperatures of 25, 40 and 50 °C
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The results of the isothermal experiments can be found in Figure V-13 (bottom). The reaction heat flow displays a catalytic kinetic behavior, with the initial reaction heat flow increasing with temperature. The missed reaction heat during the preparation procedure can be estimated by forward extrapolating the reaction heat flow of the experiment at room temperature over the 3-minute preparation time. The missed reaction heat is about $-20 \text{ J.g}^{-1}$. The preparation heat together with the reaction heat of the non-isothermal measurement, leads to the total reaction heat $-360 \text{ J.g}^{-1}$ of the MDI – DEGME mixture in stoichiometric conditions. By dividing the total reaction heat by the initial concentration of the isocyanate groups, the molar reaction enthalpy is $-88 \text{ kJ.mol}^{-1}$, which is 4 kJ.mol$^{-1}$ more exothermal than predicted by the additivity method (Table V-4), and 8 kJ.mol$^{-1}$ more exothermal than for the secondary alcohol.

Applying model free kinetic on the non-isothermal experiments, the evolution of the activation energy and kinetic function $A_f(x)$ can be determined as function of the reaction conversion (Figure V-14). The activation energy of the primary alcohol reaction is at $45.0 \pm 3.6 \text{ kJ.mol}^{-1}$ at a conversion of 15%, which is a bit lower than the activation energy of $49.4 \pm 2.1 \text{ kJ.mol}^{-1}$ of the secondary alcohols. The activation energy of the primary alcohol reaction increases significantly as the reaction progresses, reaching $54.4 \text{ kJ.mol}^{-1} \pm 5.2 \text{ kJ.mol}^{-1}$ at 50% conversion. Although the evolution of the activation energy with conversion is quite different, the continuous overlap between the 95% confidence intervals indicates the difference is not significant.

![Figure V-14. (left) Overall activation energy $E_a(x)$ and (right) kinetic function $A_f(x)$ for the cure of a stoichiometric MDI-DEGME mixture as determined by applying the Friedman isoconversional method on the non-isothermal measurements (Figure V-13) with the shaded area giving the 95% confidence interval.](image-url)
4.2.2 Effect of stoichiometry

Also for the primary alcohol, the effect of the isocyanate and alcohol concentrations on the urethane reaction was investigated using off-stoichiometric reaction mixtures. The results of non-isothermal DSC experiments for MDI-DEGME with molar ratios r1-1, r3-1 and r1-3 are given in Figure V-15 (left). In case of excess isocyanate (r3-1), a clear melting peak of the MDI can be observed. The reaction heat flows for the off-stoichiometric experiments are lower compared to one for the stoichiometric ratio. Using the molar reaction enthalpy of the primary urethane reaction, the expected total reaction heat of the off-stoichiometric experiments can be calculated (Table V-6) and the reaction conversion and conversion rate can be obtained. The conversion rates are plotted as a function of the temperature for the different mixing ratios in Figure V-15 (right). The peak in the conversion rate of the excess OH system (r1-3) begins at lower temperature compared to the other experiments. A second reaction peak is observed around 150 °C, which is not observed in the other experiments. This reaction peak is the result of the oxidation of DEGME due to the oxygen present in the DSC crucible. Note that in perforated crucibles, the oxygen present in the DSC pans is purged by purge gas of the DSC cell. The use of perforated crucibles is not suitable here, however, as the monofunctional monomers are volatile. Another option for removing the oxygen from the crucible is preparing the DSC samples in a glove box filled with inert gas. However, due to the fast nature of the polyurethane reaction this is not feasible. The oxidation is clearly prevalent in the excess alcohol mixture (r1-3), but is also likely to occur for the other mixing ratios, albeit to a lesser extent. The heat flow due to oxidation are more pronounced in experiments performed at a lower scanning rate. The oxidation is clearly visible in the stoichiometric experiment at a heating rate of 1 K.min$^{-1}$ (Figure V-13).

The reaction rate for the excess isocyanate experiment (r3-1) starts increasing slightly later than for the stoichiometric experiment, but increases more rapidly to a maximum. The conversion rate peak is narrower compared to the stoichiometric peak, indicating a higher overall activation energy (a stronger temperature dependence) than for the stoichiometric mixture. Above 150 °C, a shoulder on the conversion peak is observed for both the excess isocyanate and the stoichiometric mixture.
Table V-6 The concentrations of the different stoichiometries of MDI and DEGME with the corresponding reaction heat.

<table>
<thead>
<tr>
<th>Ratio MDI-DEGME</th>
<th>[NCO]₀ mol.kg⁻¹</th>
<th>[OH]₀ mol.kg⁻¹</th>
<th>ΔHₜₒₜ J.g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>r 3 – 1</td>
<td>5.888</td>
<td>1.963</td>
<td>-173</td>
</tr>
<tr>
<td>r 2 – 1</td>
<td>5.203</td>
<td>2.601</td>
<td>-229</td>
</tr>
<tr>
<td>r 1 – 1</td>
<td>3.857</td>
<td>3.857</td>
<td>-339</td>
</tr>
<tr>
<td>r 1 – 2</td>
<td>2.542</td>
<td>5.083</td>
<td>-224</td>
</tr>
<tr>
<td>r 1 – 3</td>
<td>1.895</td>
<td>5.686</td>
<td>-167</td>
</tr>
</tbody>
</table>

Figure V-15. Results for non-isothermal experiments at a heating rate of 10 K.min⁻¹ for MDI-DEGME mixtures having isocyanate-alcohol molar ratios of r 3 – 1, r 1 – 1 and r 3 – 1: (left) reaction heat flow and (right) conversion rate ẋ as a function of temperature.

The effect of the stoichiometry on the reaction kinetics in isothermal conditions is depicted in Figure V-12. As the lower graph shows, the conversion rates of the excess alcohol mixtures (r1-2 and r1-3) are faster than for the stoichiometric ratio. The excess isocyanate mixtures have comparable reaction rates to the stoichiometric ratios. This is in agreement with the non-isothermal results, where the conversion rate of the excess isocyanate mixtures is comparable with those for the stoichiometric ratio around 40 °C, while the conversion rate for the excess alcohol mixture is faster than for the stoichiometric mixture.
4.3 Effects of other functional groups on the kinetics

4.3.1 Effect of ether groups

The conversion of the urethane formation of primary and secondary alcohols as measured with DEGME and cyclohexanol, respectively, are compared in Figure V-18. Both display a catalytic behavior in isothermal conditions. At the start of the isothermal experiments, the conversion rate of the experiment with secondary alcohols OH$_s$ is higher than for the one with primary alcohols OH$_p$. In non-isothermal conditions, the reaction with secondary alcohols starts at lower temperature and reaches a maximum sooner than for the primary alcohols, which is consistent with the isothermal results.
Figure V-17. The comparison of the urethane reaction heat flow for the reaction of MDI with primary and secondary alcohols, investigated using stoichiometric mixtures of MDI–DEGME and MDI–Cyclohexanol. (left) isothermal reaction at 40 °C; (right) non-isothermal experiment at a heating rate of 10 K.min⁻¹

These results were unexpected, as literature clearly states that the formation rate of urethanes out of primary alcohols is faster than for secondary alcohols.⁵ The discrepancy between the obtained results and the literature can be explained by the presence of ether groups in the DEGME monomer. The ether groups can interact with the alcohol groups by forming hydrogen bonds. This reduces the concentration of free alcohol groups available for the urethane formation. A similar, retarding effect of hydrogen bonding of alcohols with ether groups on the reactivity of curing systems has been observed previously in epoxy-amine systems.¹⁸

The retarding effect of ether groups can be experimentally confirmed by replacing some of the DEGME monomer by 1-hexanol, also a primary amine. By doing so, the concentration of ether functional groups goes down, which is expected to result in an increase in free alcohol groups and an increase in reaction rate.

Figure V-18. Reaction heat flows for a stoichiometric MDI-DEGME system with 0 mol%, 25 mol %, 50 mol% of DEGME replaced with 1-hexanol: (left) isothermal experiments at 60 °C, (right) non-isothermal experiments at 10 K.min⁻¹.
Isothermal results for the effect of replacing DEGME by 0%, 25%, and 75% of hexanol can be found in Figure V-18 (left). By increasing the hexanol concentration and thus lowering the ether concentration, the reaction heat flow at the beginning of the reaction is higher, implying that the reaction rate has increased. Non-isothermal results for MDI-DEGME with 0%, 25% and 50% of the DEGME replaced by 1-hexanol are given in Figure V-18 (right). By decreasing the ether concentration, the reaction peak shifts towards lower temperatures, which is also pointing to an increased reaction rate.

The effect of ether groups on the reaction rate can also be observed in case of the reaction of MDI with secondary alcohols, by introducing ether groups in the reaction mixture of MDI and cyclohexanol. The dipropylene glycol dimethyl ether (DPGDME) has 3 ether groups. By dissolving 10 w% of DPGDME into cyclohexanol, a source of ether groups is introduced. The effect of the addition of ether groups on the reaction rate is given in Figure V-19 for isothermal experiments at 40°C for stoichiometric and off-stoichiometric mixtures. By adding DPGDME to the reactive mixture, the reaction rate is reduced over the full duration of the reaction, regardless of the mixing ratio. The retarding effect is especially strong in case of an excess alcohol mixture.

Thus, the retarding effect of ether groups on the reaction rate of the urethane formation has been experimentally confirmed for reactions with both primary and secondary alcohol groups. When building a mechanistic kinetic model, the effects of ether groups on the reaction rate must be included, as the frequently used polyether polyols contain a high amount of ether functions.

![Figure V-19. Conversion rate versus conversion for combined isothermal DSC and TAM experiments at 40 °C for MDI-cyclohexanol (full) and MDI-cyclohexanol with 10 w% DPGDME dissolved in the cyclohexanol (dashed) at mixing ratios of r1-1, r2-1 and r2-1](image-url)
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4.3.2 Effect of added urethane and allophanate formation

In literature, it is stated that urethane groups catalyze the urethane reaction. This autocatalysis is not clearly observed in the isothermal experiments, in strong contrast to the autocatalysis in epoxy-amine reactive systems, for example. To investigate the influence of urethane groups on the kinetics of the urethane reaction, molecules with urethane functional groups can be added to the reactive mixture. First results indicated the absence of a strong catalytic effect of added urethane groups (not shown).

In non-isothermal experiments on excess isocyanate mixtures, a second reaction peak was observed at higher temperatures (see section 4.1.2). The first peak is due to the urethane reaction and the second peak is attributed to allophanate formation. The latter is the result of a thermoreversible reaction between urethane and isocyanate. The thermoreversibility implies that at low temperatures the formation of allophanate is favored, while at high temperatures the allophanate dissociation is favored. The allophanate formation is an exothermic reaction and the dissociation is an endothermic reaction and both can therefore be studied in DSC.

The allophanate reaction can be investigated independently from the urethane formation by mixing urethane with isocyanate. Such a sample can be obtained by taking a fully cured excess isocyanate sample, such as those investigated in section 4.1.2 and 0. The samples were investigated using non-isothermal DSC measurement, using a heat-cool-heat cycle from a temperature of -50 °C to 200 °C, with an isothermal stabilization segment of one minute between the heating and cooling steps. During the first heating, the thermal history of the sample and the allophanate formation is erased. The cooling always was performed at a cooling rate of -50 K. min\(^{-1}\). For the second heating different heating rates were applied. The results for the second heatings are given in Figure V-20. From 90 °C onwards, an exothermic peak is observed, immediately followed by an endothermic peak. The exothermic peak is attributed to allophanate formation and the endothermic peak is the allophanate dissociation. At the lowest scanning rate, the exothermic and endothermic peak are shift to lower temperatures and the exothermic peak is also more pronounced. Due to the low scanning rate, a longer time is spent at low temperatures, where the allophanate formation is favored.
4.3.3 Effect of catalyst

By dissolving a small amount (0.04 w%) of catalyst (DABCO) in the cyclohexanol, the urethane reaction rate can be further increased. The results for an isothermal DSC experiment of the reaction of a stoichiometric mixture of MDI and cyclohexanol with added catalyst at 40 °C are shown in Figure V-21. The initial reaction heat flow of the experiment with added catalyst is higher than the reaction heat flow of the experiment without added catalyst, indicating a faster reaction. The effect of catalyst will not further be investigated in this chapter, but will be extensively investigated in Chapter VII, including the kinetic modeling of catalyzed reactions.

Figure V-21. Reaction heat flows of an isothermal combined DSC and TAM experiment for a stoichiometric MDI-cyclohexanol mixture without added catalyst and with 0.04 w% catalyst dissolved in the cyclohexanol at 40 °C.
Chapter V

5 Modeling polyurethane reactions without added catalyst

5.1 Evaluation of literature kinetic models

Although the formation of a urethane from an isocyanate and an alcohol is often written as a bimolecular elementary reaction, it has been recognized in literature that the actual mechanism is more complex (see Chapter II section 4.2).\textsuperscript{19–25} In this section, several mechanistic models presented in literature will be evaluated.

5.1.1 Evaluation of simple mechanistic models from literature

The first mechanism tested is the uncatalyzed reaction mechanism in which an isocyanate reacts directly with an alcohol through a four-membered ring transition state (see Chapter II section 4.2.1).\textsuperscript{26} The total reaction order of this mechanism is two and the partial reaction orders of alcohol and isocyanate are both one. Knowing that the total reaction order of the urethane formation changes between two and three for stoichiometric mixtures, the uncatalyzed mechanism could not model the polyurethane reaction in isothermal conditions. In non-isothermal conditions, the model worked to a certain extent, confirming that non-isothermal experiments are less discriminatory for evaluating kinetic models.

The second mechanism tested was the alcohol catalysed reaction mechanism (see Chapter II section 4.2.2).\textsuperscript{26–28} The total reaction order of the mechanism is three with partial reaction orders of the isocyanate and alcohol groups being one and two, respectively. Using this mechanism, the isothermal and non-isothermal stoichiometric measurements could be modelled. However, when applying the model in off-stoichiometric conditions no satisfactory results could be obtained in isothermal conditions. This model can be extended by implementing urethane catalysis.\textsuperscript{29} As the experiments do not show clear effects of autocatalysis, no significant improvement could be made.

5.1.2 Evaluation of a more complex mechanistic model

A third, recently developed, mechanistic model added an isocyanate catalysed pathway in addition to the alcohol catalysed pathway.\textsuperscript{17} The alcohol catalysed pathway begins with the two alcohol groups interacting with one another forming an alcohol dimer (eq. V-6). In the next step the dimer reacts with an isocyanate group, forming a urethane bond and recovering an alcohol group (eq. V-7). The isocyanate catalysed pathway begins with the formation of an isocyanate dimer (eq. V-8). The isocyanate dimer reacts with an alcohol group resulting in the formation of an allophanate (AL) (eq. V-9). The urethane bond is formed via the isocyanate pathway by dissociating the allophanate group into a urethane and an isocyanate (eq. V-10).
To obtain the kinetic parameters for this model, both isothermal and non-isothermal experiments at different mixing ratios were used, using the same approach as for the model introduced in this work, which will be described in section 5.3.1. To evaluate the fitting results, a quality of fit parameter $Q_{\text{fit}}$ is introduced. This will evaluate the maximum relative difference between the experimental ($\dot{H}_{\text{exp}}$) and modelled ($\dot{H}_{\text{mod}}$) reaction heat flow.

$$Q_{\text{fit}} = 1 - \max\left(\frac{\text{abs}(\dot{H}_{\text{exp}} - \dot{H}_{\text{mod}})}{\text{abs}(\dot{H}_{\text{exp}})}\right)$$  \hspace{1cm} (eq. V-11)

In non-isothermal conditions, due to the cold crystallization and melting of isocyanate at the start of the reaction, in addition to the complexity of the baseline estimation and the possible occurrence of oxidation, not the entire range of the measured reaction heat flow data points can be used to evaluate the quality of fit parameter. The range is limited between 33% and 67% of the peak maximum. In an isothermal measurement, start-up effects in the heat flow are interfering during the first two minutes, and therefore these data points are excluded for the quality of the fit. Data points close to the baseline, defined as points where the measured reaction heat flow becomes less than 5% of the (exothermal) maximum value, are also excluded.

First, the model is evaluated for the reaction between isocyanate and secondary alcohols using the data for MDI-cyclohexanol (Figure V-22). Looking at the reaction heat flow released during the first hour, for conversions up to 73%, the modelled and experimental data match quite nicely for both stoichiometric and off-stoichiometric conditions. When using a linear scale (Figure V-22 (left)), evaluating the match between the model and the experiments becomes difficult at higher conversion due to the high order kinetic mechanism of the urethane reaction, causing lower reaction rates. To adapt to these lower rates, the reaction heat flows are presented on a logarithmic scale for longer reaction times (Figure V-22 (right)). When critically evaluating the data using the logarithmic scale, the fit of the modelled and experimental reaction heat flow is shown to be more than one order of magnitude wrong in the more advanced stages (Figure V-22 (right)) for the stoichiometric and excess isocyanate mixtures, while a good match between the experimental and modelled data is observed for the excess alcohol mixing ratio only. These results are reflected in the quality of the fit parameter given in Table V-7.
Table V-7 Quality of the fit in isothermal conditions at 40°C for cyclohexanol and DEGME

<table>
<thead>
<tr>
<th></th>
<th>Cyclohexanol</th>
<th>DEGME</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{fit}$</td>
<td>0.327</td>
<td>0.289</td>
</tr>
<tr>
<td></td>
<td>0.893</td>
<td>0.213</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.510</td>
</tr>
<tr>
<td></td>
<td>0.679</td>
<td></td>
</tr>
</tbody>
</table>

Figure V-22. Reaction heat flows for MDI – cyclohexanol mixtures at 40°C: experiments using the combined DSC TAM method (full) and model (dashed). (left) zoom at the first hour with r2-1 shifted by -0.10 W.g$^{-1}$ and r2-1 by -0.20 W.g$^{-1}$ for clarity. (right) reaction heat flow on a logarithmic scale for evaluating the quality of fit at higher reaction conversions. The 0.05 mW.g$^{-1}$ upper limit of the logarithmic scale is taken based on the 1 µW sensitivity limit of the TAM.

The result of the fit of the model versus the experimental results in non-isothermal conditions is given in Figure V-23. The model fits the experimental data reasonably well for all the investigated heating rates, which is confirmed by the quality of the fit parameter (see Table V-8). The model deviates most from the experimental data at the higher reaction conversions at the higher temperatures. At these higher temperatures the baseline of the experimental data is less well known and this can be an explanation for the poorer fit in this region.

Table V-8 Quality of the fit for in non-isothermal conditions in a stoichiometric ratio for cyclohexanol and DEGME

<table>
<thead>
<tr>
<th>K.min$^{-1}$</th>
<th>Cyclohexanol</th>
<th>DEGME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.96</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>0.89</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Polyurethane kinetics with monofunctional alcohols

Figure V-23 Reaction heat flows for stoichiometric MDI-cyclohexanol mixtures measured at heating rates of 1, 2, 5, 10 and 20 K.min\(^{-1}\): experiments (solid) and model (dashed). (left) Reaction heat flow $\dot{H}$ in W.g\(^{-1}\), (right) and $h\dot{H}_C$ in heat capacity units J.g\(^{-1}\).K\(^{-1}\).

Next, the model is evaluated for the reaction between primary alcohol and isocyanate using the isothermal data obtained for MDI-DEGME mixtures having different mixing ratios. Figure V-24 displays the model and experimental data for isothermal reactions. The start of the measurement is not well modelled for all the investigated mixing ratios as the model is too slow compared to the experimental data. From 30 minutes, onward the model fits the experimental data quite well. When evaluating the model using the logarithmic scaled reaction heat flow (Figure V-24 (right), the model fits the experimental data in stoichiometric conditions over a broad time interval. The noise on the experimental heat flow is clearly visible when only DSC data is used. For the off-stoichiometric ratios the model fits the data and the trend. The overall quality of the fit is given in Table V-7.

Figure V-24 Reaction heat flows for MDI – DEGME mixtures at 40 °C: DSC experiments (full) and model (dashed). (left) zoom at the first hour with r2-1 shifted by -0.05 W.g\(^{-1}\) and r2-1 by -0.10 W.g\(^{-1}\) for clarity. (right) reaction heat flow on a logarithmic scale for evaluating the quality of fit at higher reaction conversions.
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The results of non-isothermal experiments for the reaction of isocyanate with primary alcohol can be found in Figure V-25. The match between the model and the experiment for the heating rates of 1 and 2 K.min\(^{-1}\) is quite good. The quality of the fit is poorer for the heating rates of 5 and 10 K.min\(^{-1}\). In these experiments the model fits the data in the lower temperature range only. The top of the reaction peak is not well represented by the model.

![Figure V-25 Reaction heat flows for stoichiometric MDI-DEGME mixtures measured at heating rates of 1, 2, 5, 10 and 20 K.min\(^{-1}\): experiments (solid) and model (dashed). (left) Reaction heat flow \(\dot{H}\) in W.g\(^{-1}\), and (right) \(\dot{H}_C\) in heat capacity units J.g\(^{-1}\).K\(^{-1}\).](image)

The results of non-isothermal experiments for off-stoichiometric mixing ratios are given in Figure V-26. The experimental and modelled curves overlap nicely over the whole temperature interval for all mixing ratios for the urethane formation exotherm. The formation of the allophanate with excess isocyanate, clearly observed experimentally, cannot be fitted by this model, notwithstanding that the allophanate formation is inherently part of the urethane reaction in this mechanistic model (eq. V-9). The development of this mechanism was supported by ab initio modelling, providing values for the reaction enthalpies and Gibbs free energy changes.\(^{17}\) These values can be compared with the values obtained with the kinetic parameters obtained from the modelling (Table V-9). For the excess isocyanate conditions, the literature value of the Gibbs free energy change at 298 K for the allophanate formation is more negative than for forming urethane and isocyanate. From a thermodynamic point of view this implies there is no driving force for the allophanate to react further to urethane. In the data derived from the kinetic model optimization performed in this work, the Gibbs free energy change of the allophanate formation is higher (even slightly positive) than for the formation of urethane and isocyanate. Therefore allophanate will act as an intermediate specie. This means that the species called allophane in the model is not an allophanate. To cope with the shortcomings of the literature kinetic models, an ionic reaction mechanism was developed in this work.
Table V-9 Thermodynamic parameters of the literature model calculated with ab initio modelling for the reaction of phenylisocyanate with 1-propanol, and the parameters calculated from the model optimization in this work.

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Species</th>
<th>$\Delta H^\circ$ (kJ.mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (kJ.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>literature</td>
<td>model</td>
</tr>
<tr>
<td>Excess Alcohol</td>
<td>NCO + (OH)$_2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>UR + OH</td>
<td>-100.9</td>
<td>-80.6</td>
</tr>
<tr>
<td>Excess Isocyanate</td>
<td>(NCO)$_2$ + OH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>AL</td>
<td>-160.1</td>
<td>-1.5</td>
</tr>
<tr>
<td></td>
<td>UR + NCO</td>
<td>-105.6</td>
<td>-79.1</td>
</tr>
</tbody>
</table>

*Reaction is a forward reaction in the model and not an equilibrium reaction and can therefore not be calculated.*

Figure V-26 Reaction heat flows for MDI-cyclohexanol mixtures having molar ratios r1-1, r3-1 and r1-3 measured at heating rates of 10 K.min$^{-1}$: experiments (solid) and model (dashed). (left) Reaction heat flow $\dot{H}$ in W.g$^{-1}$, (right) conversion rate $\dot{x}$ in s$^{-1}$, and

5.2 Building a mechanistic kinetic model

5.2.1 A proposed ionic reaction mechanism for urethane formation

The ionic reaction mechanism proposed in this work for the uncatalyzed reaction was inspired by the reaction mechanism that was proposed in literature for the urethane formation in the presence of a base catalyst (see Chapter II section 4.2.4). In this mechanism an alkoxide ion is formed by the base catalyst and the formed alkoxide ion initiates the urethane reaction.

The reaction mechanism consists of three elementary reaction steps (Figure V-27). In the first step an isocyanate acts as a base and reacts with alcohol, forming an alkoxide ion and a protonated isocyanate. Note that the reaction takes place in a relatively apolar reaction environment, meaning that the formed ions are not completely dissociated, the two ions remaining in each other’s proximity, which has a stabilizing effect. In a second step, the alkoxide ion reacts with an isocyanate group, forming an NCOO$^-$ group. Note that the NCOO$^-$
group has resonance structures that stabilize the structure formed. In the third step, the NCOO\(^{-}\) group reacts with an alcohol, forming a urethane bond and recovering the alkoxide ion.

![Proposed ionic reaction mechanism for the urethane formation](image)

**Figure V-27** Proposed ionic reaction mechanism for the urethane formation

The total and partial reaction orders of the urethane formation predicted by this mechanism can be determined analytically. Using the third reaction step, the rate of urethane formation can be written as:

\[
\frac{d[UR]}{dt} = k_3[OH][NCOO^-] \quad (eq. \text{ V-12})
\]

Assuming reaction 1 of Figure V-27 is a fast equilibrium, meaning that products of the reaction are always in equilibrium with the reagents and that the equilibrium is reached instantaneously, with an equilibrium constant \(K_1\). As a result of the fast equilibrium, the concentrations of \([\text{NCOH}^+]\) and \([\text{O}^-]\) are therefore equal. Now the concentration of \([\text{O}^-]\) can be calculated:

\[
K_1 = \frac{k_1}{k_{-1}} = \frac{[\text{NCOH}^+][\text{O}^-]}{[\text{NCO}][\text{OH}]} \quad (eq. \text{ V-13})
\]

\[
[\text{O}^-] = (K_1[\text{NCO}][\text{OH}])^{0.5} \quad (eq. \text{ V-14})
\]

Using the quasi steady state approximation (QSSA) on the intermediate NCOO\(^{-}\), the concentration of the intermediate after the start-up can be approximated:

\[
\frac{d[\text{NCOO}^-]}{dt} = k_2[\text{O}^-][\text{NCO}] - k_{-2}[\text{NCOO}^-] - k_3[\text{OH}][\text{NCOO}^-] \approx 0 \quad (eq. \text{ V-15})
\]

\[
[\text{NCOO}^-] = \frac{k_2[\text{O}^-][\text{NCO}]}{k_{-2} + k_3[\text{OH}]} \quad (eq. \text{ V-16})
\]
The concentration of $[O^-]$ obtained in (eq. V-14) can be substituted into (eq. V-16), leading to
\[
[NCOO^-] = \frac{k_2(K_1[NCO][OH])^{0.5}[NCO]}{k_{-2} + k_3[OH]} \quad (eq. V-17)
\]
Substituting (eq. V-17) into (eq. V-12) gives:
\[
\frac{d[UR]}{dt} = \frac{k_3k_2(K_1[NCO][OH])^{0.5}[NCO][OH]}{k_{-2} + k_3[OH]} \quad (eq. V-18)
\]
Assuming that $k_2 \gg k_3[OH]$, (eq. V-18) can be simplified to (eq. V-19).
\[
\frac{d[UR]}{dt} \approx k'[OH]^{1.5}[NCO]^{1.5} \quad (eq. V-19)
\]
\[
k' = \frac{(K_1)^{0.5}k_2k_3}{k_{-2}} = K_1^{0.5}K_2k_3 \quad (eq. V-20)
\]
$K_2$ is the equilibrium constant of reaction 2. The obtained partial reaction orders for both alcohol and isocyanate are 1.5 and the total reaction order is 3. The partial reaction orders of alcohol and isocyanate are equal, which was also derived from the experimental data. Another assumption which can be made is $k_3[OH] \gg k_{-2}$ reducing (eq. V-18) to (eq. V-21).
\[
\frac{d[UR]}{dt} = k''[OH]^{0.5}[NCO]^{1.5} \quad (eq. V-21)
\]
\[
k'' = K_1^{0.5}k_2K_3 \quad (eq. V-22)
\]
Where $K_3$ is the equilibrium constant of reaction 3. The partial reaction orders for alcohol and isocyanate are 0.5 and 1.5 respectively leading to a total reaction order of 2. The experimentally obtained overall reaction order for the stoichiometric ratio of MDI and cyclohexanol varied between two and three (Figure V-12 (bottom right)), which is in between the orders of the two idealized cases.

The reaction mechanism could be simplified to a single ordinary differential equation (eq. V-19) or (eq. V-21) with a single reaction rate constant $k'$ (eq. V-20) or $k''$ (eq. V-22) respectively if either of the simplifications and approximations hold. It will be seen that this is not the case in section 5.3.2.

5.2.2 Including the allophanate formation

The ionic mechanism for the urethane formation can be further extended to introduce the allophanate formation: by writing the equivalent of reaction step 3, replacing the alcohol by a urethane group. An important difference is that reaction (eq. V-23) needs to be reversible to correctly represent the reversible nature of the allophanate formation: at high temperature, the reaction equilibrium must shift to the left.
The reaction enthalpy of the allophanate formation is directly related to the activation energies \(E_4\) and \(E_{-4}\) of the forward and reverse reactions of this thermoreversible reaction.

\[
\Delta_r H^\circ_{\text{AL}} = E_4 - E_{-4}
\]

(eq. V-24)

By coupling the reaction enthalpy to the kinetic parameters and additional constraint on the kinetic parameters is introduced, hereby preventing that the optimization algorithm would change these parameters to unrealistic values. This is especially useful for the allophanate formation as the kinetic parameters of this reaction are poorly known. The software needs the formation enthalpy of each of the compound in order to calculate the heat flow. For the formation enthalpy of the allophanate group from the free isocyanates and alcohols, the formation enthalpy of the urethane group from the free isocyanates and alcohols must be combined with the reaction enthalpy of the allophanate formation.

\[
\Delta_t H^\circ_{\text{AL}} = \Delta_t H^\circ_{\text{UR}} + \Delta_t H^\circ_{\text{AL}}
\]

(eq. V-25)

5.2.3 Modelling the retarding effect of ether groups

It was assumed that the observed lower reactivity in the presence of ether groups is due to a lower activity of alcohol groups due to hydrogen bonding with these ether groups. By introducing a reversible equilibrium reaction, this effect can be introduced, as was done in earlier work for amine-cured epoxies.

\[
Et + OH \rightleftharpoons EtOH
\]

(eq. V-26)

Such a hydrogen-bonding equilibrium reaction is fast compared to the urethane reaction. So, determining the parameters of the individual rate constants is not possible, however, determining the equilibrium constant \(K_5\) is. To implement this in the kinetic software developed in this work, in which the forward and reverse reaction are always taken into consideration individually, the rate constant of the reverse reaction \(\log k_{5T}\) at a selected reference temperature can be fixed at a high value, optimizing the rate constant of the forward reaction \(\log k_{5T}\) only. Like with the allophanate formation, the reaction enthalpy of the formed hydrogen bond is related to the difference in activation energies.

\[
\Delta_t H^\circ_{\text{EtOH}} = E_5 - E_{-5}
\]

(eq. V-27)

Knowing that the hydrogen bond is a weak interaction, at least when compared to the urethane formation, this reaction enthalpy is therefore limited to a maximum of -10 kJ.mol\(^{-1}\). To model the temperature dependence of the hydrogen bond formation, only \(E_5\) and \(\Delta_t H^\circ_{\text{EtOH}}\) will be optimized.
5.3 Evaluating the model for the urethane formation

5.3.1 Data preparation and modeling strategies

The kinetic parameters \( \log k_T \) and \( E \) of all reaction steps are optimized using the reaction heat flows of isothermal and non-isothermal experiments with stoichiometric and off-stoichiometric conditions using a least square curve fitting algorithm (see Chapter III section 3.4). An overview of all conditions used is given in Table V-10.

<table>
<thead>
<tr>
<th>Isothermal (^{\circ}{\text{C}})</th>
<th>Cyclohexanol</th>
<th>DEGME</th>
</tr>
</thead>
<tbody>
<tr>
<td>r1-1</td>
<td>25, 40, 60</td>
<td>25, 40, 60</td>
</tr>
<tr>
<td>r2-1</td>
<td>25, 40</td>
<td>25, 40, 60</td>
</tr>
<tr>
<td>r2-1</td>
<td>25, 40</td>
<td>25, 40, 60</td>
</tr>
<tr>
<td>Non-isothermal ((\text{K.min}^{-1}))</td>
<td>1,2,5,10,20</td>
<td>2,5,10,20</td>
</tr>
<tr>
<td></td>
<td>2,5,10,20</td>
<td>2,5,10,20</td>
</tr>
<tr>
<td></td>
<td>1,2,5,10</td>
<td>1,2,5,10</td>
</tr>
<tr>
<td></td>
<td>1,2,5,10</td>
<td>1,2,5,10</td>
</tr>
</tbody>
</table>

**Table V-10 All the used conditions for the modelling for cyclohexanol and DEGME**

**Accounting for reaction during sample preparation**

Before the measured experimental data, an isothermal segment at 21 °C of 2-4 minutes is added to simulate the reaction during preparation, the amount of which is determined by the real preparation time and temperature of each individual experiment. Due to the high order kinetic behavior, small errors in the true preparation time and temperature propagate over the whole time range. It was decided to keep the initial isothermal temperature in the simulation constant at 21 °C, whereas in reality the sample temperature may be different due to differences in the laboratory temperature, self-heating due to reaction, and differences in the temperature of the reagents mixed. Remember that the MDI is stored in an oven at 50°C and prior to mixing the MDI is taken out of the oven and cooled down to room temperature (see Chapter III section 1.4). To account for differences in pre-insertion temperature and time, for each isothermal experiment a starting time \( t_s \) is introduced as an additional optimizable parameter. It can vary over a limited time range of 60 seconds. For non-isothermal experiments, the preparation time at 21 °C is followed by a cooling at 20 K.min\(^{-1}\) and an isothermal step of two minutes, to simulate the cooling before the measured heating step.

**Point-by-point optimization weight**

For the parameter optimization, a point by point weighing factor is defined for the experiments. If the measured reaction heat flow is unreliable or faulty, the weight is put to zero. Unreliable data points include the added preparation data points and the first two minutes of the startup of the isothermal DSC measurements. Faulty data points include data points during the cold crystallization and melting of MDI in non-isothermal experiments.
Chapter V

Optimization strategies

The optimization of all model parameters is done in several steps. In the first set of steps, only the urethane formation was modelled, excluding data points for which the allophanate reaction could be important. Once the urethane formation was sufficiently well described by the model, the allophanate formation and the corresponding data were included in the model.

In the first optimization step for the urethane formation, the $\log k_T$ parameters of all relevant reactions are optimized using only isothermal experiments at the reference temperature $T_r$ of 40 °C and for different stoichiometric ratios, until a satisfactory match between the experimental and the modeled reaction heat flows is obtained. The reaction is well measured at this temperature, being not too fast to miss a too large portion of the heat flow, while being high enough to prevent crystallization of MDI.

In the next step, the activation energies $E$ are optimized using non-isothermal experiments at different scanning rates and for different mixing ratios, while keeping the previously obtained $\log k_T$ constant. As initial values for the activation energies, the overall activation energy from the analysis using model free kinetics approaches was used (see section 4.1.1). To further improve the agreement of the model with the experiments, both $\log k_T$ and $E$ are optimized using all isothermal and non-isothermal experiments in the following step.

Once the urethane formation is satisfactorily modelled, the allophanate reaction is modelled using only the non-isothermal excess isocyanate experiments, while keeping parameters from all urethane reactions constant. The reference temperature $T_r$ for the $\log k_T$ of the allophanate reaction is 150°C, as the reaction only becomes significantly measurable in this temperature region.

In a final step all kinetic parameters are again optimized within narrow limits using all non-isothermal and isothermal experiments for all measured stoichiometries.

5.3.2 Evaluating the model in isothermal conditions

The reaction heat flows obtained using the ionic reaction model after optimization for the isothermal reactions at 40 °C of MDI with secondary alcohol cyclohexanol are given in Figure V-28. For all reaction mixtures, the experimental and the modelled reaction heat flow correspond nicely for the first hour. A reasonably good match between the experimental and modeled heat flow over the whole time interval is only obtained for the stoichiometric ratio (Figure V-28 (top right)). In the time region between two and six hours after the start of the measurement, the modeled reaction rate is somewhat too fast, while the reaction rate after ten hours is too slow. A possible explanation for this discrepancy can be found in the MDI used, which is a mixture of 63% MDI44 and 37% MDI24. According to literature, the reactivity of the isocyanate group in the 4’ position is higher than the reactivity of the isocyanate in the 2’ position. Overall, the isocyanate groups present could be split up into isocyanate groups in
the position 4’, which amounts to 81.5%, and isocyanate in the 2’ position, amounting to 18.5%. Keeping the reaction rate constant of steps 1 and 2 constant (Figure V-27) and allowing the reaction rate constant of step 3 to differ slightly for the different isocyanate groups, the model can be further improved, however in view of reducing the model complexity as much as reasonable, it was decided not to take this different reactivity into account in further steps.

For the off-stoichiometric mixtures, the model fits the experimental data reasonably well until a reaction heat flow of the order of $-10^{-3}$ W.g$^{-1}$. From this point onwards model and experiment diverge. Also here, some improvements can be made by accounting for a different reactivity of the isocyanate groups, although the improvements are less significant compared to the stoichiometric ratio.

![Graphs showing reaction heat flows and reaction conversion](https://example.com/graphs)

*Figure V-28. Reaction heat flows for MDI – cyclohexanol mixtures at 40°C: experiments using the combined DSC TAM method (full) and ionic model (dashed). (left) zoom at the first hour with r2-1 shifted by -0.10 W.g$^{-1}$ and r2-1 by -0.20 W.g$^{-1}$ for clarity. (right) reaction heat flow on a logarithmic scale for evaluating the quality of fit at higher reaction conversions. (bottom left) reaction conversion as a function of time first 3 hours (bottom right) reaction conversion as a function of time first.*

The experimental and modeled reaction conversion profiles for the different mixing ratios are given in Figure V-28 (bottom). The reaction conversion is a sensitive indicator for accumulated errors. A good match between the model and experimental is observed for all mixing ratios.
The results for the reaction of primary alcohol DEGME with isocyanate are given in Figure V-29. The model underestimates the reaction rate at the start of reaction for all stoichiometric ratios. For the stoichiometric and excess alcohol mixtures (r1-1 and r1-2), the fit improves as the reaction progresses further, however the small error accumulated over the whole measurement leads to a slight underestimation (3 %) of the final reaction conversion (Figure V-29 (bottom))\textsuperscript{b}. When evaluating the model using the logarithmic scale, the evolution of the reaction rate for the stoichiometric and excess isocyanate mixtures is quite well up to a high conversion. Also for the excess isocyanate experiment, the start of the reaction is underestimated by the model. This is followed by an overestimation starting at 10 minutes. The accumulation of this under- and overestimation of the reaction rate by the model leads to a slight underestimation (2 %) for the modelled reaction conversion over the entire time interval.

\textit{Table V-11 Quality of fit for the isothermal experiments of MDI with cyclohexanol and DEGME at 40°C.}

<table>
<thead>
<tr>
<th></th>
<th>Cyclohexanol</th>
<th>DEGME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r1-1 r2-1 r2-1</td>
<td>r1-1 r2-1 r1-2</td>
</tr>
<tr>
<td>$Q_{\text{fit}}$</td>
<td>0.885 0.710 0.880</td>
<td>0.825 0.889 0.814</td>
</tr>
</tbody>
</table>

The $Q_{\text{fit}}$ values in all cases is higher for the ionic model (Table V-11) is compared to the literature model (Table V-7)in all investigated. Comparing the results for cyclohexanol, the startup of the reaction is best modelled for both the models, but at higher conversions the literature model slows down too fast, while this is less the case for the ionic model. Comparing the result for DEGME, the reaction rate at the start is less well modelled, but the model results are better at high conversion rates for both the models.

\textsuperscript{b}the estimated error on the heat flow calibration is about 1%.
Figure V-29. The results of MDI – DEGME isothermal experiments (full) and model (dashed) at 40°C (top left) zoom at the first hour with r2-1 shifted by -0.05 W.g⁻¹ and r2-1 by -0.10 W.g⁻¹ for clarity. (top right) the reaction heat flow in a logarithmic scale in order to evaluate the model and the experiment at high reaction conversions (bottom) The experimental and modeled reaction conversion as function of time.

5.3.3 Evaluating the model in non-isothermal conditions

The reaction heat flows for stoichiometric mixtures in non-isothermal conditions at different heating rates are given in Figure V-30. The modelled and experimental profiles correspond nicely for all investigated heating rates and over the whole temperature range. The match between the model and the experiment is somewhat less good at low and high temperatures. In these temperature ranges, the reaction heat flow is the lowest and the experimental data is more affected by errors on the baseline construction.
Chapter V

Figure V-30 Reaction heat flows for stoichiometric MDI-cyclohexanol mixtures measured at heating rates of 1, 2, 5, 10 and 20 K.min\(^{-1}\): experiments (solid) and ionic model (dashed). (left) Reaction heat flow \(\dot{H}\) in W.g\(^{-1}\) and (right) \(\dot{H}_c\) in heat capacity units J.g\(^{-1}\).K\(^{-1}\).

The model and experimental reaction heat flow for off-stoichiometric ratios of MDI-cyclohexanol measured at 10 K.min\(^{-1}\) are given in Figure V-31. A good match between the experimental and modelled curves is seen. For the excess isocyanate mixture, the secondary peak caused by the succession of allophanate formation and dissociation is modelled well. The production rate of allophanate is most prevalent in the excess isocyanate mixtures, but also takes place in the stoichiometric mixtures, while almost no allophanate is formed in the excess alcohol mixtures.

Table V-12 Quality of the fit for the reaction of stoichiometric mixtures of MDI with cyclohexanol and DEGME for non-isothermal conditions.

<table>
<thead>
<tr>
<th>K.min(^{-1})</th>
<th>Cyclohexanol</th>
<th>DEGME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>(Q_{\text{fit}})</td>
<td>0.941</td>
<td>0.917</td>
</tr>
</tbody>
</table>
The results of the fit for the reaction of MDI with primary alcohol cyclohexanol can be found in Figure V-32. Of course, the secondary peak observed at high temperatures, which is likely caused by the oxidation of the DEGME, is not fitted by the model. Excluding these high temperature ranges, the quality of the fit is less good near the peak maximum for the heating rates of 5 and 10 K.min^-1. The cold crystallization and melting of the MDI, which is clearly visible for the experiment done at 2 K. min^-1 does not seem to influence the reaction compared to the model.

The $Q_{fit}$ values in all cases are comparable for ionic model (Table V-12) and the literature model (Table V-8) which was not the case for the isothermal measurements. This can be explained by the fact that non-isothermal measurements are less sensitive in determining reaction mechanisms. However, the allophanate formation in the literature model is not well modelled but due to the investigated range of the $Q_{fit}$ is has no impact on its value.
5.3.4 Evaluation of the kinetic parameters

The kinetic parameters after optimization for the MDI - cyclohexanol model system are given in Table V-13. Filling in the kinetic parameters into (eq. V-20) provides values of $k'$ and its kinetic parameters $\log k'_{Tr}$ at the reference temperature of 313.13 K and $E'$ with values $-3.80 \log(\text{kg}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1})$ and 47.2 kJ.mol$^{-1}$ respectively. The value of this activation energy is close to the value obtained by model free kinetics (see section 4.2.1).

By changing the values of $k_1$, $k_{-1}$, $k_2$, $k_{-2}$ and $k_3$ while keeping $k'$ constant and looking at the effect on the heat flow, the coupling between parameters can be evaluated. Additionally, the approximation made for the calculation of $k'$ needs to be checked. Note that the power of 0.5 for the parameters of the $k_1$ and $k_{-1}$ in (eq. V-18) must be considered. By changing the parameters of $k_1$ and $k_3$ or $k_{-1}$ and $k_3$, simultaneously did not influence the simulation results. This means that these parameters are strongly coupled and cannot be independently determined. Obtaining the exact values for $k_1$, $k_{-1}$ and $k_3$ therefore becomes impossible. These values can only be determined accurately by measuring the concentrations of the reactive ions, which cannot be achieved. Another effect of this coupling is that the concentration of the alkoxide ion $\text{RO}^-$ can be changed, as it is the result of reaction step 1 in Figure V-27. This is valuable information when developing the model for reactions in the presence of a catalyst. In this model additional alkoxide ion will be formed as a result of the catalyst and the concentration of the alkoxide ion resulting from isocyanate can thus be tuned to be at the right level with respect to the values obtained induced by the catalyst (see Chapter VII). When changing $k_2$ or $k_{-2}$ in combination with the other kinetic parameters $k_1$, $k_{-1}$ and $k_3$, while keeping $k'$ constant, different results for the modelled reaction heat flow were obtained. This implies that the steady state approximation used to derive (eq. V-20) is not completely valid.
Table V-13 Kinetic parameters for the MDI-cyclohexanol mixture. The values for $\log k_{TR}$ are given at the reference temperature of 313.15 K (40°C); $\log k$ and $\log(A)$ are in kg.mol$^{-1}$.s$^{-1}$, except parameters marked with * are given in s$^{-1}$; the activation energy is given in kJ.mol$^{-1}$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log k_{TR}$</th>
<th>$\log(A)$</th>
<th>$E$</th>
<th>$\log k_{TR}$</th>
<th>$\log(A)$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCO + OH ⇌ NCOH$^+$ + O$^-$</td>
<td>-6.93</td>
<td>-6.09</td>
<td>5.0</td>
<td>2.00</td>
<td>2.83</td>
<td>5.0</td>
</tr>
<tr>
<td>NCO + O$^-$ ⇌ NCOO$^-$</td>
<td>2.30</td>
<td>2.88</td>
<td>4.9</td>
<td>2.73*</td>
<td>4.33*</td>
<td>9.6</td>
</tr>
<tr>
<td>NCOO$^-$ + OH → UR + O$^-$</td>
<td>1.09</td>
<td>9.76</td>
<td>51.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NCOO$^-$ + UR ⇌ AL + O$^-$</td>
<td>-3.05</td>
<td>12.8</td>
<td>95.0</td>
<td>1.67</td>
<td>-8.34</td>
<td>155.0</td>
</tr>
</tbody>
</table>

The model free kinetic method can also be applied to the heat flow profiles simulated using the ionic kinetic model. The resulting activation energy and reaction rate are given in Figure V-33 by a dashed line and compared with the experimentally obtained results. Comparing the model and experimental activation energy profiles for the reaction of the secondary alcohols, the values of the model are found to be within the confidence interval of the experimental values and follow a similar trend. For the primary alcohols, this is not the case.

Figure V-33. Activation energy $E_x$ and kinetic function $A.f(x)$ versus conversion as determined by the Friedman isoconversional method based on data for reaction in non-isothermal conditions: experimental (full line) and model (dashed line), with the shaded area giving the 95% confidence interval of the experimental results.

6 Conclusion

The thermochemistry of the polyurethane reaction was first investigated using group additivity method. Because the values of the formation enthalpy in the liquid state of the groups CB-(CNO)(CB)$_2$, CO-(N)(O) and N-(H)(CB)(CO) were not tabulated in literature, these were estimated using formation enthalpies of reference molecules and reaction enthalpies of reference reactions. The formation enthalpy of the CO-(N)(O) group depends on the polarity of the reaction environment, probably due to the high polarity of the group itself. Using these groups, the reaction enthalpy of the formation of UR$_p$ and UR$_s$ from isocyanate and alcohol was found to be -83.9 and -77.3 kJ.mol$^{-1}$. With the same approach, the reaction enthalpy for the allophanate formation was calculated to be -58.0 kJ.mol$^{-1}$. 
Chapter V

Next, the polyurethane reaction kinetics was investigated experimentally using two monofunctional monomers, cyclohexanol and DEGME, as model systems for reactions with secondary and primary alcohols, respectively. The reaction kinetics were investigated isothermally and non-isothermally for different mixing ratios. It was found that the partial reaction order of both alcohol and isocyanate groups were about equal and that the total reaction order of for the urethane formation varies between two and three in stoichiometric conditions. In the absence of ether groups, the conversion rate of the off-stoichiometric mixtures is higher than in stoichiometric conditions, which indicate isocyanate and alcohol catalysis. It was also observed that when ether groups are present in the reaction mixture the overall reaction rate is lower. This was attributed to hydrogen bonds being established between alcohol and ether groups, resulting in a lowering of the concentration of available alcohol groups, slowing down the overall reaction. In non-isothermal experiments for excess isocyanate systems, the formation and dissociation of the allophanate groups was observed starting from a temperature of 150 °C onwards.

Mechanisms presented in literature were implemented to model the urethane reaction without the addition of catalysts. Models without catalytic effects of any of the functional groups could not model the experimentally obtained heat flow. For models with alcohol catalysis, the stoichiometric conditions and excess alcohol mixtures could be modelled, but excess isocyanate systems were not well modelled. The literature model that could model the experimental results best, was a model with alcohol and isocyanate catalyzed pathways. The isocyanate catalyzed pathway uses allophanate as an intermediate to form urethane. It was shown that this is not viable solution due to the thermodynamics of the allophanate formation.

An ionic mechanism with the formation of an alkoxide ion, inspired by the reaction mechanism in catalyzed conditions, was developed in this work to model the kinetics of the urethane formation. Using the steady state approximation on the reactions with the intermediates, the partial reaction orders for isocyanate and alcohol groups were found to be 1.5 for both, adding up to a total reaction order of three. The ionic mechanism was extended to include allophanate formation and dissociation at higher temperatures. To incorporate the retarding effects of ether groups, a hydrogen-bonding equilibrium reaction between the ether groups and the alcohol groups was introduced. The mechanistic model was able to fit the experimental results in both isothermal and non-isothermal conditions for all investigated mixing ratios.
7 References

15. https://webbook.nist.gov/cgi/cbook.cgi?ID=C598550&Units=SI.


CHAPTER VI

REACTION BETWEEN DIPROPYLENE GLYCOL AND MDI

1 Introduction

In the previous chapter, the urethane formation kinetics were studied using monofunctional alcohols. In this chapter, the kinetics are investigated with dipropylene glycol (DPG), a bifunctional monomer. DGP is a mixture of isomers having primary and secondary alcohol functional groups (see Chapter III). As stated in literature and shown in Chapter V, the different alcohols have different reaction rates.\(^{1-6}\)

By combining DPG with MDI, a linear polymer chain will be formed. As a result of the increasing molar mass, the glass transition temperature will increase as the reaction progresses. In case of isothermal measurement, the glass transition temperature may rise to and above the isothermal temperature causing the material to vitrify. This vitrification will reduce the overall reaction rate, as the mobility of the polymer chains will become the determining factor for the kinetics rather than the chemical rate. Reactions in diffusion-controlled conditions will not be studied in this work.

Starting from the mechanistic ionic model, developed in Chapter V, the reaction model will be extended to handle the simultaneous reaction of both primary and secondary alcohol groups.

2 Materials

The materials used in this chapter are MDI and DPG (see Chapter III). The mixing ratios and their corresponding initial concentrations are given in Table VI-1.

<table>
<thead>
<tr>
<th>Ratio MDI-DPG</th>
<th>[NCO]_0 mol.kg(^{-1})</th>
<th>[OH(_p)]_0 mol.kg(^{-1})</th>
<th>[OH(_s)]_0 mol.kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>r 3 – 1</td>
<td>6.780</td>
<td>0.542</td>
<td>1.718</td>
</tr>
<tr>
<td>r 2 – 1</td>
<td>6.302</td>
<td>0.756</td>
<td>2.395</td>
</tr>
<tr>
<td>r 1 – 1</td>
<td>5.203</td>
<td>1.249</td>
<td>3.954</td>
</tr>
<tr>
<td>r 1 – 2</td>
<td>3.857</td>
<td>1.851</td>
<td>5.862</td>
</tr>
<tr>
<td>r 1 – 3</td>
<td>3.064</td>
<td>2.206</td>
<td>6.986</td>
</tr>
</tbody>
</table>

Table VI-1 The concentrations of the different stoichiometries of MDI and DPG
Chapter VI

3 Experimental evaluation of the kinetics

3.1 Non-isothermal measurements

3.1.1 Heat-cool-heat cycle

A typical measurement of a heat-cool-heat cycle of a stoichiometric mixture of MDI with DPG at a heating rate of 10 K.min$^{-1}$ is given in Figure VI-1, where only the heatings are shown. In the first heating, the exothermic reaction peak of the urethane formation is observed. In the second heating, the glass transition temperature at full cure $T_g$ is observed at 97 °C. It is important to note that the $T_g$ is well above 40°C, a typical isothermal temperature used throughout this work, meaning that during isothermal cure the sample will vitrify (see section 0). Using the techniques described in Chapter IV, a baseline is constructed. As the reaction is still going on at 200 °C, full cure was not achieved during the first heating. The reaction heat released during the reaction was 437 J.g$^{-1}$ or 84.0 kJ.mol$^{-1}$.

![Figure VI-1. Heat flow measured by DSC for a stoichiometric mixture of MDI – DPG at a scanning rate of 10 K. min$^{-1}$ showing the first heating, the second heating and the baseline.](image)

The reaction heat flow for this experiment is compared with the results obtained with monofunctional alcohols cyclohexanol and DEGME in Figure VI-2 (left). The reaction peak for cyclohexanol starts first, around 0°C, while the reaction peaks for DEGME and DPG start around 10 °C. This delayed start is attributed to the presence of ether groups, which are present in both DPG and DEGME, and not in cyclohexanol (see Chapter V).
3.1.2 Effect of the heating rate

Results of experiments for stoichiometric MDI-DPG measured at different scanning rates can be found in Figure VI-3. Before the reaction peak, the cold crystallization and melting of the MDI can be seen in all experiments (Figure VI-3 (left)). At higher scanning rates, the reaction peaks shift towards higher temperatures, with intensifying maximum.

3.1.3 Off-stoichiometric compositions

The result of non-isothermal experiments for MDI-DPG mixtures with an increasing excess of alcohol are given in Figure VI-4. At the start of the reaction (below a temperature of 50 °C), the reaction heat flows overlap for all investigated concentrations (Figure VI-4 (top left)). At higher temperatures, the heat flows start to diverge and with increasing excess of alcohol the overall reaction heat is lowered. When analyzing the conversion rate for the different stoichiometries, the conversion rate is actually increasing with increasing alcohol concentration (Figure VI-4 (top right)). This was also observed for the reaction of MDI with monofunctional

Figure VI-2. DSC results for a stoichiometric mixture of MDI – Cyclohexanol, MDI – DEGME and MDI – DPG at a scanning rate of 10 K. min\(^{-1}\): (left) reaction heat flow, (right) conversion rates.

Figure VI-3. Reaction heat flows for a stoichiometric mixture of MDI – DPG at heating rates of 1, 2, 5, 10 and 20 K.min\(^{-1}\): (left) heat flow and (right) heat flow in heat capacity units.

Figure VI-4. Reaction heat flows for a stoichiometric mixture of MDI – DPG at heating rates of 1, 2, 5, 10 and 20 K.min\(^{-1}\): (left) heat flow and (right) heat flow in heat capacity units.

alcohols (Chapter V). The heat flow of the second heating, given in Figure VI-4 (bottom left), shows the glass transition temperature $T_{g1}$ for the fully cured samples. The evolution of the fully cured glass transition temperature as function of the initial alcohol concentration is given in Figure VI-4 (bottom right). The more off-stoichiometric the reaction mixture is, the lower $T_{g1}$ is, because the average molar mass of the polymer chains is reduced. The lower limit of the glass transition temperature $T_{g0}$ is given by the zero-cure glass transition temperature (indicated with the dashed line).

![Figure VI-4](image)

Figure VI-4. Results for off-stoichiometric MDI – DPG mixtures with a mixing ratio of $r_{1-1}$, $r_{1-1.2}$, $r_{1-1.5}$, $r_{1-2}$ and $r_{1-3}$, measured at 10 K. min$^{-1}$. (top left) reaction heat flow of the first heating, (top right) conversion rates, (bottom left) heat flow of the second heating showing the full cure glass transitions, (bottom right) full cure glass transition temperatures as a function of the initial alcohol concentration ($x$) and the initial glass transition temperature of a stoichiometric mixture $T_{g0}$ (dashed).
3.2 Isothermal measurements

3.2.1 Stoichiometric composition

The heat flow of an isothermal measurement at 40 °C for a stoichiometric mixture of MDI – DPG is given in Figure VI-5. The first 10 minutes of the experiment were measured by conventional DSC, while the remaining time was measured in modulated mode with an amplitude of 0.5 K and a period of 60 seconds, as was done for the measurements of MDI with cyclohexanol (Chapter V section 4.1.1). The reaction rate is the fastest at start of the measurement and gradually decreases as the reaction progresses, as observed for monofunctional alcohols (cyclohexanol and DEGME).

![Figure VI-5](image)

Figure VI-5. The heat flow and reversing heat capacity curves measured in DSC/MTDSC at 40 °C for a stoichiometric mixture of MDI – DPG, with the first 10 minutes being measured in conventional DSC, and the remaining time measured with MDSC with an amplitude of 0.5 K and a period of 60 s: (left) zoom on the first hour, (right) the complete experiment.

The reversing heat capacity signal $C_{p,rev}$, only measured in modulated mode, is maximal at the start and decreases gradually as the reaction progresses till 2.5 hours ($t_{vit,start}$). Then a faster, gradually decelerating drop in heat capacity is observed, extending till the end of the measurement. This drop corresponds with vitrification of polymerizing material. To characterize vitrification, a mobility factor $MF$ was introduced and is defined as follows: \(^7,8\)

$$MF(t) = \frac{C_p(t) - C_{p,g}}{C_{p,l} - C_{p,g}} \quad \text{(eq. VI-1)}$$

Where $C_{p,g}$ is the measured heat capacity of the material at the end of the isothermal measurement, when the material is (nearly) fully vitrified and thus behaves glassy, while $C_{p,l}$ is the measured heat capacity of the sample at the start of the vitrification when the material behaves as a liquid. This mobility factor is useful to study the reaction in diffusion-limited conditions and can be linked to the diffusion factor (eq. II-62). \(^7,8\) The material is fully mobile when $MF$ is equal to one and the reaction kinetics are unaffected by diffusion. When $MF$ is equal to zero, the material is vitrified and the reaction rate is also reduced to zero. When $MF$ is
equal to 0.5, the material is partially vitrified. The time corresponding with $MF = 0.5$, $t_{vitr,mid}$, is indicated in Figure VI-5 (right).

After the isothermal step, the sample was cooled down and a heat-cool-heat cycle at 5 K.min$^{-1}$ from -70 °C to 200 °C was applied. The measured heat flow of the two heatings is given in Figure VI-6. In the first heating, an endothermic step around 55 °C is followed by an endothermic peak, immediately followed by an exothermic peak. The step corresponds with the glass transition $T_{g,iso40}$ achieved during the isothermal reaction at 40°C. The endothermic peak superimposed on it corresponds with an enthalpy relaxation or enthalpy recovery. Going through the glass transition, the sample regains mobility, meaning the urethane reaction is happening without diffusion limitations, leading to the exothermic peak starting from 62 °C and continuing until 200 °C. In the second heating, the glass transition temperature at full cure is observed at 97 °C. A baseline was constructed by drawing a linear line using the evolution of the heat flow of the second heating from 150 °C to 200 °C. The residual reaction heat $\Delta H_{res}$ occurring during the first heating is calculated by integrating the heat flow with respect to this baseline (see the colored area). This will be used for constructing the $T_g - x$ evolution (see section 3.3).

The vitrification line of a TTT-diagram can be constructed by plotting the time to reach vitrification $t_{vitr,mid}$ at the corresponding reaction temperatures (Figure VI-7 (left)). At 10 °C, it takes nearly to reach vitrification. By increasing the isothermal temperature, the time to vitrify is reduced and the glass transition temperature reached isothermally is increased, with the fastest time to vitrify being 2.3 hours for an isothermal temperature of 70 °C. Increasing the isothermal temperature from 70 °C onwards, leads to higher glass transition temperatures, but longer vitrification times. Because of the high order reaction kinetics of the urethane formation, significantly lowering conversion rate at high conversion, it takes more time to reach the high conversions needed to vitrify at temperatures close to the $T_g$ of the fully cured material, which is observed at temperatures above 70 °C.
The measured extent of reaction is given as a function of time for the different isothermal measurements in (Figure VI-7 (right)). When looking at the results of the measurement done at 25 °C, the conversion obtained during the isothermal reaction is limited to 82% due to diffusion limitations and full cure will never be obtained isothermally. The maximum conversion in isothermal conditions can be increased to 97% by increasing the temperature to 80 °C.

Figure VI-7. (left) Construction of a TTT-diagram using experimental data points for the isothermal measurement done at 10, 25, 30, 40, 50, 60, 70, 80 and 90 °C by plotting $t_{vit,mid}$ for the corresponding cure temperature; the dashed line is the glass transition temperature at full cure $T_{g1}$ (right). Measured extent of reaction at isothermal temperatures of 25, 30, 40, 50 and 80 °C; the dashed curve corresponds with full cure $x=1$.

### 3.2.2 Off-stoichiometric compositions

The effect of the stoichiometry on the isothermal reactivity of MDI – DPG mixtures is shown in Figure VI-8. The initial heat flow of the r 3-1 excess isocyanate system is the lowest and as the amount of alcohol is increased the initial heat flow is increased. A maximum is achieved at a ratio of r 1-2. When comparing the conversion rates to one another (Figure VI-8 (right)), it can be noted that the initial conversion rate of the stoichiometric mixture is the lowest and both excess alcohol and isocyanate system have higher initial conversion rates, with the highest initial conversion rate observed for the r 1-3 excess alcohol system. This catalytic effect for excess alcohol systems was also observed with the monofunctional alcohols (Chapter V).
Figure VI-8. (left) The reaction heat flow at 40 °C for reactive mixtures of MDI and DPG for mixing ratios of $r_{3-1}$, $r_{2-1}$, $r_{1-1}$, $r_{1-2}$ and $r_{1-3}$. (right) the conversion rate calculated using the isothermal measurements.

3.3 Measuring and building a $T_g - x$ relationship

The position of the glass transition temperature will have an impact on the viscosity of the polymer, the viscosity of a polymer increases when $T - T_g$ decreases, and as the $T_g$ increases with increasing extent of reaction it is essential to predict this evolution. The $T_g - x$ relation can be measured experimentally using partially cured samples made by curing the sample isothermally for a certain selected time. In the case of MDI – DPG, a temperature of 30 °C and 40 °C is chosen, not too high to well-control the cure. After the isothermal step, the sample is cooled down at 20 K.min$^{-1}$ to -90 °C. In the next step, a heat-cool-heat cycle is applied, heating the sample from -90 °C to 200 °C at 5 K.min$^{-1}$ and cooling the sample at 20 K.min$^{-1}$. During the first heating, a $T_g$ is observed, followed by a reaction peak (see Figure VI-9). These heat flows are comparable to the ones measured in the HCH cycle after the isothermal measurement (Figure VI-6), but no or a very small enthalpy relaxation is observed.

Figure VI-9 Heat flow curves for a stoichiometric mixture of MDI – DPG measured in the first heating after a reaction at 30 °C for a period of 5, 10, 20, 30, 40 and 50 min.
The measured $T_g$ corresponds with the extent of reaction achieved after reacting during the preparation time, the isothermal cure time and the cooling down of the sample. From the residual reaction heat $\Delta H_{\text{res}}$, obtained by integration of the residual reaction peak, the extent of conversion corresponding with the measured $T_g$ can be calculated by following formula:

$$x_{\text{iso}} = 1 - \frac{\Delta H_{\text{res}}}{\Delta H_{\text{tot}}} \quad \text{(eq. VI-2)}$$

Where $\Delta H_{\text{tot}}$ is the total heat released for 100% reaction (437 J.g$^{-1}$). The heating rate of 5 K.min$^{-1}$ is chosen as it is slow enough for the sample to reach full cure during the first heating, while being sufficiently high to clearly observe a $T_g$. By increasing the isothermal reaction time, the conversion and $T_g$ at the end of the isothermal segment increase, while the residual reaction heat is decreased. The results of the measured reaction heats and glass transitions of the partially cured samples are given in Table VI-2. The reaction heat missed $\Delta H_{\text{miss}}$ during sample preparation and the time it takes to start the measurement can be estimated by subtracting the reaction heat measured during the isothermal $\Delta H_{\text{iso}}$ and the residual from the total reaction heat:

$$\Delta H_{\text{miss}} = \Delta H_{\text{tot}} - \Delta H_{\text{iso}} - \Delta H_{\text{res}} \quad \text{(eq. VI-3)}$$

The missed heat for the experiments measured at 30 °C varies between -32 to -56 J.g$^{-1}$, which corresponds with a conversion of 7% and 12% respectively. The missed heat measured for the isothermal temperatures of 50 and 60 °C are -93 and -140 J.g$^{-1}$, respectively corresponding with 21% and 32%. As the DSC samples are inserted at a higher isothermal temperature in these experiments, more heat is missed during the startup of the measurement.

<table>
<thead>
<tr>
<th>$T_{\text{iso}}$ °C</th>
<th>$t_{\text{iso}}$ min</th>
<th>$\Delta H_{\text{iso}}$ J.g$^{-1}$</th>
<th>$\Delta H_{\text{res}}$ J.g$^{-1}$</th>
<th>$\Delta H_{\text{miss}}$ J.g$^{-1}$</th>
<th>$x_{\text{iso}}$ %</th>
<th>$T_g(x_{\text{iso}})$ °C</th>
</tr>
</thead>
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<td>60</td>
<td>60</td>
<td>-250</td>
<td>-47</td>
<td>-140</td>
<td>89</td>
<td>45</td>
</tr>
</tbody>
</table>

These measured conversion $x$ and their corresponding $T_g$ are plotted in Figure VI-10 for partial cure and regular isothermal experiments. By fitting the DiBenedetto equation (eq. II-27) to these data, the $T_g$ can be calculated as a function of the extent of reaction. The optimized parameters of $T_{g0}$, $T_{g1}$ and $\lambda$ are -69 °C, 97 °C and 0.35, respectively.
Figure VI-10. \( T_g - x \) relationship for stoichiometric MDI – DPG mixtures determined using partial cure experiments (Table VI-2) and isothermal experiments (Figure VI-7).

4 Reaction kinetics model and diffusion control

4.1 Combining primary and secondary alcohols

The ionic model developed in Chapter V is used as a start to model the reaction of the MDI – DPG mixtures. As in DPG both primary and secondary alcohols are present, the ionic model has to be extended to incorporate both alcohols. So reactions (Chapter V section 5.2.1) are duplicated and to the alcohol compound as suffix of “p” or “s” is added to indicate a primary or secondary alcohols, or a species derived from them. These result in (eq. VI-4) till (eq. VI-15).

\[
\begin{align*}
NCO + OH_p & \rightleftharpoons k_1 \ NCOH^+ + O_p^- & (eq. VI-4) \\
NCO + O_p^- & \rightleftharpoons k_2 \ NCOO_p^- & (eq. VI-5) \\
NCOO_p^- + OH_p & \rightarrow k_3 \ UR_p + O_p^- & (eq. VI-6) \\
NCOO_p^- + UR_p & \rightleftharpoons k_4 \ AL_p + O_p^- & (eq. VI-7) \\
Et + OH_p & \rightleftharpoons k_5 \ EtOH_p & (eq. VI-8) \\
Et + UR_p & \rightleftharpoons k_6 \ EtUR_p & (eq. VI-9)
\end{align*}
\]
Reaction between dipropylene glycol and MDI

\[
\begin{align*}
\text{NCO} + \text{OH}_s \quad & \quad \frac{k_1}{k_{-1}} \quad \text{NCOH}^+ + \text{O}_s^- \quad (\text{eq. VI-10}) \\
\text{NCO} + \text{O}_s^- \quad & \quad \frac{k_2}{k_{-2}} \quad \text{NCOO}_s^- \quad (\text{eq. VI-11}) \\
\text{NCOO}_s^- + \text{OH}_s \quad & \quad \frac{k_3}{k_{-3}} \quad \text{UR}_s + \text{O}_s^- \quad (\text{eq. VI-12}) \\
\text{NCOO}_s^- + \text{UR}_s \quad & \quad \frac{k_4}{k_{-4}} \quad \text{AL}_s + \text{O}_s^- \quad (\text{eq. VI-13}) \\
\text{Et} + \text{OH}_s \quad & \quad \frac{k_5}{k_{-5}} \quad \text{EtOH}_s \quad (\text{eq. VI-14}) \\
\text{Et} + \text{UR}_s \quad & \quad \frac{k_6}{k_{-6}} \quad \text{EtUR}_s \quad (\text{eq. VI-15})
\end{align*}
\]

In addition to these reactions, two additional reactions have to be added for reactions involving more than one alcohol, in case one of each of the alcohols types is involved in the reaction. This is the case for the reaction of the NCOO$^-$ complex with an alcohol group, resulting in reactions (eq. VI-16) and (eq. VI-17).

\[
\begin{align*}
\text{NCOO}_p^- + \text{OH}_p \quad & \quad \frac{k_3}{k_{-3}} \quad \text{UR}_p + \text{O}_p^- \quad (\text{eq. VI-16}) \\
\text{NCOO}_p^- + \text{OH}_s \quad & \quad \frac{k_3}{k_{-3}} \quad \text{UR}_s + \text{O}_p^- \quad (\text{eq. VI-17})
\end{align*}
\]

The parameters of this extended ionic mechanism were optimized as before (see Chapter V). The initial parameter values were those obtained with the monofunctional monomers (see Chapter V). Both isothermal and non-isothermal experiments were used for the optimization. In this ionic model no diffusion restrictions were implemented. Hence, the point based weights for the isothermal experiments are reduced to zero when for data points for which the reaction time exceeds $t_{\text{vit,start}}$, to exclude these points for the optimization.

4.2 Isothermal experiments including diffusion limitations

The result of the model fitting for a stoichiometric mixture of MDI and DPG at 40 °C after optimization of the chemical reaction kinetics is given in Figure VI-11. In this experiment, the sample vitrifies and only the time region from the start of the measurement up to two hours, the onset of vitrification as seen from the heat capacity, was taken into account for the optimization of the chemical kinetics model parameters. In a first impression, the model and the experiment seem to coincide over the complete time interval. When zooming in on the baseline, it is clear
model and experiment start to deviate from one another about two hours after the start of the measurement, with the heat flow of the experiment going to zero more quickly compared to the modelled heat flow. The slowing down of the reaction starts even before the sample begins to vitrify. As the effect of diffusion limitations resulting from vitrification are not taken into account by the reaction model, this explains the divergence between model and experiment.

![Figure VI-11. Heat flow for the reaction of a stoichiometric MDI – DPG mixture at 40 °C as measured with DSC/MTDSC and the model results (dashed) as well as the measured reversing heat capacity: (left) full data. (right) zoom on baseline to magnify the heat flow around the vitrification.](image)

The effect of the vitrification is more clearly seen when plotting the extent of reaction as a function of the time (Figure VI-12), calculated by partial integration of the reaction heat flow. The measured and the modeled conversion profiles overlap up to about two hours after the start of the measurement, then the experimental curve flattens as the reaction rate is reduced by diffusion limitations, while the modelled conversion curve still increases monotonously.

![Figure VI-12. Conversion versus time for the reaction of a stoichiometric MDI - DPG mixture at 40 °C, derived from the experiment and calculated using the model.](image)
The effect of the diffusion limitations can be accounted for by introducing a diffusion factor $DF$ (see Chapter II section 3.2.5), as studied extensively at FYSC for epoxy–amine$^9$ and epoxy–anhydride$^7,8$ reactive systems. The diffusion-controlled reaction rate is given by (eq. VI-18).

$$
\dot{x}_{\text{diff}}(x) = \dot{x}_{\text{chem}}(x)DF(x) \tag{eq. VI-18}
$$

Where $\dot{x}_{\text{diff}}(x)$ is the diffusion-affected reaction rate for a certain conversion $x$, $\dot{x}_{\text{chem}}(x)$ is the rate of the reaction only determined by the chemical kinetics at the same conversion $x$. The variation of the diffusion factor along the reaction can thus be estimated using the measured reaction rate and the conversion rate obtained from the kinetic modelling by rearranging by (eq. VI-18):

$$
DF(t) = \frac{\dot{x}_{\text{diff}}(x)}{\dot{x}_{\text{chem}}(x)} = \frac{\dot{x}_{\exp}(x_{\exp})}{\dot{x}_{\text{mod}}(x_{\exp})} \tag{eq. VI-19}
$$

The conversion rate derived from the mechanistic kinetic model $\dot{x}_{\text{mod}}(x)$ is equal to the chemical reaction rate (both in the absence of diffusion effects), while the conversion rate as measured $\dot{x}_{\exp}(x)$ is the overall conversion rate including diffusion, both evaluated at selected experimental conversions. Note that the experimental conversion and conversion rate are affected the quality of the measurement, baseline selection and experimental noise. The variation of $DF$ derived in this way is compared to the mobility factor calculated with (eq. VI-1) (see Figure VI-13). The $DF$ has a value close to one when the time is below two hours. From two hours onwards the $DF$ drops gradually to a value close to zero, which it approaches after about 10 hours. The noise coming from the experimental conversion rate needed for calculated diffusion factor is clearly observed. The $C_p$-derived mobility factor starts at a value above one, as the heat capacity of the material just before vitrification $C_{pl}$ is lower than the heat capacity at the start. The vitrification process starts when $MF$ becomes lower than one, about 2.5 hours after the start of the measurement. From this time onwards, the mobility factor gradually decreases, approaching zero after ten hours. For the epoxy-amine$^9$ systems, the mobility and diffusion factor were very comparable in shape and position, implying that the mobility of the functional groups needed for reaction (or the characteristic length scale for the reaction) was similar to the mobility frozen in upon vitrification (or the characteristic length scale for cooperative motions at the glass transition) when evaluated on a 60 s time scale (the modulation period). For the MDI-DPG system, the diffusion factor starts declining much earlier and more rapid compared to the mobility factor. This implies that the mobility needed for the polyurethane reaction is at a larger length scale than the one of the cooperative motions at the glass transition (evaluated at 60 s). This causes the urethane reaction to be reduced earlier in time and conversion than vitrification as measured by MTDSC.
4.3 Isothermal effect of stoichiometry

The measured and modelled reaction heat flow of mixtures of MDI and DPG for the different stoichiometric ratios is given in Figure VI-14. Only the first hour of the reaction was modelled to make sure that diffusion limitations did not affect the kinetic parameters. An overall good match between experiment and the model is observed. The model slightly underestimates the initial reaction rate for the excess isocyanate mixtures (r3-1 and r2-1). For the stoichiometric ratios and the excess alcohol mixtures, a good match between measured and modelled heat flow is observed.

Figure VI-14. Reaction heat flow for MDI - DPG mixtures at 40 °C, for mixing ratios of r3-1, r2-1, r1-1, r1-2 and r1-3: measured heat flow (solid) and model (dashed). The curves are shifted 0.3 W.g⁻¹ from one another for clarity.
4.4 Non-isothermal conditions

The result of the fitting of the model for non-isothermal conditions is given in Figure VI-15. When looking at the reaction heat flow in heat capacity units, it can be seen that the modelled reaction heat flow at the start of the reaction is higher than the measured heat flow, and that the peak maximum of the model is also a few degrees lower, but slightly higher in heat flow value, and this for all heating rates. After the peak maximum, the measured and experimental curves converge to one another.

![Figure VI-15. Reaction heat flow for a stoichiometric MDI – DPG mixture at heating rates of 1, 2, 5, 10 and 20 K.min⁻¹: (left) heat flow and (right) heat flow in heat capacity units for experiments (solid) and model (dashed).]

4.5 Model parameters

The kinetic parameters found after optimization for MDI-DPG are given in Table VI-3. These parameters were obtained by first optimizing the isothermal experiments of MDI-DPG at 40°C for the different compositions. The \( \log k_{TR} \) of the reactions between isocyanate and secondary alcohol ((eq. VI-10) till (eq. VI-15)) were first optimized. The kinetic parameters of the reactions between isocyanate and primary alcohol ((eq. VI-4) till (eq. VI-9)) and the reaction with both primary and secondary alcohols ((eq. VI-15) and (eq. VI-16)) were defined relative to the kinetic parameters of the secondary alcohol. How this is done is described in Chapter III section 3.2.1. The advantage of using this approach is that the kinetic parameters of related reactions having similar parameters can be optimized together, while constraining their kinetic parameters to physically realistic differences. As was mentioned in Chapter V, due to the strong coupling of the parameters with one another, determining the individual values of the parameters not possible, making the comparison of the reaction rates between the primary and secondary alcohols based on the kinetic parameters difficult. In order to compare the difference in reaction rate between primary and secondary alcohols, the conversion rate of the primary and secondary alcohols based on the model was calculated (Figure VI-12). The conversion rate of the primary alcohol at the start of the reaction is 33% faster compared to the conversion rate of
the secondary alcohol. This is a more limited difference than the double or triple reaction rate reported in literature.\textsuperscript{1,2}

![Figure VI-16. The modelled conversion rate of primary \( \dot{x}_p \) and secondary \( \dot{x}_s \) alcohols for a stoichiometric mixture of MDI - DPG at 40 °C](image)

**Table VI-3 Kinetic parameters of the MDI-DPG mixture.** The \( \log k_{TR} \) are given at the reference temperature of 313.13 K (40°C); \( \log k_{TR} \) and \( \log(A) \) are in kg.mol\(^{-1}\).s\(^{-1}\), expect parameters marked with * that are given in s\(^{-1}\); the activation energy is given in kJ.mol\(^{-1}\).

<table>
<thead>
<tr>
<th>reaction</th>
<th>forward reaction</th>
<th>reverse reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \log k_{TR} )</td>
<td>( \log(A) )</td>
</tr>
<tr>
<td>NCO + OH(_p) ⇌ NCOH(^+) + O(_p)(^-)</td>
<td>-3.46</td>
<td>-2.63</td>
</tr>
<tr>
<td>NCO + O(_p)(^-) ⇌ NCOO(_p)(^-)</td>
<td>4.42</td>
<td>5.25</td>
</tr>
<tr>
<td>NCOO(_p)(^-) + OH(_p) → UR(_p) + O(_p)(^-)</td>
<td>3.74</td>
<td>12.97</td>
</tr>
<tr>
<td>NCOO(_p)(^-) + UR(_p) ⇌ Al(_p)(^+) + O(_p)(^-)</td>
<td>-3.05</td>
<td>12.80</td>
</tr>
<tr>
<td>Et + OH(_p) ⇌ EtOHp</td>
<td>4.61</td>
<td>5.96</td>
</tr>
<tr>
<td>Et + UR(_p) ⇌ EtUR(_p)</td>
<td>-2.24</td>
<td>-0.41</td>
</tr>
<tr>
<td>NCO + OH(_s) ⇌ NCOH(^+) + O(_s)</td>
<td>-4.11</td>
<td>-3.28</td>
</tr>
<tr>
<td>NCO + O(_s)(^-) ⇌ NCOO(_s)(^-)</td>
<td>4.46</td>
<td>5.29</td>
</tr>
<tr>
<td>NCOO(_s)(^-) + OH(_s) → UR(_p) + O(_s)</td>
<td>3.23</td>
<td>11.62</td>
</tr>
<tr>
<td>NCOO(_s)(^-) + UR(_s) ⇌ Al(_p)(^+) + O(_p)(^-)</td>
<td>-3.05</td>
<td>12.80</td>
</tr>
<tr>
<td>Et + OH(_s) ⇌ EtOH(_s)</td>
<td>4.03</td>
<td>5.38</td>
</tr>
<tr>
<td>Et + UR(_s) ⇌ EtUR(_s)</td>
<td>-2.76</td>
<td>-0.92</td>
</tr>
<tr>
<td>NCOO(_s)(^-) + OH(_p) → UR(_s) + O(_p)(^-)</td>
<td>3.46</td>
<td>-1.26</td>
</tr>
<tr>
<td>NCOO(_p)(^-) + OH(_s) → UR(_p) + O(_s)</td>
<td>3.24</td>
<td>11.85</td>
</tr>
</tbody>
</table>
5 Conclusion

The kinetics of the reaction between MDI and DPG, resulting a linear polyurethane, were investigated. The glass transition temperature of a fully cured stoichiometric system was found to be 97 °C. When measuring the kinetics below this maximum glass transition temperature, vitrification is observed in MTDSC, and due to the vitrification, the reaction rate will be reduced. Modeling the reaction rate in the vitrified state has already been done successfully for epoxy-amine systems by introducing a diffusion factor. The onset for this study is given, but a full study of the polyurethane reaction in the vitrified state is beyond the scope of this PhD work. The ionic reaction kinetic model developed for the formation of urethanes in Chapter V was extended to include the urethane formation in the presence of both primary and secondary alcohols. The model could predict the reaction progress reasonably well at 40 °C, but the model was worse in predicting the urethane formation in non-isothermal conditions. In order to investigate the chemorheology of the polyurethane formation, a model system resulting in a linear polymer is needed. Due to the occurrence of vitrification and the complications of diffusion-controlled reactions, the system composed of MDI and DPG is not suitable for this purpose. The vitrification can be avoided by using longer polyol monomers, however, and the rheokinetics will be investigated in the next chapter.
6 References


CHAPTER VII

POLYURETHANE KINETICS WITH POLYPROPYLENE GLYCOLS

IN THE PRESENCE OF A CATALYST

1 Introduction

Depending on the required outcome, a polyurethane or a polyisocyanurate, different types of catalyst were developed.\textsuperscript{1–3} As established in previous chapters, the urethane reaction is quite fast, even at room temperature, and by adding catalysts to the mixture, this reaction rate will be further increased. To keep the reaction and sample handling manageable, the reaction rate of the uncatalyzed system needs to be reduced first, before the effects of catalyst can be investigated. Knowing that the urethane formation is a high order reaction, reducing the concentrations of either or both isocyanate and alcohol is an effective strategy. This can be achieved by either using solvents, or by increasing the length of the monomers involved. The disadvantage of using solvents is that solvents can have interactions with the monomers, which makes extrapolating the obtained results to more concentrated cases difficult. Additionally, industry will avoid using solvents where possible. Therefore, base compounds with higher molar masses, more specifically polypropylene glycols (PPGs), will be used, a polyol often used in polyurethanes. The common synthesis route of PPG leads to an atactic polymer and the terminal alcohol groups are a mixture of primary and secondary alcohols, with the relative amount of secondary alcohols increasing as the length of the PPG increases.\textsuperscript{4,5}

The goal of this chapter is to gain insight in the effect of adding a catalyst to the reactive mixture, and to build upon the proposed ionic mechanistic model to include the influence of the catalyst. This is achieved by first studying the effect of the catalyst experimentally using calorimetry and in following steps building the mechanistic model and optimizing the kinetic parameters.

2 Materials

The isocyanate used in this chapter is MDI, which is a mixture of 44’MDI and 24’MDI in a mixing ratio of 63 w% and 37 w%, respectively (see Chapter III). Polypropylene glycols of different lengths (PPG4000, PPG1000, PPG425) were evaluated for the kinetic study with a catalyst. It was found that PPG425 was the only suitable candidate for a further investigation of the reaction in the presence of an added catalyst (see section 3.2).

The effect of catalyst 1,4-diazabicyclo[2.2.2]octane, also known as DABCO in industry, was evaluated. DABCO (powder) was supplied by Huntsman. To add it to the reactive mixture, the catalyst was first dissolved in the polyol (in most cases PPG-425), as described in in Chapter III.
The catalyst concentrations in the reactive mixtures for the different stoichiometric ratios and catalyst weight fractions are given in Table VII-1.

**Table VII-1 Concentration of the catalyst in the reactive mixtures with PPG-425**

<table>
<thead>
<tr>
<th>Amount of DABCO added in polyol</th>
<th>Catalyst concentration in mixture µmol.kg⁻¹</th>
<th>r 2-1</th>
<th>r 1-1</th>
<th>r 1-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 w%</td>
<td></td>
<td>0.41</td>
<td>0.56</td>
<td>0.69</td>
</tr>
<tr>
<td>0.02 w%</td>
<td></td>
<td>0.82</td>
<td>1.12</td>
<td>1.38</td>
</tr>
<tr>
<td>0.04 w%</td>
<td></td>
<td>1.64</td>
<td>2.24</td>
<td>2.75</td>
</tr>
<tr>
<td>0.06 w%</td>
<td></td>
<td>2.46</td>
<td>3.37</td>
<td>4.13</td>
</tr>
</tbody>
</table>

3 Experimental evaluation of the reaction kinetics

3.1 Occurrence of oxidation for small sample masses

The reaction heat flow of stoichiometric mixtures with PPG-1000 measured at different heating rates can be seen in Figure VII-1 (left). Two superimposed reaction peaks are observed. The first reaction peak is a broad exothermic peak starting from around 10 °C, while the second reaction peak is a sharper exothermic peak with an onset around 160 °C. This second reaction peak was not reproducible. However, it was observed that larger (2nd) reaction peaks corresponded with lower sample masses.

An explanation for this phenomenon is the presence of oxygen in the crucible and a reaction of one of the components with oxygen. In such a case, the reaction heat is directly correlated with the amount of oxygen present relative to the sample mass. As the sample mass goes up, the
amount of air in the DSC crucible relative to the sample mass goes down, thus a reaction peak involving oxygen gets smaller (Figure VII-2). By perforating the hermetic crucibles, this unwanted effect is avoided, because as the DSC cell is flushed with nitrogen gas, the oxygen is removed within minutes after inserting the crucible into the DSC. The difference between measurements in perforated and unperforated crucibles can be seen in Figure VII-1 (right): in the perforated crucible, the oxygen induced reaction peak is absent.

Figure VII-2. Illustration of a DSC crucible with a higher or lower sample mass and air encapsulation.

3.2 Influence of the PPG chain length

The reaction heat flow for stoichiometric mixtures of MDI with polyols of different lengths (DPG, PPG-425, PPG-1000 and PPG-4000) are given in Figure VII-3. The peak maximum is less exothermic, the peak shifts to higher temperatures, and the reaction heat (the area) decreases as the length of the polyol increases. This is explained by the decreasing concentration of the isocyanate and alcohol groups as the molar mass of the polyol goes up. In addition, larger PPGs have more ether groups, lowering the reaction rate (see also Chapter V section 4.3.1). As mentioned before, the heat flow and thus the reaction rate of the DPG mixture is high around room temperature and it is therefore not a suitable polyol for catalytic studies. The reactive mixture of PPG-4000 has a very broad and shallow heat flow peak, making the correct choice of the baseline difficult, making it also less suitable for catalytic studies. The reaction mixtures of PPG-425 and PPG-1000 are a good compromise between slower reactivity and high enough intensity.

Figure VII-3. Reaction heat flows for stoichiometric mixtures of MDI with different polyols measured by DSC at 5 K.min\(^{-1}\). DPG, PPG-425, PPG-1000 and PPG-4000.
The reaction between of PPG-1000 and MDI was investigated at 25 °C in TAM for different mixing ratios (Figure VII-4). The exothermic heat flow for the excess alcohol (r1-2 and r1-3) experiment decreases monotonically after the stabilization period at the start of the measurement. For stoichiometric (r1-1) and excess isocyanate (r2-1 and r3-1) experiments, a second peak is observed, superimposed upon the decreasing heat flow. The peak is observed earlier for higher concentrations of isocyanate. As the reacted mixtures had an opaque appearance, a plausible explanation for this second peak is reaction-induced phase separation, occurring as a result of the increasing molar mass and the changing chemical environment. Because of the phase separation, some domains are enriched in reactive groups and while others are depleted, with the enriched zones leading to an acceleration of the reaction. This increase in reaction rate is than observed as a second peak in heat flow. As reaction-induced phase separation strongly complicates the kinetic modelling, the reaction of MDI with PPG-1000 was not further investigated.

The reaction between PPG-425 and MDI with different mixing ratios was investigated at 25 °C in TAM and the results are given in Figure VII-5 (left). In all cases the reaction heat flow displays a monotonically decreasing trend and no secondary peaks are observed. After the cure in the TAM, none of the samples were opaque. So, no or very limited phase separation occurs during the reaction of MDI-PPG-425 mixtures having different mixing ratios. Therefore PPG-425 was selected for investigating the reaction kinetics in the presence of a catalyst.

The reaction heat flow of the excess isocyanate system is higher than for the stoichiometric ratio. Looking at the conversion rate (Figure VII-5 (right)), the excess isocyanate mixture reacts faster than excess OH, and the stoichiometric ratio has the rate. The conversion rates for the reaction of isocyanates with secondary alcohols in the absence of ether groups were about equal for off-stoichiometric conditions with the same relative amount of excess (see Chapter V, Figure V-12). For the PPG-425 this is not observed, which is probably due to the presence of
ether groups. In excess alcohol mixtures, more PPG-425 is used, and therefore the relative amount of ether groups is higher. This results in a lowering of the conversion rate.

The measured specific and molar reaction heats of the isothermal measurements during 15 hours is given in Table VII-2. When only the urethane formation was measured, the molar reaction heat should be the same for all mixing ratios and should be equal to the reaction enthalpy if no reaction heat is missed at the start of the measurement and full cure is achieved. The reaction enthalpy of the urethane reaction of an aromatic isocyanate group with an aliphatic secondary alcohol group was estimated with group contribution methods in Chapter V to be -77.3 kJ.mol⁻¹. The experimentally obtained reaction enthalpy for an MDI – cyclohexanol system is -80 kJ.mol⁻¹. The molar reaction heat of the excess isocyanate system (r2-1) exceeds this value with -26 kJ.mol⁻¹, which is too high to be caused by experimental or calculation errors, for example due to an inappropriate baseline. A more reasonable explanation is that a reaction with isocyanate groups takes place in parallel to the urethane formation, the isocyanurate reaction.

<table>
<thead>
<tr>
<th>Mixing Ratio</th>
<th>Reaction heat J.g⁻¹</th>
<th>Molar reaction enthalpy kJ.mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>r 1-1</td>
<td>-236</td>
<td>-80</td>
</tr>
<tr>
<td>r 2-1</td>
<td>-228</td>
<td>-106</td>
</tr>
<tr>
<td>r 1-2</td>
<td>-120</td>
<td>-65</td>
</tr>
</tbody>
</table>

The results of non-isothermal experiments at 10 K.min⁻¹ for different stoichiometric ratios are given in Figure VII-6. When analyzing the shape of the reaction peaks, visually it is clear that the reaction peak is not symmetrical. It starts around 0 °C and gradually increases. When a temperature of about 75 °C is reached, the reaction accelerates more quickly. This might indicate that a parallel reaction mechanism becomes more prevalent. This signature of different
mechanisms was not (as clearly) observed for the reaction between MDI and cyclohexanol (Figure V-11). The reaction peak for an excess isocyanate is the highest, followed by the stoichiometric mixture, and the excess alcohol, which was also observed in the isothermal experiments.

![Figure VII-6. Non-isothermal measurements at 10 K.min\(^{-1}\) for MDI-PPG-425 mixtures with different stoichiometries r1-1, r2-1 and r1-2. (left) reaction heat flow, (right) conversion rate.](image1)

3.3 The effects of adding catalyst

3.3.1 Effect of catalyst concentration

The effect of the catalyst concentration for the reaction in non-isothermal conditions can be found in Figure VII-7 (left). The reaction peak shifts to lower temperatures by increasing the catalyst concentration, indicating a faster reaction. The shape of the reaction peak for the measurements with added catalyst is very similar. For the measurement without added catalyst, a somewhat sharper peak is seen at higher temperature.

![Figure VII-7. Reaction heat flow for a stoichiometric MDI – PPG-425 mixture with 0.00 w%, 0.02 w%, 0.04 w% and 0.06 w% added catalyst measured at 10 K.min\(^{-1}\).](image2)

The results for isothermal measurements at 40 °C using the combined DSC/TAM method is given in Figure VII-8 (left). Regardless of the catalyst concentration, a high order kinetic...
behavior is observed. The initial reaction rate increases as the catalyst concentration is increased, except for 0.06 w% catalyst. This is because a larger portion of the reaction is missed for the 0.06 w% mixture because of its higher reactivity. The total reaction order evolution can be found in Figure VII-8 (right). The reaction order of the systems without added catalyst and with catalyst vary in very similar ways, indicating that the reaction mechanism for both systems should be quite similar.

Figure VII-8. Results of isothermal measurements at 40 °C for stoichiometric MDI – PPG-425 mixtures with 0.00 w%, 0.01 w%, 0.02 w%, 0.04 w% and 0.06 w% added catalyst. (left) reaction heat flow, (right) corresponding reaction orders.

The reaction rate is given as a function of the extent of reaction in Figure VII-9 (left). When looking at a fixed extent of reaction, it can clearly be seen that by increasing the amount of catalyst the reaction rate increases. This can also be evaluated by taking the mixture with 0.02 w% catalyst as reference system. By dividing the conversion rates of the different mixtures by the reference, a relative rate increase is given Figure VII-9 (right).

Figure VII-9. Results of isothermal measurements at 40 °C for stoichiometric MDI – PPG-425 mixtures with 0.00 w%, 0.01 w%, 0.02 w%, 0.04 w% and 0.06 w% added catalyst. (left) conversion rate and (right) relative conversion rate versus 0.02 w% as reference as a function of the extent of reaction.
Chapter VII

Using the assumption that the reaction mechanisms active in the absence catalyst, reacts in parallel with the catalyzed reaction, and that they are not influencing one another, the conversion rate of adding catalyst only can be calculated as followed:

\[
\dot{x}_{\text{cat only}}(x) = \dot{x}(x) - \dot{x}_{0.00\text{w} \%}(x) \tag{eq. VII-1}
\]

This estimated catalyst conversion rate corresponding with a conversion of 30% is given in Figure VII-10, showing a linearly increasing trend, having a slope of 0.607 kg.µmol\(^{-1}\).s\(^{-1}\) and an intercept of 0.055 s\(^{-1}\). The intercept of the line ideally should go through zero. A possible explanation for the deviation can be that the assumption that reaction of the uncatalyzed and the catalyzed reaction are not independent from one another is not correct.

3.3.2 Effect of stoichiometry

The reaction heat flow of a non-isothermal measurement at 10 K.min\(^{-1}\) for stoichiometric, excess OH and excess NCO mixtures is given in Figure VII-11 (top left). A broad urethane reaction peak is observed over a temperature range starting from 0°C, with the reaction not being finished at 200°C, and with a peak maximum around 100°C. This broad reaction peak is an indication of a low apparent activation energy for the overall process. The conversion rate as a function of temperature is given in Figure VII-11 (top right). The conversion rates of the off-stoichiometric mixtures are faster compared to the stoichiometric ratio. This was also observed for the reaction of the monofunctional group without addition of catalyst (see Chapter V section 4.1.2).
Polyurethane kinetics with polypropylene glycols in the presence of a catalyst

Figure VII-11. Results of non-isothermal measurements at 10 K.min\(^{-1}\) for MDI – PPG-425 mixtures with 0.04 w% added catalyst and having different stoichiometric ratios: r1-1, r2-1 and r1-2. (left) reaction heat flow; (right) conversion rate.

In isothermal conditions, the initial reaction heat flow of the stoichiometric mixture is more exothermic than for the off-stoichiometric ratios (Figure VII-12 (top left)). However, when looking at the conversion rates (Figure VII-12 (top right)), it becomes clear that the off-stoichiometric ratios have faster conversion rates than the stoichiometric mixture, which is consistent with the non-isothermal measurements.

For all stoichiometries, a high order reaction kinetic behaviour is observed. The reaction orders for the urethane formation are given in Figure VII-12 (bottom) for the different mixing ratios. The reaction order of the stoichiometric ratio with 0.04 w% added catalyst varies between two and three in the measured conversion region. The reaction orders of the excess OH and NCO systems are between 2.5 and 1.5, and they vary in a similar way. This implies that the partial reaction order of NCO and OH are similar. This was also observed for the system with MDI and cyclohexanol without added catalyst. The partial reaction orders of the systems with added catalyst seem not to be impacted by the catalyst. The mechanism with catalyst and without catalyst should therefore by quite similar.
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Figure VII-12. Results of isothermal measurements at 40 °C for MDI – PPG-425 mixtures with 0.04 w% added catalyst with different stoichiometric ratios: r1-1, r2-1 and r1-2. (top left) reaction heat flow; (top right) conversion rate; (bottom) total reaction order n as a function of the extent of reaction.

The reaction heat and molar heat released during the isothermal measurements with 0.04 w% catalyst is given in Table VII-3 for the different stoichiometries. The molar reaction heats for the different stoichiometries are close to one another and are close to the value of -80 kJ.mol⁻¹ observed with cyclohexanol, especially knowing that some reaction heat is missed during mixing procedure. This is in contrast to the results for the system without catalyst (see Table VII-2) and it implies that in the catalyzed excess isocyanate system only limited side reactions take place.

Table VII-3 Experimental reaction heat and molar reaction enthalpy for an MDI – PPG425 system with 0.04 w% catalyst with different stoichiometries

<table>
<thead>
<tr>
<th>Mixing Ratio</th>
<th>Reaction heat J.g⁻¹</th>
<th>Molar reaction enthalpy kJ.mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>r 1-1</td>
<td>-220</td>
<td>-74</td>
</tr>
<tr>
<td>r 2-1</td>
<td>-178</td>
<td>-82</td>
</tr>
<tr>
<td>r 1-2</td>
<td>-141</td>
<td>-77</td>
</tr>
</tbody>
</table>
3.3.3 Effect of heating rate and temperature

The results of the reaction heat flow of non-isothermal measurements for a stoichiometric ratio of MDI-PPG-425 with 0.04 w% added catalyst are given in Figure VII-13. The reaction peak of the experiment performed at lowest scanning rate of 5 K.min\(^{-1}\) starts a lower temperature compared to the experiments performed at higher scanning rates (Figure VII-13 (right)). The experiments reach a peak maximum around 90 °C, 100 °C and 120 °C for the scanning rates of 5, 10 and 20 K.min\(^{-1}\), respectively. The reaction peak is visibly more symmetric around the peak maximum as compared to the experiments without added catalyst (see section 3.2).

![Graphs showing reaction heat flow and heat capacity units](image)

*Figure VII-13. Results of non-isothermal measurements at 5, 10 and 20 K.min\(^{-1}\) for a stoichiometric MDI – PPG-425 mixture with 0.04 w% added catalyst. (left) reaction heat flow; (right) reaction heat flow in heat capacity units.*

4 Modeling polyurethane reactions with catalyst

4.1 Extending the mechanistic model with catalyst

The effect of the catalyst is introduced through the formation of an alkoxide ion via an equilibrium reaction between the catalyst and the alcohol group (eq. VII-8). By increasing the alkoxide ion concentration, the reaction rate is increased.\(^\text{1,2}\)

\[
\begin{align*}
\text{NCO} + \text{OH} & \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad \text{NCOH}^+ + \text{O}^- & \text{(eq. VII-2)} \\
\text{NCO} + \text{O}^- & \quad \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad \text{NCOO}^- & \text{(eq. VII-3)} \\
\text{NCOO}^- + \text{OH} & \quad \underset{k_{-4}}{\overset{k_3}{\rightarrow}} \quad \text{UR} + \text{O}^- & \text{(eq. VII-4)} \\
\text{NCOO}^- + \text{UR} & \quad \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \quad \text{AL} + \text{O}^- & \text{(eq. VII-5)}
\end{align*}
\]
Chapter VII

\[
\begin{align*}
\text{Et} + \text{OH} & \quad \frac{k_5}{k_{-5}} \rightarrow \text{EtOH} \\
\text{Et} + \text{UR} & \quad \frac{k_6}{k_{-6}} \rightarrow \text{EtUR} \\
\text{Cat} + \text{OH} & \quad \frac{k_7}{k_{-7}} \rightarrow \text{CatH}^+ + \text{O}^- 
\end{align*}
\]

(eq. VII-6)

(eq. VII-7)

(eq. VII-8)

The overall reaction order of the urethane reaction and the partial reaction orders of the alcohol, isocyanate and catalyst that this mechanism predicts can be estimated. For reaction (eq. VII-8), the equilibrium constant \( K_7 \) can be written as follows:

\[
K_7 = \frac{k_7}{k_{-7}} = \frac{[\text{CatH}^+][\text{O}^-]}{[\text{Cat}][\text{OH}]} \quad \text{(eq. VII-9)}
\]

A case is a huge amount of catalyst is present and the reaction is driven predominantly by the alkoxide ions created by the added catalyst is studied. Assuming (eq. VII-8) is a fast equilibrium and a lot of catalyst is present, meaning nearly all alkoxide ions are formed as a result of the catalyst, \([\text{NCO}^+]\) would be approximately zero, leading to following derivation:

\[
[\text{CatH}^+] \approx [\text{O}^-] \quad \text{(eq. VII-10)}
\]

\[
[\text{O}^-] = (K_7[\text{Cat}][\text{OH}])^{0.5} \quad \text{(eq. VII-11)}
\]

By substituting (eq. VII-11) into (eq. V-16) followed by (eq. VII-12), (eq. VII-13) is found, which can be simplified to (eq. VII-13) and (eq. VII-14) by assuming \( k_3[\text{OH}] \) is much smaller than \( k_{-2} \).

\[
\frac{d[\text{UR}]}{dt} = \frac{k_3k_2(K_7[\text{Cat}][\text{OH}])^{0.5}[\text{NCO}][\text{OH}]}{k_{-2} + k_3[\text{OH}]} \quad \text{(eq. VII-12)}
\]

\[
\frac{d[\text{UR}]}{dt} \approx k'[\text{OH}]^{1.5}[\text{NCO}][\text{Cat}]^{0.5} \quad \text{(eq. VII-13)}
\]

\[
k' = \frac{(K_7)^{0.5}k_2k_3}{k_{-2}} = (K_7)^{0.5}K_2k_3 \quad \text{(eq. VII-14)}
\]

Equation (eq. VII-13) shows that in case the reaction is catalyzed predominantly by the catalyst, the partial reaction orders of the alcohol, isocyanate and catalyst are 1.5, 1 and 0.5, respectively. The order of the catalyst is 0.5, which less than the order of one deduced from the linearity of Figure VII-10.
4.2 Evaluation of the model

4.2.1 Without added catalyst

The modelling results for the reaction of different mixing ratios of MDI - PPG425 without added catalyst at 40 °C are given in Figure VII-14. For the stoichiometric mixture, the start of the measurement is fitted quite well. After one hour, the modelled reaction rate slows down more rapidly than the measured reaction rate. This becomes clearer when the heat flow is plotted on a logarithmic scale. For the excess alcohol system, the first hour is not well fitted by the model, as the reaction rate is overestimated. From one hour onwards the model and the experiment fit much better. This is again more clearly seen in the logarithmic graph, where the model only starts to deviate from the experiment from 10 hours onwards. The model does not fit the experiment of the excess isocyanate system well. The initial reaction rate is overestimated and after 0.8 hours the rate is underestimated. The total reaction heat of the experiment and the model, which are -228 and -180 J.g\(^{-1}\) respectively, do not match. The experimental reaction heat of the experiment is higher than expected, which can be caused by an additional parallel reaction with isocyanate groups like the isocyanurate reaction, which is unaccounted for in the model. This might explain why the model fits the excess alcohol experiment the best.

![Figure VII-14. Reaction heat flows of isothermal measurements at 40 °C for MDI – PPG-425 mixtures without added catalyst having different stoichiometric ratios: r1-1, r2-1 and r1-2: experiment (solid) and model (dashed). (left) Linear scale, curves are shifted 0.25 W.g\(^{-1}\) apart for clarity, (right) logarithmic scale.](image)

4.2.2 Effect of catalyst concentration

The modelling results after optimization for stoichiometric MDI – PPG-425 mixtures with different catalyst concentrations can be found in Figure VII-15. When looking at the first three hours of the reaction, an overall good match between the modelled and the experimental reaction heat flow is observed. The biggest deviation between the model and the experiment is observed at the start of the reaction and experiments with a lower amount of added catalyst have slightly bigger deviations.
When evaluating the reaction over a more extended reaction time, still a good match between the model and the experiment is observed when plotting the heat flow on a logarithmic scale (Figure VII-15 (right)). Here, a slightly bigger difference between the model and the experiment is observed when the amount of catalyst is reduced, as was observed in the first hours of the measurement. As the concentration of catalyst is reduced, the mixture more closely resembles the situation without added catalyst and as was discussed in the previous section (section 4.2.1), it is possible that processes taking place in parallel are unaccounted for. This can explain why the deviation between the experiment and the model at the lower catalyst concentrations are bigger than for mixtures with higher amounts of catalyst.

Figure VII-16. Conversion rate as a function of (1-x) for isothermal measurements at 40 °C for stoichiometric MDI – PPG-425 mixtures with 0.01 w%, 0.02 w%, 0.04 w% and 0.06 w% added catalyst: experiment (solid) and model (dashed).
Polyurethane kinetics with polypropylene glycols in the presence of a catalyst

The model fits the experiments over nearly whole conversion and more than 2 orders of magnitude in conversion rate, as can be seen in Figure VII-16. It is important to note that the model fits the data up to high conversion, as this is crucial for predicting the final molar mass, as in the step growth polymerization of linear polymers, high molar mass polymer is only formed in stoichiometric conditions and at high conversions.

The comparison of model and experiments for reactions with different catalyst concentrations in non-isothermal conditions is given in Figure VII-17. At temperatures below 100°C, the match between the model and the experiment is quite good. At the peak of the reaction, somewhat bigger deviations between the model and the experiment are observed. The smaller peak height observed for the experiment with 0.04 w% catalyst, is explained by a longer preparation time, and by accounting for this preparation time this can also compensated by the model.

![Figure VII-17. Reaction heat flow for non-isothermal measurements at 5 K.min^{-1} for stoichiometric MDI – PPG-425 mixtures with 0.02 w%, 0.04 w% and 0.06 w% added catalyst: experiment (solid) and model (dashed).](image)

4.2.3 Effect of stoichiometry

The measured and simulated reaction heat flow of catalysed mixtures of MDI with PPG-425 at different stoichiometric ratios is shown in Figure VII-18. An overall good match between experiment and model is observed when looking at the first three hours of the reaction (Figure VII-18 (left)), although the model underestimated the initial reaction rate. On a logarithmic scale (Figure VII-18 (right)), a good match between the model and the experiment is observed over the whole time interval for the stoichiometric mixture. For the excess isocyanate mixture an acceptable match is observed for times below three hours. From three hours onwards, a bigger deviation between model and experiment is observed, with the model underestimating the reaction rate. A possible explanation for this, is again the contribution of a second reaction process. For the excess alcohol mixture, a good match between model and experiment is observed up to four hours after the beginning of the reaction. After the first four hours, the model and the experiments start to deviate significantly, even more than the mixture with excess isocyanate.
Figure VII-18. Reaction heat flows of isothermal measurements at 40 °C for MDI – PPG-425 mixtures with 0.04 w% added catalyst and different stoichiometric ratios: \( r1-1, r2-1 \) and \( r1-2 \): experiment (solid) and model (dashed). (left) linear scale, curves shifted 0.5 \( W.g^{-1} \) apart for clarity; (right) logarithmic scale.

The results for mixtures having different stoichiometries in non-isothermal conditions are given in Figure VII-19. A nice overlap between the heat flow of the model and experiment is observed for the stoichiometric system. Before the peak maximum, the predicted reaction rate is slightly higher than the experimental observed reaction rate, and the position of the peak maximum is at a slightly lower temperature (4 K) compared to the experiment. For the excess alcohol system \( r1-2 \), an overall good match between the experiment and the model is observed. At a temperature 130 °C the model slows down more quickly than the experimental curve. For the excess isocyanate system \( r2-1 \), the start of the reaction is modelled adequately. Closer to the peak maximum, around 70 °C, model and experiment diverge. The biggest difference between experimental and modelled heat flow is observed around the peak maximum. The area under the curve, representing the total reaction heat, is lower for the model than for the experiment. A possible explanation for the discrepancy between model and experiment can again be a parallel reaction of the isocyanate groups, e.g., the isocyanurate formation.
4.2.4 Effect of heating rate

The results for reactions of a stoichiometric mixture of MDI-PPG-425 with 0.04 w% added catalyst studied, at heating rates of 5, 10 and 20 K.min⁻¹ can be found in Figure VII-20. For all investigated heating rates, a good match between model and experiment is observed. The match is best at lower temperatures, below the peak maximum. When plotting the heat flow in heat capacity units (Figure VII-20 (right)), a clear difference between model and experiment is seen around the peak maximum for scanning rates of 5 and 10 K.min⁻¹, while a better match between the two is seen for the scanning rate of 20 K.min⁻¹.
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4.2.5 Kinetic parameters with added catalyst

Table VII-4 shows the kinetic parameters for the kinetic model optimized on the experimental data for the MDI-PPG425, with and without added catalyst. The parameters before optimization were initialized with the optimum parameters found for MDI-cyclohexanol (Table V-13). First only the isothermal experiments at 40°C of MDI-cyclohexanol and MDI-PPG425, with the different catalyst concentrations and stoichiometric ratios, were used to optimize the \( \log k_{TR} \) of the different reactions. The experiments of MDI-cyclohexanol were included to aid the optimization algorithm to obtain physically realistic parameters. Once a reasonable fit between the experiments and the model was obtained for the isothermal experiments, non-isothermal experiments with MDI-PPG425 were used to determine the activation energies \( E \) of the different reactions.

In Chapter V, a simplified formula (eq. V-20) for the reaction rate constant in the absence of catalyst \( (k') \) was derived. The reaction rate \( \log k'_{TR} \) at the reference temperature of 313.13 K obtained in Chapter V for MDI-cyclohexanol is -3.80 \( \log(\text{kg}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}) \). Using the same approximations the \( \log k'_{TR} \) for MDI-PPG425 results in -3.94 \( \log(\text{kg}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}) \) which is close to the values obtained with cyclohexanol. As discussed in Chapter V section 5.3.4, the sum of the kinetic parameters in the MDI – cyclohexanol reaction model are strongly coupled and cannot be independently determined, hence one should not compare the \( \log(A) \) and \( E \) of individual reaction steps. Also for the catalyzed reaction model couplings between the parameters exist which reduced the conclusions one can draw from a sensitivity analysis.

<table>
<thead>
<tr>
<th>reaction</th>
<th>forward reaction</th>
<th>backward reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_{TR} )</td>
<td>( \log(A) )</td>
</tr>
<tr>
<td>NCO + OH ⇌ NCOH(^+) + O(^-)</td>
<td>-4.00</td>
<td>-3.17</td>
</tr>
<tr>
<td>NCO + O(^-) ⇌ NCOO(^-)</td>
<td>4.10</td>
<td>4.93</td>
</tr>
<tr>
<td>NCOO(^-) + OH → UR + O(^-)</td>
<td>3.16</td>
<td>9.22</td>
</tr>
<tr>
<td>NCOO(^-) + UR ⇌ AL + O(^-)</td>
<td>-3.05</td>
<td>12.8</td>
</tr>
<tr>
<td>Et + OH ⇌ EtOH</td>
<td>3.18</td>
<td>4.54</td>
</tr>
<tr>
<td>Et + UR ⇌ EtUR</td>
<td>0.31</td>
<td>2.14</td>
</tr>
<tr>
<td>Cat + OH ⇌ CatH(^+) + O(^-)</td>
<td>5.19</td>
<td>6.05</td>
</tr>
</tbody>
</table>

Table VII-4 Kinetic parameters of the MDI-PPG425 mixture. The \( k_{TR} \) are given at the reference temperature of 313.13 K (40°C); \( \log k_{TR} \) and \( \log(A) \) are in \( \text{kg}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1} \), except parameters marked with *, which are given in \( \text{s}^{-1} \); the activation energy is given in kJ.mol\(^{-1}\).
5 Conclusions

In search for a good polyol to investigate the urethane reaction in the presence of added DABCO catalyst, an influence of the presence of oxygen in the DSC crucible was observed. The oxygen leads to an additional reaction peak starting around 160°C and was sample mass dependent. By perforating the DSC crucible and thereby removing the oxygen using the N₂ purge gas of the DSC, the oxidation reaction could be prevented. Three polypropylene glycols of different lengths, about 425, 1000 and 4000 g.mol⁻¹, were investigated without added catalyst. As the length of the PPG chain is increased, the reaction heat flow and the reaction heat are decreased. Using a PPG-4000, the reaction heat flow and heat are decreased too extensively for a good kinetic analysis. When investigating the urethane reaction of the PPG-1000 isothermally at 25 °C with and excess of alcohol, phase separation was observed, and therefore also PPG-1000 was excluded for the study with added catalyst.

Investigating the reaction between MDI and PPG-425 without added catalyst in isothermal conditions, no clear indication of phase separation was observed. Nevertheless, a discrepancy between the measured reaction heat which is higher and the expected heat based on the measurement of MDI with cyclohexanol was observed. This effect was most pronounced when an excess of isocyanate was present. The most likely explanation for this effect is that a parallel reaction takes place, and that this is observed because of the lowered urethane reaction rate resulting from the higher relative amount of retarding ether groups. By adding catalyst and therefore speeding up the urethane formation, this effect could be reduced again.

The effect of added catalyst on the MDI-PPG-425 reaction kinetics was investigated. The overall reaction order of the urethane formation at 40 °C was calculated and was found to be 3.5 and 1.8 for the experiments with added catalyst, with the reaction order being the highest at the beginning of the reaction and gradually decreasing. This evolution was also observed in the experiments of MDI and cyclohexanol without added catalyst, implying that the reaction mechanisms with and without added catalyst are comparable.

Starting from the ionic reaction mechanism without added catalyst, a new equilibrium reaction was added to account for the added catalyst. The equilibrium reaction consists of an interaction of the catalyst with an OH group, forming an O⁻ ion and CatH⁺ ion. The catalytic effect is achieved by increasing the concentration of the O⁻ ions. Using the quasi stationary state and fast equilibrium approximations, the overall reaction rates could be deduced to be around 2.5 when the reactive O⁻ alkoxide ion is predominantly formed by catalyst, which is in the range of experimentally calculated reaction orders.

The model, after parameter optimization, was evaluated by comparing it to the experimentally obtained results. A good match was found between the experiments and the model for the stoichiometric mixture with different catalyst concentrations, both in isothermal conditions at 40 °C and in non-isothermal ones. For the off-stoichiometric ratios, the model could predict the
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isothermal experiment quite well for the first couple of hours, but as the extent of reaction is increased model and experiment start to deviate from one another. In non-isothermal conditions, the excess alcohol condition was well predicted by the model, but the prediction for the excess isocyanate condition was less successful.

A model system able to form linear polymers which can be modelled with a mechanistic model including a catalyst is now available. This was a necessary requirement to study the properties of the produced polymers as a function of the molar mass. In the next chapter, a recursive algorithm will be developed to calculate average molar masses and other properties. This recursive algorithm will be applied together with the monomers and the kinetic model in Chapter IX.

6 References


CHAPTER VIII
STRUCTURE EVOLUTION

1 Introduction

The molecular architecture of polymers defines to a large extent the macroscopic properties of the polymeric system. To characterize and understand the physical properties of linear and branched polymers essential to know their molar mass distribution while for network polymer the molecular architecture of the polymer network is needed. Different theoretical models have been developed to predict the molar mass distribution based on the reaction kinetics of the polymerization. Often, detailed knowledge of the full molar mass distribution is not needed to predict certain properties. With a good estimation of the molar mass averages of a polymer, properties, like viscosity, gelation, crosslink density and rubber elastic behavior, can be predicted to a certain degree.\(^1\) Using probability generating functions, Gordon derived average properties of polymer systems.\(^2\) The advantage of this approach is that it is not necessary for the whole distribution to be calculated. A disadvantage is that the abstract mathematics and the formulation of the equations for molecular mass averages are not straightforward.\(^1\) Macosko and Miller\(^3,4\) proposed a method using the recursive elements of a polymer network to calculate the average molar masses directly, hereby bypassing the use of probability generating functions. To be able to calculate these average molar masses assumptions first proposed by Flory\(^5\) were made:

- all functional groups of the same type are assumed to be equally reactive, independent of the length of the molecule they are part of.
- all functional groups react independently from one another.
- no intramolecular reactions occur in finite species.

In addition to the weight average molar mass \(M_w\), other properties can be calculated, such as the \(z\)-average molar mass \(M_z\) in the pre-gel phase, and the mass fractions of the sol, pending and elastic effective phase and the crosslink density in the post-gel phase. Since the development of this method, continued interest in the results and formulas of the developed method was shown, leading to adapted formulas, so that Flory’s assumptions could be somewhat relaxed, taking into account, among others, the effects of unequal reactivity,\(^6\) the effect of substitution on the reactivity of remaining functional groups,\(^7,8\) and formulas for higher order average molar masses\(^1\). These results were later used to calculate the viscosity evolution in the pre-gel phase\(^9,10\) and the viscoelastic properties.\(^11–13\)

In this chapter, is a method is described to calculate the number, weight and higher order molar masses and related pre-gel properties, as well as the post-gel properties, for general step-growth polymerization reactions, where unequal reactivity, substitution effects and competing parallel
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reactions can all be combined. Different (hypothetical) polyurethane systems were investigated as case studies for the algorithm implemented. Due to the large number of possible reactions, complex molecular architectures can be obtained. In order to describe the evolution of average molar masses and mechanical properties, a method capable of the handling these complexities is needed. To validate the algorithm described in this work, the results will be compared to results of calculations published in literature.

2 Theory

2.1 Estimation of pre-gel properties

The derivation presented in this chapter is based on the *in-out* recursive probability modeling first presented by Macosko and Miller. This approach can be used to calculate average molar masses for step-growth polymerizations. To calculate the average molecular mass several parameters must be known a priori: (i) the molar mass of the monomer units, (ii) the number of functional groups present on the monomer units, and (iii) the mass fractions of these monomer units. Additionally, the concentrations of the functional groups and the concentrations of the linking groups are assumed to be known. The concentrations can be determined using spectroscopic techniques or be calculated using a model based on a reaction mechanism of the polymerization. During the polymerization the reactive mixture is assumed to remain homogeneous and in the pre-gel stage it is assumed that no cyclization occurs. In previously published papers, a method and reaction systems are usually described, and the results are limited to a specific case. In this chapter, a more general method is proposed that can be used for both homo- and copolymerization, account unequal reactivity, and allows the calculation of higher-order molecular mass averages, which is useful to describe the polydispersity. First, the derivation of the calculation of the weight average molar mass will be given and the way to extend this approach to higher-order weight averages, with explicit formulation of the z-average molar mass. Next, the number average and weight average number of branching points will be calculated, which are used to calculate the number average molar mass and the $g$ factor. To end this section, the molar mass average calculations are used to predict the viscosity evolutions.

2.1.1 Weight-Average Molar Mass $M_w$

The derivation of the formulas and the basis of the algorithm is based on a thought experiment, which is illustrated schematically in Figure VIII-1. The polymer molecule that is depicted schematically in Figure VIII-1c is constituted out of monomers $C_i$ depicted in Figure VIII-1b, whose (reactive) functional groups $A_j$ reacted forming the linking functional groups $B_k$ following the rules $R_k$ set forward in Figure VIII-1a. To illustrate the recursive analysis of a polymer molecule, one first selects a root monomer, an arbitrary starting point, indicated by an asterisk in Figure VIII-1c and Figure VIII-1d, somewhere on the polymer molecule. From this starting point one “walks” in all possible chain directions through the molecule or network, noting the size of the branches ahead.
Figure VIII-1. a) The functional groups ($A_i$) and the connectivity scheme leading to the linking functional groups ($B_k$), b) The monomer units ($C_i$) present in the polymer chain, c) Schematic representation of a randomly chosen root monomer (indicated by an asterisk *) as the starting point for the molecular mass calculations in a random polymer molecule. d) The steps to “walk” through the polymer to calculate the mass of the polymer, starting from the root monomer.

This is shown schematically in Figure VIII-1d, where in each successive step the chains are followed one step further away from the starting point, keeping track of the molar mass of each successive section as we go along. As the mass is a stochastic variable, the most likely mass of the polymer can be calculated, corresponding to the weight average molar mass.

To explain this process in more detail, first several parameters need to be defined. A polymer consists of many monomer units, each belonging to one of the $n_C$ types of monomers, which are identified as $C_i$ in our thought experiment and Figure VIII-1b. In the example, the polymer has four types of monomers units. These monomers units have functional groups that can react to form a polymer chain. In the example (Figure VIII-1a), the functional groups are represented by three shapes (●, □, ◆), while in the algorithm the functional groups will be denoted by $A_i$. Note that in one monomer unit multiple and different functional groups can be present, as is the case for $C_3$ and $C_4$ in the example. The total number of different functional groups is represented by $n_A$. For each monomer, the functional groups and their functionality are stored in a functionality matrix $f$. In this matrix, each row with index $i$ corresponds to monomer type $C_i$,
and each column with index $j$ corresponds to functional group type $A_j$. Matrix $f$ is thus a $n_C$ by $n_A$ matrix. The functionality matrix $f$ of the example is given by (eq. VIII-1).

$$f = \begin{bmatrix} 2 & 0 & 0 \\ 0 & 3 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{bmatrix} \quad (eq. \text{VIII-1})$$

Investigating $C_2$ as an example (Figure VIII-1b), note that there are three $A_2$ and no other functional groups, so the value of $f_{2,2}$ is three, while $f_{2,1}$ and $f_{2,3}$ are zero. Specific combinations of functional groups present on the monomers can react with each other, forming a link and extending the monomers to polymer chains and networks. In the example, two types of links can be formed, as illustrated by the linking rules $R_k$ in Figure VIII-1a. A first type of linking functional group $B_1$ is formed by combining one functional group $A_1$ with one $A_2$, as a result of reaction $R_1$. Note that strictly speaking $R_k$ is not required to be a reaction: it could also be a physical interaction linking two functional groups, but the lifetime of this interaction should be longer than the timescale of the investigated properties. In the polyurethane chemistry, a similar linking rule would correspond to the formation of urethane through the reaction of an isocyanate group with an alcohol group. The second type of link is formed by combining one $A_2$ and two $A_3$ functional groups, leading to linking functional group $B_2$. A similar link between three groups could be used to represent the allophanate formation from two isocyanate groups and one alcohol group. In general, $R_k$ and $B_k$ correspond to the $k^{th}$ linking reaction and the $k^{th}$ linking functional group, respectively. The number of linking functional groups is represented by $n_R$. This information can be represented by a connectivity matrix $\alpha$, where the row with index $k$ corresponds to the type of link $R_k$ and linking group $B_k$, while the column with index $j$ corresponds to the functional group $A_j$. Matrix $\alpha$ is thus an $n_R$ by $n_A$ matrix. The connectivity matrix $\alpha$ for the example of Figure VIII-1 is given by (eq. VIII-2)

$$\alpha = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 1 & 2 \end{bmatrix} \quad (eq. \text{VIII-2})$$

For estimating the weight average molar mass, the thought experiment starts by selecting a root monomer unit at random (chosen by mass) from the mixture. $W$ is defined as a stochastic variable corresponding to the mass of the whole molecule that contains the root monomer unit. In the example, the root monomer unit is of the $C_2$ type and is marked by an asterisk * (Figure VIII-1c). The probability of selecting a certain monomer as root monomer unit depends on the mass fraction of its monomer type present in the mixture (eq. VIII-3).

$$W = \begin{cases} W_1 \text{ if random root is a monomer unit of type } C_1 \\ ... \\ W_i \text{ if random root is a monomer unit of type } C_i \\ ... \\ W_{n_C} \text{ if random root is a monomer unit of type } C_{n_C} \end{cases} \quad (eq. \text{VIII-3})$$
If the root monomer is of type $C_i$, the total mass of the polymer molecule is equal to the mass of the root monomer $M_i^{\text{w}}$ plus the mass of all chains attached to the (reacted) functional groups of the monomer. This was called the ‘out’ mass for functional group $j$ of the polymer molecule with root monomer type $C_i$, $W_{ij}^{\text{out}}$, by Macosko and Miller.3,4

$$W_i = M_i^{\text{w}} + \sum_{j=1}^{n_A} \sum_{l=1}^{f_{ij}} (W_{ij}^{\text{out}})_l \quad (\text{eq. VIII-4})$$

The way to “walk” stepwise through all branches of the molecule emanating from the root monomer unit is illustrated in Figure VIII-1d. In step I of Figure VIII-1d, three $A_2$ functional groups are present on the root monomer. Thus, the total mass of the polymer molecule is the mass of monomer unit $C_2$ plus the mass of the chains attached to the three $A_2$ functional groups, represented by $(W_{22}^{\text{out}})_1$ and $(W_{22}^{\text{out}})_2$. The next step is to determine the value of $W_{ij}^{\text{out}}$. This mass depends on whether the functional group $A_j$ of monomer $C_i$ has reacted and, if so, which type of linking functional group $B_k$ it has formed, as summarized in (eq. VIII-5).

$$W_{ij}^{\text{out}} = \begin{cases} 0 & \text{if } A_j \text{ from } C_i \text{ has not reacted} \\ W_{ij1}^{\text{out}} & \text{if } A_j \text{ from } C_i \text{ reacted into } B_1 \\ \cdots & \cdots \\ W_{ijk}^{\text{out}} & \text{if } A_j \text{ from } C_i \text{ reacted into } B_k \\ \cdots & \cdots \\ W_{ijnR}^{\text{out}} & \text{if } A_j \text{ from } C_i \text{ reacted into } B_{n_R} \end{cases} \quad (\text{eq. VIII-5})$$

The simplest case is if the functional group has not reacted. In this case, the mass of the chain attached to the group is zero. In the example, this is the case for the group giving $(W_{22}^{\text{out}})_3$. For the groups leading to $(W_{22}^{\text{out}})_1$ and $(W_{22}^{\text{out}})_2$, a $B_2$ and $B_1$ type of linking group were formed, respectively (Figure VIII-1d, step II), with $B_2$ built up out of one $A_2$ and two $A_3$ functional groups, following the connectivity scheme (Figure VIII-1b). In general, the “outlooking” mass of each linking group $B_k$, written as $W_{ijk}^{\text{out}}$, is calculated by summing the masses of the chains attached to this linking group, excluding the chain from which the linking group was reached. Each linking group $B_k$ is built up from functional groups as is defined by $R_k$ in the connectivity scheme. Thus, to know the mass of all chains attached by linking group $B_k$, one must look “into” the chains connected via each of the functional groups forming $B_k$. Writing the mass attached to a specific group $A_j$ as $W_{ij}^{\text{in}}$, $W_{ijk}^{\text{out}}$ is given by (eq. VIII-6). The first term corresponds with the functional group type $A_j$ from which linking group $B_k$ was reached (so one less is available), while the second term corresponds to the other types of functional groups that can partake in linking processes ($A_p$ with $p \neq j$).

$$W_{ijk}^{\text{out}} = \sum_{l=1}^{\alpha_{kj}-1} (W_{ij}^{\text{in}})_l + \sum_{p=1}^{n_A} \sum_{l=1}^{\alpha_{kp}} (W_{p}^{\text{in}})_l \quad (\text{eq. VIII-6})$$
All monomer units containing a functional group that can be used to build up the linking group can be used to extend the polymer chain (Figure VIII-1d, step III). The mass of the branch belonging to the functional group is determined by knowing the mass of the monomer unit and what is connected to it, which is determined by looking ‘into’ the monomer unit.

\[
W_{ij}^{\text{in}} = \begin{cases} 
W_{ij}^{\text{in}} & \text{if } A_j \text{ belongs to a monomer unit of type } C_i \\
\ldots & \\
W_{ij}^{\text{in}} & \text{if } A_j \text{ belongs to a monomer unit of type } C_i \\
\ldots & \\
W_{ncl}^{\text{in}} & \text{if } A_j \text{ belongs to a monomer unit of type } C_{ncl} 
\end{cases} \quad (\text{eq. VIII-7})
\]

In the example of linking group \( B_2 \) in Figure VIII-1d (step IV), there are two possible sources of functional group \( A_3 \): a monomer unit of type \( C_3 \) or one of type \( C_4 \). The mass \( W_{ij}^{\text{in}} \) of the chain connected via a functional group \( A_j \) of monomer type \( C_i \) can be calculated by adding together the mass of the monomer unit itself and the masses of the chains attached to the functional groups of this monomer unit, looking outward and excluding the functional group from which the monomer unit was reached in the previous step (eq. VIII-8).

\[
W_{ij}^{\text{in}} = M_i^w + \sum_{l=1}^{f_{ij}-1} (W_{ij}^{\text{out}})_l + \sum_{p=1}^{n_A} \sum_{l=1}^{f_{ip}} (W_{ip}^{\text{out}})_l \quad (\text{eq. VIII-8})
\]

The first term in (eq. VIII-8) corresponds to the molar mass of the monomer unit itself, the second term adds all the masses of the functional groups of type \( A_j \) from which the monomer unit was reached (one was used for reaching the monomer unit), and the last term accounts for the masses connected to all other functional groups present on the monomer unit.

Next, the masses looking outwards from the monomer unit need to be calculated, which can be accomplished following the same procedure as described by (eq. VIII-5). In Figure VIII-1d, step I and step V illustrate the same procedure. The next step in the algorithm is performing the same procedure as in step II, and so on. Hence, a recursive method can be developed to calculate the molar mass \( W \) of a random polymer chain.

As the molar mass \( W \) of the molecule is a stochastic variable, the most likely value can be calculated and corresponds to the weight average molar mass \( M_w \). To do this, the expected value operator \( \mathbb{E}[] \) is used on (eq. VIII-3), leading to (eq. VIII-9). The likelihood that a monomer unit of type \( C_i \) is selected as root monomer unit increases with the mass-based amount that is present (assuming that the heavier or the larger the monomer unit is, the more likely it is to be chosen), which is defined by the mass fraction \( w_i^f \) of the monomer unit type used in the original reactive mixture. The higher the amount of monomer unit is present, the higher the likelihood that it will be selected.
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\[ M_w = \text{E}[W] = \sum_{i=1}^{n_C} w_i^l \cdot \text{E}[W_i] \quad (eq. \text{VIII-9}) \]

The expected value \( \text{E}[W_i] \) of \( W_i \) as defined by (eq. VIII-4) can be transformed into (eq. VIII-10)

\[ E[W_i] = \text{E} \left[ M_i^w + \sum_{j=1}^{n_A} \sum_{l=1}^{f_{ij}} (W_{ij}^\text{out})_l \right] \quad (eq. \text{VIII-10}) \]

The masses of the different connected chains, indexed by \( l \), are independent from one another, assuming no cyclization occurs. As the expected value of a sum of independent stochastic variables is equal to the sum of the expected values of the stochastic variables, (eq. VIII-10) can be rewritten as (eq. VIII-11).

\[ E[W_i] = M_i^w + \sum_{j=1}^{n_A} \sum_{l=1}^{f_{ij}} \text{E}[W_{ij}^\text{out}] = M_i^w + \sum_{j=1}^{n_A} f_{ij} \text{E}[W_{ij}^\text{out}] \quad (eq. \text{VIII-11}) \]

To calculate the likelihood that a (reactive) functional group of type \( A_j \) has reacted, in literature\(^1,3,4,6,7,10,14,15\) a conversion based on the concentrations of the functional groups is used.

Here, the conversion is calculated using a mass-based concentration of the linking groups \([B_k]\), which needs to be adjusted to take account for off-stoichiometric systems by calculating the limiting functional group concentration for \( B_k \), called \([B_k]_{\text{lim}}\). The latter corresponds to the concentration of the least abundant functional group used in \( B_k \), taking into account its stoichiometry with respect to \( B_k \). This limiting concentration is thus given by (eq. VIII-12).

\[ [B_k]_{\text{lim}} = \min \left( \frac{[A_1]_0}{\alpha_{k1}}, \ldots, \frac{[A_l]_0}{\alpha_{k\ell}}, \ldots, \frac{[A_{n_A}]_0}{\alpha_{k\text{n}_A}} \right) \text{ with } \alpha_{kj} > 0 \quad (eq. \text{VIII-12}) \]

The conversion \( x_k \) of the linking group \( B_k \) is then defined by dividing its concentration by its limiting concentration, as shown in (eq. VIII-13). This conversion \( x_k \) is the fraction of linking groups \( B_k \) formed with respect to the theoretical maximum based on the initial composition and the connectivity scheme.

\[ x_k = \frac{[B_k]}{[B_k]_{\text{lim}}} \quad (eq. \text{VIII-13}) \]

To correct for the stoichiometric imbalance of the individual functional groups \( A_j \) in the expected value of the outlooking molar masses \( \text{E}[W_{ij}^\text{out}] \), a factor \( g_{kj}^{\text{off}} \) is defined by dividing the concentration of the linking groups by the rescaled initial concentrations of the functional groups:
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\[ g_{kj}^{\text{off}} = \frac{[B_k]_{\text{lim}}}{[A_j]_0} \]  

(eq. VIII-14)

To calculate the likelihood that a functional group has reacted and formed a linking group, the linking group conversion is multiplied by factor expressing the stoichiometric imbalance of the functional group. Using this factor, the expected value \( E[W_{ij}^{\text{out}}] \) can now be calculated leading to (eq. VIII-15).

\[
E[W_{ij}^{\text{out}}] = \sum_{k=1}^{n_R} x_k g_{kj}^{\text{off}} E[W_{ijk}^{\text{out}}]
\]

(eq. VIII-15)

The expected value of (eq. VIII-6) can be calculated in an analogous way to (eq. VIII-10).

\[
E[W_{ijk}^{\text{out}}] = E \left[ \sum_{l=1}^{\alpha_{kj}^{-1}} (W_j^{\text{in}})_l + \sum_{p=1}^{n_A} \sum_{l=1}^{\alpha_{kp}^{-1}} (W_p^{\text{in}})_l \right] = \sum_{l=1}^{\alpha_{kj}^{-1}} E[W_j^{\text{in}}] + \sum_{p=1}^{n_A} \sum_{l=1}^{\alpha_{kp}^{-1}} E[W_p^{\text{in}}]
\]

\[
E[W_{ijk}^{\text{out}}] = E \left[ (\alpha_{kj} - 1)E[W_j^{\text{in}}] + \sum_{p=1}^{n_A} \alpha_{kp} E[W_p^{\text{in}}] \right] = \sum_{p=1}^{n_A} \alpha_{kp} E[W_p^{\text{in}}] - E[W_j^{\text{in}}]
\]

(eq. VIII-16)

(eq. VIII-16) is only valid if functional group \( A_j \) is part of the connectivity scheme \( R_k \), or in other words, if \( \alpha_{kj} \) is greater than zero. If this is not the case, \( E[W_{ijk}^{\text{out}}] \) is zero, leading to (eq. VIII-17). Note that the right-hand side of (eq. VIII-17) is independent of the monomer \( C_i \) from which linking group \( B_k \) was entered, meaning that \( E[W_{ijk}^{\text{out}}] \) is the same for all monomer units that have a functional group \( A_j \) and a connection \( B_k \).

\[
E[W_{ijk}^{\text{out}}] = \begin{cases} 
\sum_{p=1}^{n_A} \alpha_{kp} E[W_p^{\text{in}}] - E[W_j^{\text{in}}] & \text{if } \alpha_{kj} > 0 \\
0 & \text{if } \alpha_{kj} = 0
\end{cases}
\]

(eq. VIII-17)

To calculate the expected value of (eq. VIII-7), the likelihood that a functional group \( A_j \) is part of a monomer unit of type \( C_i \) is needed, which equals the (initial) molar fraction \( \rho_{ij} \) of functional groups \( A_j \) on monomer units \( C_i \). First, the initial mass-based concentration \([A_j]_{C_i,0}\) of functional
group $A_j$ contributed by monomer units of type $C_i$ is calculated as the initial mass-based concentration of the monomer in the mixture $[C_i]_0$ multiplied by the functionality of the functional group. This can be rewritten as the mass fraction of monomer units of type $C_i$, $w_i^f$, divided by their molar mass $M_i^w$, as shown in (eq. VIII-18).

$$[A_j]_{C,0} = f_{ij} [C_i]_0 = f_{ij} \frac{w_i^f}{M_i^w} \quad \text{(eq. VIII-18)}$$

To obtain the molar fraction $\rho_{ij}$, this concentration needs to be divided by the initial concentration of the functional group $[A_j]_{tot,0}$, which equals the sum of all initial concentrations of that functional group over all monomer units, leading to (eq. VIII-19):

$$\rho_{ij} = \frac{[A_j]_{C,0}}{[A_j]_{tot,0}} = \frac{f_{ij} w_i^f}{\sum_{l=1}^{n_c} f_{il} [C_l]_0} = \frac{f_{ij} w_i^f}{\sum_{l=1}^{n_c} f_{il} \frac{w_l^f}{M_l^w}} \quad \text{(eq. VIII-19)}$$

Next, the expected value of (eq. VIII-7) can be calculated:

$$E[W_{ij}^{in}] = \sum_{i=1}^{n_c} \rho_{ij} E[W_{ij}^{in}] \quad \text{(eq. VIII-20)}$$

Similar to (eq. VIII-10) and (eq. VIII-17), the expected value of (eq. VIII-8) can be transformed into (eq. VIII-21).

$$E[W_{ij}^{in}] = E \left[ M_i^w + \sum_{l=1}^{f_{ij}-1} (W_{ij}^{out})_l + \sum_{p=1}^{n_A} \sum_{l=1}^{f_{ip}} (W_{ip}^{out})_l \right]$$

$$= M_i^w + \sum_{l=1}^{f_{ij}-1} E[W_{ij}^{out}] + \sum_{p=1}^{n_A} \sum_{l=1}^{f_{ip}} E[W_{ip}^{out}]$$

$$= M_i^w + (f_{ij} - 1) E[W_{ij}^{out}] + \sum_{p=1}^{n_A} f_{ip} E[W_{ip}^{out}]$$

$$E[W_{ij}^{in}] = M_i^w - E[W_{ij}^{out}] + \sum_{p=1}^{n_A} f_{ip} E[W_{ip}^{out}] \quad \text{(eq. VIII-21)}$$

This is only valid if the functional group $A_j$ is present in monomer unit $C_i$ or, equivalently, if $f_{ij}$ is larger than zero. If this is not the case, the expected value is of $W_{ij}^{in}$ is equal to zero:
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\[
E[W_{ij}^{\text{in}}] = \begin{cases} 
M_i^w - E[W_{ij}^{\text{out}}] + \sum_{p=1}^{n_A} f_{ip}E[W_{ip}^{\text{out}}] & f_{pj} > 0 \\
0 & f_{pj} = 0
\end{cases} \quad (\text{eq. VIII-22})
\]

In a final step, successively substituting (eq. VIII-22) into (eq. VIII-20), into (eq. VIII-17), and into (eq. VIII-15), results in a set of \(n_C\) by \(n_A\) equations in unknowns \(E[W_{ij}^{\text{out}}]\). This set of equations can be solved numerically using a Newton-Raphson method or by transforming the formulas into a symbolic equation using commercial software packages like Matlab® and solve it in a symbolic way. Finally, the resulting expressions for \(E[W_{ij}^{\text{out}}]\) can be substituted into (eq. VIII-11) and the result substituted into (eq. VIII-9) to obtain a formula for the mass average molar mass \(M_w\). The parameters that will govern the obtained formula for the evolution of the molar mass are the mass fraction \((w_f)\) of the monomer units and the concentration profiles of the functional groups \([A_i]\) and linking groups \([B_k]\).

2.1.2 Z-Average Molar Mass \(M_z\)

Using a similar approach as for the weight-average molar mass \(M_w\), higher order molar masses can be calculated, starting with Z-average molar mass \(M_z\). This was performed using techniques first described by Shiau et al. for a copolymerization of type \(A_t + B_g\). \(M_z\) is defined as the ratio of the second moment of the mass distribution \(E[W^2]\) to the first moment \(E[W]\).

\[
M_z = \frac{E[W^2]}{E[W]} \quad (\text{eq. VIII-23})
\]

Note that formula for \(E[W]\) has already been calculated as it equals \(M_w\) and that \(E[W^2]\) corresponds to the variance of \(M_w\). To calculate \(E[W^2]\), the expected value of the squares of (eq. VIII-3) to (eq. VIII-8) need to be calculated. For (eq. VIII-3) this leads to:

\[
E[W^2] = \sum_{i=1}^{n_C} w_i^t E[W_i^2] \quad (\text{eq. VIII-24})
\]

The formula based on (eq. VIII-4) is derived as follows:

\[
E[W_i^2] = E\left[\left(M_i^w + \sum_{j=1}^{n_A} \sum_{l=1}^{f_{ij}} (W_{ij}^{\text{out}})_l\right)^2\right]
\]

\[
E[W_i^2] = M_i^{w^2} + 2M_i^w \sum_{j=1}^{n_A} f_{ij} E[W_{ij}^{\text{out}}] + E\left[\left(\sum_{j=1}^{n_A} \sum_{l=1}^{f_{ij}} (W_{ij}^{\text{out}})_l\right)^2\right]
\]
Structure evolution

\[
E[W_i^2] = M_i^w + 2M_i^w \sum_{i=1}^{n_A} f_{ij}E[W_{ij}^{out}] + \sum_{j=1}^{n_A} f_{ij}E[(W_{ij}^{out})^2]
\]

\[
- \sum_{j=1}^{n_A} f_{ij}E[W_{ij}^{out}]^2 + \left(\sum_{j=1}^{n_A} f_{ij}E[W_{ij}^{out}]\right)^2
\]

(eq. VIII-25)

The results for (eq. VIII-5) to (eq. VIII-8) are given by (eq. VIII-26) to (eq. VIII-29). To solve (eq. VIII-24) the substitution of (eq. VIII-25) in (eq. VIII-29) using the calculated results from (eq. VIII-9) to (eq. VIII-22) is needed.

\[
E[W_{ij}^{out}] = \sum_{k=1}^{n_R} x_k g_{kj}E[W_{ij}^{out}]
\]

(eq. VIII-26)

\[
E[W_{ijk}^{out}] = 2E[W_i^{in}]^2 - E[W_i^{in}] + \sum_{p=1}^{n_A} \alpha_{kp}E[W_p^{in}^2] - \sum_{p=1}^{n_A} \alpha_{kp}E[W_p^{in}]^2
\]

\[+ \left(\sum_{p=1}^{n_A} \alpha_{kp}E[W_p^{in}]\right)^2 - 2E[W_i^{in}]\sum_{p=1}^{n_A} \alpha_{kp}E[W_p^{in}]
\]

(eq. VIII-27)

\[
E[W_i^{in}] = \sum_{i=1}^{n_C} \rho_{ij}E[W_i^{in}]
\]

(eq. VIII-28)

\[
E[W_i^{in}^2] = M_i^w - E[W_i^{out}] + 2E[W_i^{out}]^2 + \sum_{p=1}^{n_A} f_{ip}E[W_{ip}^{out}]
\]

\[- \sum_{p=1}^{n_A} f_{ip}E[W_{ip}^{out}]^2 + \left(\sum_{p=1}^{n_A} f_{ip}E[W_{ip}^{out}]\right)^2
\]

(eq. VIII-29)

Now that \(M_w\) and \(M_z\) can be calculated, higher order moment molecular mass averages can be derived in a similar way. Note that higher order moments require all lower order moments to be calculated, thus increasing the computational cost. Using the recursive algorithm, the number average molar mass cannot be derived. To calculate it, the number average of branching points is needed.
2.1.3 Number and weight average number of branching points

Two mechanisms can lead to branching during polymerization. The first type of branches occurs when three or more functional groups of a monomer unit have reacted, requiring that the functionality of that type of monomer units is higher than two. The second type of branching occurs when three or more functional groups are used to form a linking group in the connection scheme $R_k$, as is the case for $B_2$ in the example in Figure VIII-1b. In addition, there are two ways of counting the number of branching points. A first approach is to count each monomer unit for which three or more of its functional groups have reacted as one branching point. A second approach is to consider the so-called “effectiveness” of the branching point. In this method, the branching points (monomers) are counted in a way that the functionality of the monomer is accounted for. For example, a monomer unit which has three reacted functional groups will count as one branching point, a monomer unit which has four reacted functional groups will count as two, and in general a monomer unit which $\lambda$ reacted groups will count is $\lambda$-2 branching points. The branching points will be denoted with $T$, while the effective number of branching points will be denoted with $\tilde{T}$.

First, for calculating the branching points caused by monomer units, denoted $T_C$, the likelihood that a functional group $A_j$ has reacted $P(A_j^{\text{reacted}})$ is determined by summing the conversion of the linking group scaled by the stoichiometry factor $g_{kj}^{\text{off}}$ (eq. VIII-30). Note that if the functional group $A_j$ is not used in connection scheme $R_k$, $\alpha_{kj}$ is zero and thus $g_{kj}^{\text{off}}$ equals zero.

$$P(A_j^{\text{reacted}}) = \sum_{k=1}^{n_R} x_k g_{kj}^{\text{off}}$$

(eq. VIII-30)

The likelihood that the reacted functional group $A_j$ belongs to monomer unit $C_i$, $P(A_i^{\text{reacted}})$, is calculated by multiplying the likelihood that the it has reacted by the (initial) molar fraction $\rho_{ij}$ of functional groups $A_j$ on monomer units $C_i$ (eq. VIII-19):

$$P(A_i^{\text{reacted}}) = \rho_{ij} P(A_j^{\text{reacted}})$$

(eq. VIII-31)

Monomer unit $C_i$ is a branching node of degree $\lambda$ if exactly $\lambda$ functional groups have reacted. This can be divided into branches resulting from different functional groups. A binomial probability $P_n$ is used to account for the different configurations:

$$P(T_i^{\lambda_j}) = P_n \left( T_i^{\lambda_j} | C_i A_j \right) = \binom{\lambda_j}{\lambda} P(A_i^{\text{reacted}})^{\lambda_j} (1 - P(A_i^{\text{reacted}}))^{\lambda_j - \lambda_j}$$

(eq. VIII-32)

The probability that a given monomer unit $C_i$ will lead to a branching node of degree $\lambda$ is calculated by combining the probabilities of the different functional groups present on the monomer unit:
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\[ \text{P}(T_\lambda^i) = \sum_{\lambda_1,...,\lambda_j,...,\lambda_{n_A}} \text{P}(T_{i_1}^{\lambda_1}) \ast ... \ast \text{P}(T_{i_j}^{\lambda_j}) \ast ... \ast \text{P}(T_{i_{n_A}}^{\lambda_{n_A}}) \]  

(eq. VIII-33)

if \( \lambda = \sum_{j=1}^{n_A} \lambda_j \)

The mass-based concentration \([T_i^\lambda]\) of nodes of branching degree \(\lambda\) due to monomer units of type \(C_i\) is calculated by multiplying \(\text{P}(T_i^\lambda)\) by the mass-based concentration of the monomer unit \(C_i\) (eq. VIII-18):

\[ T_i^\lambda = [C_i]\text{P}(T_i^\lambda) = \frac{w^f}{M^w} \text{P}(T_i^\lambda) \]  

(eq. VIII-34)

The overall concentration of nodes of branching of degree \(\lambda\) is then calculated by summing the contributions for all types of monomer units:

\[ T_C^\lambda = \sum_{i=1}^{n_C} T_i^\lambda \]  

(eq. VIII-35)

Next, the branching points caused by the linking groups are calculated, denoted with \(T_B\). The likelihood that such a branching point is formed is equal to the conversion of the linking group, and the concentration of these branching points is then equal to the concentration of the linking group. The overall concentration of branching points of degree \(\lambda\) is calculated by summing over all linking groups of degree \(\lambda\).

\[ T_B^\lambda = \sum_{k=1}^{n_R} [B_k] \text{ for all } k \text{ for which } \sum_{j=1}^{n_A} \alpha_{kj} = \lambda \]  

(eq. VIII-36)

The overall concentration of branching points of degree \(\lambda\), taking into account both branching due to the monomer unit and branching due to the connection scheme, is the sum of the two concentrations:

\[ T^\lambda = T_C^\lambda + T_B^\lambda \]  

(eq. VIII-37)

The concentration of branching points is calculated by adding all branching points of at least three as lower degrees cannot be counted as real branching points. For the effective number of branching points, the same is done, but taking into account the effectiveness.

\[ T = \sum_{\lambda \geq 2} T^\lambda \]  

(eq. VIII-38)

\[ \tilde{T} = \sum_{\lambda \geq 2} (\lambda - 2)T^\lambda \]  

(eq. VIII-39)

This was first done by Miller\textsuperscript{10} for two reaction monomers of type \(A_f + B_g\). Here the general solution will be presented. The mass average number of branching points will be denoted with \(T_w\), while the effective number of branching points will be denoted with \(\tilde{T}_w\). Analogously to
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VIII-9), a root monomer unit is selected, and the number of branching points is counted while walking through the branches of the molecule. This can be done for both the number and the effective number of branching points.

\[
T_w = \sum_{i=1}^{n_c} w_i E[T_{wi}] \quad (eq. \ VIII-40)
\]

As was done in (eq. VIII-11), the number of branching points is the expected value of branching points caused by the monomer unit \( T_i \) plus the ones caused by the chains attached to the monomer unit and thus the functional groups looking outwards. The expected number of branching points caused by a monomer unit be calculated by adding all branching points of monomer unit \( C_i \) of different orders (eq. VIII-34), starting from order three.

\[
E[T_{wi}] = \sum_{\lambda>2} T_i^\lambda + \sum_{j=1}^{n_A} f_{ij} E[T_{wijd}] \quad (eq. \ VIII-41)
\]

Similar to what was done in (eq. VIII-15), the branching points looking outwards from the functional groups present on the monomer unit depend on which type of linking group was formed and the likelihood of that linking group to be formed.

\[
E[T^\text{out}_{wijd}] = \sum_{k=1}^{n_R} x_k g_{kj} E[T^\text{out}_{wijkd}] \quad (eq. \ VIII-42)
\]

The linking group can be a source of branching if more than two functional groups are needed to form the bond. If the sum of the number of functional groups needed to form the linking group is two, then the connection is made between two monomer units without forming a new branching point. Using the same approach as in (eq. VIII-17) this will lead to:

\[
E[T^\text{out}_{wijd}] = \begin{cases} 
1 + \sum_{p=1}^{n_A} \alpha_{pj} E[T^\text{in}_{wijd}] - E[T^\text{in}_{wijd}] & \text{if } \alpha_{kj} > 0 \text{ and } \sum_{p=1}^{n_A} \alpha_{pj} > 2 \\
\sum_{p=1}^{n_A} \alpha_{pj} E[T^\text{in}_{wijd}] - E[T^\text{in}_{wijd}] & \text{if } \alpha_{kj} > 0 \text{ and } \sum_{p=1}^{n_A} \alpha_{pj} = 2 \\
0 & \text{if } \alpha_{kj} = 0
\end{cases} \quad (eq. \ VIII-43)
\]

The number of branching points looking in caused by functional \( A_j \) will depend on the functional group it belongs to, scaled by the amount of those functional groups present due to the monomer unit, as in (eq. VIII-20).

\[
E[T^\text{in}_{wijd}] = \sum_{i=1}^{n_c} \rho_{ij} E[T^\text{in}_{wijd}] \quad (eq. \ VIII-44)
\]

The branching points attached to the monomer unit, thus looking outwards, plus the expected value depending on whether the monomer unit itself will be a branching point, is equal to the
number of branching points caused by the monomer unit entered from functional group $A_j$. Similar to what was done in (eq. VIII-22), the following equation is obtained.

$$E[T_{ij}^{\text{in}}] = \begin{cases} \sum_{\lambda > 1} T_i^\lambda - E[T_{ij}^{\text{out}}] + \sum_{k=1}^{n_A} f_{ik} E[T_{ik}^{\text{out}}] & f_{kj} > 0 \\ 0 & f_{kj} = 0 \end{cases}$$  \hspace{1cm} (eq. VIII-45)

Using (eq. VIII-42) till and a Newton-Raphson algorithm the expected value $E[T_{ij}^{\text{out}}]$ can be calculated. This in turn can be inserted into (eq. VIII-41) and its solution into (eq. VIII-40) to get the weight average number of branching points. The weight average of effective branching points is calculated via a similar approach, with the exception that the effectiveness of the branch is accounted for, leading to (eq. VIII-46) till (eq. VIII-51).

Using the number and effective number of branching points, the average number of chains per molecule can be calculated, also called the “complexity” of the molecule ($Z$) by Flory$^{10,16}$. Using the weight average number and effective number of branching points, the weight average number of chains per molecule ($Z_w$) can be calculated instead.

$$Z = 1 + T + \tilde{T}$$  \hspace{1cm} (eq. VIII-52)

$$Z_w = E[Z] = E[1 + T + \tilde{T}] = 1 + T_w + \tilde{T}_w$$  \hspace{1cm} (eq. VIII-53)
2.1.4 Number-average molar mass $M_n$

The number average molar mass $M_n$ is calculated by dividing the total mass $m_{\text{total}}$ by the total number of molecules present $n_{\text{total}}$, which is equivalent to taking the inverse of the mass-based concentration of all molecules present $[N]$.

$$M_n = \frac{m_{\text{total}}}{n_{\text{total}}} = [N]^{-1} \quad (eq. \text{VIII-54})$$

Using the formula for the branching concentration (eq. VIII-37), the concentration $[N]$ can be calculated. All monomer units that have not reacted (branching points of order 0) are contributing one-on-one to the number of molecules. Monomer units that have reacted only once (branching points of order 1) are the chain-ends of a polymer. When only mono- or bifunctional monomer units are used and only two functional groups are linked in the connectivity scheme, linear polymers are formed. The concentration of these linear polymers is equal to the concentration of chain-ends divided by two. When monomer units have functionalities higher than two or when the connectivity scheme connects at least three functional groups, this will lead to (hyper-) branched polymers. To calculate the concentrations of these branched polymers, the concentration of chain-ends can be used as well. A branch of order three would lead to an additional chain end. A branch of order four would lead to two additional chain-ends. In general, a branch of order $\lambda$ would lead to $\lambda-2$ additional chain-ends. The sum of the concentration of unreacted monomer units and the concentration of linear and branched polymers, calculated using the chain-ends, equals the total concentration of all molecules in the system:

$$[N] = T^0 + \frac{1}{2} \left( T^1 - \sum_{\lambda > 2} (\lambda - 2)T^\lambda \right) = T^0 + \frac{1}{2} (T^1 - T)$$

This can be simplified to:

$$[N] = \sum_{\lambda=0} \left(1 - \frac{\lambda}{2}\right) T^\lambda \quad (eq. \text{VIII-55})$$

The total concentration of all molecules calculated in (eq. VIII-55) can be substituted into (eq. VIII-54) to calculate the number-average molar mass. By dividing the weight-average molecular mass calculated in (eq. VIII-9) by the number-average molecular mass calculated in (eq. VIII-55), the polydispersity index $PDI$ can be determined:

$$PDI = \frac{M_w}{M_n} \quad (eq. \text{VIII-56})$$

As the number, weight and z-average molar masses have been determined, information about the shape of the size distribution is gained without needing to calculate the distribution curve of the polymer in all detail.
Structure evolution

All derivations in Sections 2.1.1 to 2.1.4 are generalized forms, valid for any (known) mixtures of monomers, any number of reactions and linking functional groups, any stoichiometric ratio,… Explicit formulas for average number, weight and z-average molar mass for some common homopolymerization and copolymerization (type A \(_f \) + B \(_g \)) combinations of idealized monomer units in stoichiometric ratios can be found in Table VIII-1.

2.1.5 The radius of gyration contraction factor or the \( g \)-factor

The viscosity of (hyper-) branched polymers does not purely depend on the average molar mass of the polymer, but rather on the gyration radius of the polymer\(^{17–20} \). Zimm and Stockmayer\(^{17} \) calculated the \( g \)-factor, by taking the ratio of the gyration radius of the branched polymer over the gyration radius of the linear polymer. It is assumed that both the linear and branched polymers consist out of the same monomer units. For polymers consisting out of monomer units of a certain functionality \( f \) and the functional groups can react with one another, if these reacted functional groups are randomly distributed, the \( g \)-factor is given by following formula:

\[
g_t = \frac{(3(1-\alpha)^2(1-(f-1)\alpha)G_t(\alpha))}{(f-1)^{\gamma(f-1)}} \quad (eq. \ VIII-57)
\]

\[
G_t(\alpha) = \int_0^\alpha \frac{4-f}{z^{f-1}} \frac{1}{(1-(f-1)z)(1-z)^{f-1}} \, dz \quad (eq. \ VIII-58)
\]

\[
\beta = \alpha(1-\alpha)^{f-2} \quad (eq. \ VIII-59)
\]

Where \( \alpha \) is the branching probability as defined by Flory\(^{16} \). This branching probability can be expressed as function of the weight average number of branching points\(^{21} \):

\[
\alpha = \frac{T_w}{2 + (f-1)T_w} \quad (eq. \ VIII-60)
\]

Using the formulas above, the solutions of the \( g \)-factor calculation for monomer units with functionality of three and four are given. In the paper of Zimm\(^{17} \) the derivation of these formulas can be found.

\[
g_3 = \frac{6}{T_w} \left( \frac{1}{2} \left( \frac{(2 - T_w)}{T_w} \right)^{1/2} \ln \left( \frac{(2 + T_w)^{1/2} + T_w^{1/2}}{2 + T_w^{1/2} - T_w^{1/2}} \right) - 1 \right) \quad (eq. \ VIII-61)
\]

\[
g_4 = \frac{1}{T_w} \ln(1 + T_w) \quad (eq. \ VIII-62)
\]
Table VIII-1. Summary of the expressions for number, weight and z-average molar masses for selected connectivity schemes and monomer unit functionalities as a function of the reaction conversion \(x\). In these simplified formulas, it is assumed that there is no stoichiometric imbalance and that all monomer units have the same molar mass (\(M_wC\)).

<table>
<thead>
<tr>
<th>Connectivity</th>
<th>Monomer Units</th>
<th>(x_{gel})</th>
<th>(M_n / M_wC)</th>
<th>(M_w / M_wC)</th>
<th>(M_z / M_wC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_2)</td>
<td>1.000</td>
<td>(\frac{1}{1-x})</td>
<td>(\frac{x+1}{1-x})</td>
<td>(\frac{x^2+4x+1}{1-x^2})</td>
<td></td>
</tr>
<tr>
<td>(A_3)</td>
<td>0.500</td>
<td>(\frac{2}{2-3x})</td>
<td>(\frac{x+1}{1-2x})</td>
<td>(\frac{-2x^3-6x^2+3x+1}{(1-2x)^2(1+x)})</td>
<td></td>
</tr>
<tr>
<td>(A_4)</td>
<td>0.333</td>
<td>(\frac{1}{1-2x})</td>
<td>(\frac{x+1}{1-3x})</td>
<td>(\frac{-3x^3-9x^2+3x+1}{(1-3x)^2(1+x)})</td>
<td></td>
</tr>
<tr>
<td>(A_f)</td>
<td>(\frac{1}{f-1})</td>
<td>(\frac{2}{2-fx})</td>
<td>(\frac{x+1}{1-(f-1)x})</td>
<td>(\frac{(1-f)x^3-3(1-f)x^2+3x+1}{(1-(f-1)x)^2(1+x)})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Connectivity</th>
<th>Monomer Units</th>
<th>(x_{gel})</th>
<th>(M_n / M_wC)</th>
<th>(M_w / M_wC)</th>
<th>(M_z / M_wC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_2)</td>
<td>0.500</td>
<td>(\frac{6}{6-7x})</td>
<td>(\frac{2x+1}{1-2x})</td>
<td>(\frac{-8x^3-12x^2+10x+1}{(1-2x)^2(1+2x)})</td>
<td></td>
</tr>
<tr>
<td>(A_3)</td>
<td>0.250</td>
<td>(\frac{3}{3-5x})</td>
<td>(\frac{2x+1}{1-4x})</td>
<td>(\frac{-16x^3-24x^2+12x+1}{(1-4x)^2(1+2x)})</td>
<td></td>
</tr>
<tr>
<td>(A_4)</td>
<td>0.167</td>
<td>(\frac{6}{6-13x})</td>
<td>(\frac{2x+1}{1-6x})</td>
<td>(\frac{-24x^3-36x^2+14x+1}{(1-6x)^2(1+2x)})</td>
<td></td>
</tr>
<tr>
<td>(A_f)</td>
<td>(\frac{1}{2(f-1)})</td>
<td>(\frac{6}{6-(1+3f)x})</td>
<td>(\frac{2x+1}{1-2(f-1)x})</td>
<td>(\frac{8(1-f)x^3+12(1-f)x^2+(6+2f)x+1}{(1-2(f-1)x)^2(1+2x)})</td>
<td></td>
</tr>
<tr>
<td>Connectivity</td>
<td>Monomer Units</td>
<td>$x_{gel}$</td>
<td>$M_n / M_w$</td>
<td>$M_w / M_{wC}$</td>
<td>$M_z / M_{wC}$</td>
</tr>
<tr>
<td>--------------</td>
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<td>-------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>A + B &gt;&gt; C</td>
<td>$A_2 + B_2$</td>
<td>1.000</td>
<td>$\frac{1}{1-x}$</td>
<td>$\frac{x+1}{1-x}$</td>
<td>$\frac{x^2 + 4x + 1}{1-x^2}$</td>
</tr>
<tr>
<td></td>
<td>$A_2 + B_3$</td>
<td>0.707</td>
<td>$\frac{4}{4-5x}$</td>
<td>$\frac{3x^2 + 5x + 2}{2(1-2x^2)}$</td>
<td>$\frac{-10x^5 + 34x^4 - 14x^3 + 18x^2 + 13x + 2}{(1-2x^2)(2+3x)}$</td>
</tr>
<tr>
<td></td>
<td>$A_2 + B_4$</td>
<td>0.577</td>
<td>$\frac{2}{2-3x}$</td>
<td>$\frac{2x^2 + 3x + 1}{(1-3x^2)}$</td>
<td>$\frac{-15x^5 + 36x^4 - 9x^3 + 15x^2 + 8x + 1}{(1-3x^2)(1+2x)}$</td>
</tr>
<tr>
<td></td>
<td>$A_2 + B_f$</td>
<td>$\frac{1}{\sqrt{f-1}}$</td>
<td>$\frac{4}{4-(2+f)x}$</td>
<td>$\frac{(x+1)(2+f)x}{2(1-(f-1)x^2)}$</td>
<td>$\frac{[(-f^3 + 3f^2 - 4f + 2)x^5 + (-7f^2 + 11f - 4)x^4 + (f^2 - 11f + 10)x^3 + (f^2 + 5f - 6)x^2 + (3f + 4)x + 2]}{(1-(f-1)x^2)(2+f)x}$</td>
</tr>
</tbody>
</table>
2.2 Viscosity calculation using average molar mass

The weight average molar mass $M_w$ will have a direct influence on the zero-shear viscosity. For linear polymers, the following relation is used for both polymers in concentrated solutions and in bulk:

$\eta_0 = KM_w^a$  \hspace{1cm} (eq. VIII-63)

Here $\eta_0$ is the zero-shear viscosity, $K$ is a temperature dependent constant and $a$ a constant. The value of parameter $a$ changes depending on the weight average molar mass: if $M_w$ is larger than a critical molar mass ($M_c$), the value of $a$ equals 3.4, if $M_w$ is lower than $M_c$, $a$ ranges between 1 and 2.5. The critical molar mass corresponds with the molar mass beyond which chain entanglements become important.\(^2\) For branched polymers, this relationship no longer holds. Due to the branches, the viscosity is lower than for linear polymers of the same weight average molar mass. Graessley\(^2,23\) experimentally measured the zero shear viscosity for different branched molecules and found a good correlation between the viscosity and the weight average molar mass by introducing the $g$-factor as follows:

$\eta_0 = K(gM_w)^a$  \hspace{1cm} (eq. VIII-64)

Using the formulas describing the $g$-factor developed in section 2.1.5 and the formulas for the weight average molar mass from section 2.1.1, the viscosity for branched polymers can be estimated during polymerization (increasing conversion).

2.3 Gelation and Post-gel Properties

Depending on the building blocks, the reaction chemistry and the stoichiometry of the reactive groups, the weight-average molar mass can become infinite as the extent of reaction is increased. At this point, an infinite network has formed and rheological properties abruptly change as the material changes from a liquid-like to a solid-like elastic behavior – the polymer has gelled. This is reflected in the formulas that are used to calculate the polymer properties. No simple, generalized closed formula for the gelation point can be given. Entering the input values beyond the gel point into the $M_w$ formula will result in negative output values, without any physical meaning. From the gel point onwards, the $M_w$ formula can no longer be used, however, meaningful calculations can still be performed in the gelled state by using the probabilities of finite branches to calculate the different fractions (sol, pending and elastic effective fraction) in the reactive mixture, as well as crosslink densities, which in turn can be used to predict the mechanical properties of the developing polymer network.

2.3.1 Probability of finite branches

Beyond the gel conversion, polymer chains can be either part of the infinite network structure, called the gel, or be still independent and part of the so-called sol, the soluble fraction. Using a recursive algorithm, it can be checked whether a randomly selected polymer chain is part of the
sol fraction: a requirement for a polymer molecule to be part of the sol fraction is that its molar
mass \( W \) is lower than infinity. As in the previous derivations (Figure VIII-1), a random root
monomer unit is selected. The probability of selecting a root monomer from a polymer molecule
that is part of the sol fraction corresponds to the probability of a finite branch (eq. VIII-65). To
simplify the notation, this probability is represented by the stochastic variable \( F \):

\[
P(W_i < \infty) \equiv P(F_i)
\]  
(eq. VIII-65)

Using (eq. VIII-4) - (eq. VIII-8) this probability can be calculated. The root monomer unit \( C_i \) is
finite \( P(F_i) \) if the masses of all chains connected to outgoing functional groups \( A_j \) on the
monomer unit are finite, the probability of which is given by \( P(F_{ij}^{out}) \).

\[
P(F_i) = P\left( \prod_{j=1}^{n_A} \prod_{l=1}^{f_{ij}} (F_{ij}^{out})_l \right) = P\left( \prod_{j=1}^{n_A} \prod_{l=1}^{f_{ij}} (W_{ij}^{out} < \infty)_l \right)
\]  
(eq. VIII-66)

The likelihood that the functional group looking outwards is a finite branch, is independent of
the other branches attached to the functional groups on the monomer unit. Knowing that
probability of the intersection of independent events is the product of probabilities of the
individual events, (eq. VIII-66) can be simplified to (eq. VIII-67), taking into account that for
each functional group of type \( A_j \) on a monomer of type \( C_i \), the probability is the same.

\[
P(F_i) = \prod_{j=1}^{n_A} \prod_{l=1}^{f_{ij}} P\left( (F_{ij}^{out})_l \right)
\]

(eq. VIII-67)

On the one hand, if the functional group on the monomer unit has not reacted, no branch is
attached to it, implying that the branch attached to the functional group is finite. The likelihood
that a functional group from a monomer unit has not reacted is one minus the likelihood that a
functional group has reacted, which is given by (eq. VIII-30). On the other hand, if the
functional group has reacted, whether the branch on it is finite will depend on whether all
branches attached via the linking group are finite \( P(F_{ijk}^{out}) \). The likelihood that a functional
group has reacted, forming a linking group, is proportional to the conversion of that linking
group, taking into account the stoichiometric imbalance. The likelihood that all branches
connected to the functional groups \( A_j \) of monomer unit \( C_i \) are finite, \( P(F_{ij}^{out}) \), is the sum of the
probability that the groups \( A_j \) have not reacted and the probability that they are finite when they
have reacted.

\[
P(F_{ij}^{out}) = 1 - \sum_{k=1}^{n_R} x_k g_k^{off} + \sum_{k=1}^{n_R} x_k g_k^{off} P(F_{ijk}^{out})
\]  
(eq. VIII-68)
In the next step, the likelihood that all branches connected to the linking group are finite \( P(F_{ij}^{out}) \) is calculated. The whole link is finite if all other chains connected to the functional groups of the monomer unit connected via the linking group are finite, excluding the functional group from which the monomer unit was reached:

\[
P(F_{ij}^{out}) = P \left( \left( \bigcap_{l=1}^{\alpha_{kl}^{-1}} (F_{ij}^{in})_l \right) \bigcap \left( \bigcap_{p=1}^{n_A} \bigcap_{l=1}^{\alpha_{kp}} (F_p^{in})_l \right) \right) \]  
\text{(eq. VIII-69)}

The likelihoods that the branches attached to a functional group \( A_j \) of the monomer unit reached via the linking group have a finite length, \( P(F_j^{in}) \), are independent from one another. Therefore (eq. VIII-69) can be reduced to (eq. VIII-70).

\[
P(F_{ij}^{out}) = \prod_{l=1}^{\alpha_{kl}^{-1}} P \left( (F_j^{in})_l \right) \prod_{p=1}^{n_A} \prod_{p \neq j}^{\alpha_{kp}} P \left( (F_p^{in})_l \right) 
= P(F_j^{in})^{\alpha_{kj}^{-1}} \prod_{p=1}^{n_A} P(F_p^{in})^{\alpha_{kp}}
\]

\[
P(F_{ij}^{out}) = P(F_j^{in})^{-1} \prod_{p=1}^{n_A} P(F_p^{in})^{\alpha_{kp}} \]  
\text{(eq. VIII-70)}

The likelihood that the chain attached the functional group, building the linking group, is finite, depends on the monomer unit that supplied the functional group for the link. The probability that a molecule of monomer unit type \( C_i \) has supplied a functional group \( A_j \) is proportional to the molar fraction of the functional group present on molecules of that type of monomer units: \( \rho_{ij} \).

\[
P(F_j^{in}) = \sum_{i=1}^{n_{ci}} \rho_{ij} P(F_{ij}^{in}) \]  
\text{(eq. VIII-71)}

The entered monomer unit \( C_i \) and all its connecting branches are considered finite, if all other chains attached to the functional groups present on the monomer unit are finite, excluding the one from which the monomer unit was entered into.

\[
P(F_{ij}^{in}) = P \left( \left( \bigcap_{l=1}^{f_{ij}^{-1}} (F_{ij}^{out})_l \right) \bigcap \left( \bigcap_{p=1}^{n_A} \bigcap_{l=1}^{f_{jp}^{out}} (F_{ij}^{out})_l \right) \right) \]  
\text{(eq. VIII-72)}
The events whether the chains connected to the functional groups are finite are again independent from one another, thus (eq. VIII-72) can be rewritten as (eq. VIII-73):

\[
P(F_{ij}^n) = \prod_{i=1}^{f_{ij}-1} P\left(F_{ij}^{\text{out}}\right) \prod_{p=1}^{n_A} \prod_{i=1}^{f_{ip}} P\left(F_{ip}^{\text{out}}\right)
\]

\[
= P(F_{ij}^{\text{out}})^{f_{ij}-1} \prod_{p=1}^{n_A} P(F_{ip}^{\text{out}})^{f_{ip}}
\]

\[
P(F_{ij}^n) = P(F_{ij}^{\text{out}})^{-1} \prod_{p=1}^{n_A} P(F_{ip}^{\text{out}})^{f_{ip}}
\]  

(eq. VIII-73)

Substituting (eq. VIII-70) to (eq. VIII-73) into (eq. VIII-68) results in a polynomial equation in the probability \(P(F_{ij}^{\text{out}})\) with at least two roots. One of the roots is equal to one and is a trivial solution. The other root, having a value between zero and one, corresponds to the physically realistic solution of the equation. In general, no simple formula for the roots can be found and thus the roots should be calculated numerically by an algorithm with an initial guess for the solution between zero and one, e.g. Newton-Raphson.

2.3.2 Sol, Pending and Elastic Effective Fractions

The probability that a polymer branch containing a monomer unit \(i\) is not connected to the infinite network \(P(F_i)\) is derived in Section 2.3.1 and can be used to calculate the mass fraction of polymer that is still in the sol phase (\(w_{fs}\)). For a molecule to be in part of the sol phase, all branches attached to the root monomer unit should be finite. The mass fraction of a certain type of monomer unit \(C_i\) that is still in the sol phase is equal to this monomer unit’s mass fraction in the mixture multiplied by the likelihood that the chains attached to the monomer unit are finite (eq. VIII-71). By adding these mass fractions in the sol phase for all types of monomer unit, the mass fraction of the sol phase \(w_{fs}\) in the total reactive mixture is obtained:

\[
w_{fs} = \sum_{i=1}^{n_c} w_i P(F_i)
\]  

(eq. VIII-74)

In addition to the sol fraction, the mass fraction of the pending chains (\(w_{fp}\)) can be calculated. A pending polymer chain is a chain with exactly one connection to the polymer network. To determine the pending fraction, the likelihood \(P(P_i)\) that a monomer unit \(C_i\) is pending, meaning that only one of its functional groups is connected to the infinite network, is required. First, the likelihood \(P(P_{ij})\) is calculated, which is the likelihood that only one functional group \(A_j\) from a monomer unit \(C_i\) is not attached to the infinite network, while all other \(f_{ij}-1\) functional groups \(A_j\) are finite branches and all other functional groups of other types are finite branches as well. The event that a chain is not finite is represented by an overbar \(\overline{F_{ij}^{\text{out}}}\):
The likelihood that a branch is not finite equals one minus the likelihood that a branch is finite. Knowing that the likelihood that the chains are finite are independent from one another, (eq. VIII-75) can be simplified into (eq. VIII-76) using (eq. VIII-67).

\[
P(P_{ij}) = f_{ij} \left(1 - P(F_{ij}^{\text{out}})\right) \left(P(F_{ij}^{\text{out}})\right)^{-1} \prod_{p=1}^{n_A} P(F_{ip}^{\text{out}})^{f_{ip}}
\]

The likelihood that a pending chain in monomer unit \(C_i\) is caused by a certain functional group is independent of the likelihood of another functional group being present in the monomer unit. The likelihood that a monomer unit is part of a pending chain of a monomer unit \(P(P_i)\) can thus be calculated by adding all the probabilities of pending chains of a monomer unit \(C_i\) for the different functional groups:

\[
P(P_i) = \sum_{j=1}^{n_A} P(P_{ij}) \quad (eq. VIII-77)
\]

The mass fraction of the pending chains \(wfp\) can then be calculated by summing over all the pending probabilities of the monomer units scaled by their mass fractions present:

\[
wfp = \sum_{i=1}^{n_c} w_i^f P(P_i) \quad (eq. VIII-78)
\]

Finally, the elastic effective fraction \(wfe\) is what remains after the sol fraction and pending fractions are subtracted:

\[
wfe = 1 - wfs - wfp \quad (eq. VIII-79)
\]

Together, the elastic effective fraction and the pending fraction form the gel fraction, the insoluble part of the growing or fully polymerized material.
2.4 Crosslink Density and Elastic Effective Junctions

Before calculating the crosslink density, first, the concept of elastic effective network junctions needs to be defined. An elastic network junction is of degree \( \lambda \) if exactly \( \lambda \) connections are made to the infinite network. Two types of network junction can be made.

The first type is a network junction based on monomers units (\( Y \)), where the connections to the infinite network are made with the functional groups present on the monomer unit. A schematic presentation of the different order junctions for a monomer with four functional groups is shown in Figure VIII-6. Note that a junction of order one has only one connection to the infinite network and therefore do not contribute to the mechanical properties and cannot be seen as an elastic effective junction but as a pending chain.

![Figure VIII-2. The schematic representation of the different network junctions a monomer unit with four functional groups ranging from orders one to four. The connections with the infinite network are represented by the ground symbol (three vertical lines). The other chains are free to move and are therefore dangling chains.](image)

The probability that a monomer unit of type \( C_l \) forms an effective junction of degree \( \lambda_j \) through functional groups of type \( A_j \), has a binomial probability:

\[
P(Y_{ij}^{\lambda_j}) = P_n(Y_{ij}^{\lambda_j}|C_l A_j) = \binom{\lambda_j}{\lambda_j} \left(1 - P(F_{ij}^{\text{out}})\right)^{\lambda_j} P(F_{ij}^{\text{out}})^{\lambda_j - \lambda_j} \quad (\text{eq. VIII-80})
\]

The probability that a given monomer unit \( C_l \) will lead to an effective junction of degree \( \lambda \) is:

\[
P(Y_1^{\lambda}) = \sum_{\lambda_1, \ldots, \lambda_n} P(Y_{11}^{\lambda_1}) \ast \ldots \ast P(Y_{in}^{\lambda_i}) \ast \ldots \ast P(Y_{in}^{\lambda_n}) \quad (\text{eq. VIII-81})
\]

with \( \lambda = \sum_{j=1}^{n} \lambda_j \)

Note that a junction of degree one corresponds with the formula of a pending chain (eq. VIII-77).

The concentration of junctions coming from a given monomer unit \( C_l \) is calculated by multiplying the probability of having a junction of degree \( \lambda \) for that monomer unit with the concentration of the monomer unit. Summing for all types of monomer units \( n_C \) leads to the overall concentration of monomer-unit-based effective junctions of degree \( \lambda \), \([Y^{\lambda}]\).
Chapter VIII

\[ [Y] = \sum_{i=1}^{n_c} [C_i] P(Y_i^\lambda) = \sum_{i=1}^{n_c} \frac{w_i}{M_i^w} P(Y_i^\lambda) \quad \text{(eq. VIII-82)} \]

The second type are network junctions formed by a linking group \( (Z) \), where the connections to the infinite network are made by the functional groups present in the linking group. The calculation is similar to that for the junctions coming from the functional groups. The probability that a given connectivity scheme \( R_k \) and a given functional group \( A_j \) will lead to an effective junction of degree \( \lambda \) has a binomial probability:

\[ P(Z_i^\lambda) = P_n(Z_i^\lambda | R_k A_i) = \left( \frac{\alpha_{kj}}{\lambda} \right) \left( 1 - P(F_{ij}^{\text{in}}) \right)^\lambda P(F_{ij}^{\text{in}})^{\alpha_{kj}-\lambda} \quad \text{(eq. VIII-83)} \]

The probability that a given connectivity scheme \( R_k \) will lead to an effective junction of degree \( \lambda \) is:

\[ P(Z_k^\lambda) = \sum_{\lambda_1, \ldots, \lambda_p} P(Z_{k1}^{\lambda_1}) \ast \ldots \ast P(Z_{kp}^{\lambda_p}) \ast \ldots \ast P(Z_{kn}^{\lambda_n}) \quad \text{(eq. VIII-84)} \]

if \( \lambda = \sum_{i=1}^{n_R} \lambda_i \)

The concentration of junctions attributed to the connectivity scheme is calculated by multiplying the probability of having a junction of degree \( \lambda \) in a connectivity scheme \( R_k \) with the concentration of that linking group. Summing for all types of linking groups leads to the overall concentration of connectivity scheme based effective junction of degree \( \lambda \), \([Z^\lambda]\).

\[ [Z^\lambda] = \sum_{k=1}^{n_R} [B_k] P(Z_k^\lambda) \quad \text{(eq. VIII-85)} \]

By adding the elastic effective junction concentrations of both types, the overall concentration \([X^\lambda]\) is calculated.

\[ [X^\lambda] = [Y^\lambda] + [Z^\lambda] \quad \text{(eq. VIII-86)} \]

The crosslink density \([X]\) of the system, expressed in mol of elastic effective junctions per unit of mass of material, can be calculated by summing over all elastic effective junction starting from order 3.\n
\[ X = \sum_{\lambda \geq 3} [X^\lambda] \quad \text{(eq. VIII-87)} \]

An elastic effective chain is a polymer chain that connects two elastic effective junctions. Using the elastic effective junctions, the concentration of elastic effective chains can be calculated:\n
\[ J = \sum_{\lambda \geq 3} \frac{\lambda}{2} [X^\lambda] \quad \text{(eq. VIII-88)} \]
3 Calculation of material properties

The crosslink density and the elastic effective junctions can be used to calculate the elastic modulus $G$ of polymers in the rubbery state. The two classical models to describe rubber elasticity are the so-called phantom network and affine deformation approaches. In these theories, the network is modelled by a collection of Gaussian chains, meaning that the spatial position of the chains is independent of the location of the neighboring chains.\(^{24}\)

3.1.1 Phantom network and affine deformation

The phantom network model assumes that the position of chain ends may fluctuate unhindered about their equilibrium position. The elastic modulus is then described by following formula.

$$G = (J - X) \rho RT \quad (eq. \text{VIII-89})$$

Where $\rho$ is density of the polymer, $R$ is the universal gas constant, $T$ is the absolute temperature, $J$ is the concentration of effective junctions and $X$ is the crosslink density, as defined in section 2.4. In case that the chain ends cannot fluctuate unhindered and are thus constrained by the neighboring crosslinks, this can be described by the affine deformation.

$$G = J \rho RT \quad (eq. \text{VIII-90})$$

3.1.2 Chain entanglements in the gelled state

In case of a low crosslink density, chain entanglements causing physical crosslinks will significantly contribute to the elastic modulus, while in highly crosslinked systems their effect might be negligible. Miller and Macosko\(^4\) first described a method to calculate the entanglements using the recursive algorithm for a case with a short poly-functional monomer crosslinker combined with a long bifunctional chain extender. Miller and Macosko assumed that due to its longer length the chain extender would contribute to the entanglements while the cross linker would not lead to entanglements. This is a valid approximation if there is a large difference in length of the monomer units, but when the crosslinker and chain extender are of similar lengths, the likelihood that the crosslinker monomer units can lead to entanglements will increase. A different approach to calculate chain entanglements in the gelled material is given here, taking into account possibility of entanglements by the crosslinker, by using the recursive algorithm calculation described above.

For chain entanglement to contribute to the elastic properties of the polymer, the four chain ends of the two entangled chains have to be immobilized. This trapped entanglement is achieved if the chain ends are connected to the infinite network. Therefore, the likelihood that the arms of the monomer units are attached to the infinite network will be calculated. An arm of a monomer unit is defined as the piece of the monomer units, starting from the crosslinking center of the monomer unit and stops at the functional group. For an arm to be part of the elastic effective chain entanglements denoted with $E_{\text{arm}}$, the monomer unit attached to it as well as the chain attached to the functional group have to be connected to the infinite network. Or
equivalently, using the likelihood of finite branches as defined in section 2.3.1, both the chain attached to the functional group and the monomer unit should not be finite, leading to following expression for the likelihood:

$$P(E_{ij}^{\text{arm}}) = P(F_{ij}^{\text{in}}) \cdot P(F_{ij}^{\text{in}}) \quad (\text{eq. VIII-91})$$

The likelihood of an arm of a certain monomer unit with a certain functional group to be selected depends on the number of arms present in that monomer unit and the number of functional groups present on the monomer unit, or equivalently, on the relative amount of functional groups of a certain type present on the monomer unit.

$$f_{ij}^{\text{rel}} = f_{ij} / \sum_{l=1}^{n_A} f_{il} \quad (\text{eq. VIII-92})$$

The likelihood that a monomer unit, selected at random, is attached to the elastic network through any of its arms, is equal to sum of the likelihoods for all arms with a certain functional group present on the monomer unit multiplied with their relative amount functional groups.

$$P(E_{i}^{\text{arm}}) = \sum_{j=1}^{n_A} f_{ij}^{\text{rel}} P(E_{ij}^{\text{arm}}) \quad (\text{eq. VIII-93})$$

The likelihood that an arm, selected at random, is attached to the infinite network is equal to the sum of likelihoods for all arms coming from a monomer unit times their relative amount.

$$P(E_{\text{arm}}) = \sum_{i=1}^{n_C} w_i P(E_{i}^{\text{arm}}) \quad (\text{eq. VIII-94})$$

For a chain entanglement to be elastic effective the two chains have to be attached to the infinite network. The probability of chain entanglement $T_e$ also called the entanglement trapping factor, is calculated by selecting to two arms at random attached to the elastic network.

$$T_e = P(E_{\text{arm}})^2 \quad (\text{eq. VIII-95})$$

There are no dangling chains in a perfect, fully cured network, meaning that the $T_e$ value will be one. Langley calculated the concentration of physical (entanglement) crosslinks by multiplying the probability of the chain entanglement by a an effective concentration $\epsilon$.

$$X_e = \epsilon T_e \quad (\text{eq. VIII-96})$$

3.1.3 Combined Models

The phantom network and affine deformation models can be combined into a single formula by using a fitting parameter $h$, and the effect of the chain entanglements can be taken in to account as follows:

$$G = (J - hX) \rho RT + G_e T_e \quad (\text{eq. VIII-97})$$
Structure evolution

Where \( G_e \) is the entanglement modulus and \( T_e \) entanglement trapping factor. The fitting parameter \( h \) has a value between 0 and 1. When \( h \) is equal to zero, the model corresponds to affine deformation model, while if \( h \) is equal to one, the model corresponds to the phantom network model. The entanglement modulus corresponds with the maximum contribution to the modulus of the chain entanglements and is closely related with \( G_N^0 \), the modulus of the rubbery plateau of linear polymers.

4 Structure formation and kinetics

4.1 Simplified kinetics of the polyurethane chemistry and monomers

Different polymer systems can be defined for investigating the algorithm. Some numerical examples based on the isocyanate and urethane chemistry will be shown here to illustrate the capabilities of this generalized algorithm. Firstly, isocyanurate homopolymerization is investigated and compared with literature values. Next, polyurethane formation, also studied in literature is investigated. Thirdly, gradually more complexity will be added by accounting for a different reactivity between the alcohol groups due to a substitution effect. In a fourth and final step, the combination of polyurethane and isocyanurate chemistry will be investigated to showcase the possibilities of the newly developed, generalized method.

To accurately describe the molar mass build up during reaction, one must know the reaction mechanism behind the urethane and isocyanurate formations. The kinetic model developed in Chapters V to VII can be used for molar mass calculations, which will be presented in Chapter IX. To focus just on the molar mass evolutions in this chapter, the reaction mechanism is simplified by proposing a bimolecular reaction for the urethane formation (eq. VIII-98) and a trimolecular reaction for the isocyanurate formation (eq. VIII-99). It is assumed that no other reaction takes place. The rate constants of the urethane formation are taken as \( 10^{-3} \) kg.mol\(^{-1}\).s\(^{-1}\) and \( 10^{-5} \) kg\(^2\).mol\(^{-2}\).s\(^{-1}\). The monomers units with their molar mass and functionality are given in Table VIII-2.

\[
\begin{align*}
1 \text{OH} + 1 \text{NCO} & \xrightarrow{k_{UR}} \text{UR} \quad (eq. \ VIII-98) \\
3 \text{NCO} & \xrightarrow{k_{IR}} \text{IR} \quad (eq. \ VIII-99)
\end{align*}
\]

4.2 Structure development with isocyanate homopolymerization

As a first study, the homopolymerization of isocyanate to isocyanurate will be investigated (eq. VIII-99). Here, the reaction mixture contains HDI only. The increase of the molar mass as a function of the extent of reaction is given in Figure VIII-3. The reactive mixture gels at an extent of reaction of 50.0%, as seen by \( M_w \) and \( M_z \) going to infinity at this conversion. Note that \( M_n \) remains finite when the mixture gels. Throughout the pre-gel phase, the value \( M_z \) is above \( M_w \), which is above \( M_n \) for the same conversion, which is in accord with the definitions
of $M_n$, $M_w$ and $M_z$. In Figure VIII-3, the results for the simulation of $M_w$ are compared with values calculated by Pascault\textsuperscript{33} based on the method developed by Macosko and Miller. The results coincide with our simulation, validating the newly developed generalized method.

Table VIII-2. The monomers units, molar mass and functionality

<table>
<thead>
<tr>
<th>Monomer Units</th>
<th>Molar mass g.mol\textsuperscript{-1}</th>
<th>Reactive functional group and functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylene diisocyanate (HDI)</td>
<td>168</td>
<td>NCO: 2</td>
</tr>
<tr>
<td>Pentaerythritol (PETO)</td>
<td>136</td>
<td>OH: 4</td>
</tr>
<tr>
<td>1,1,5,5-Pentanetetrol (PTO)</td>
<td>136</td>
<td>(OH)\textsubscript{2}: 2</td>
</tr>
<tr>
<td>1,6-Hexanediol (HDO)</td>
<td>118</td>
<td>OH: 2</td>
</tr>
</tbody>
</table>

Figure VIII-3 $M_n$, $M_w$ and $M_z$ and sol-, pending- and elastic effective mass fraction as a function of the extent of reaction for an isocyanurate system. The results from this work are shown as curves, the data obtained by Pascault\textsuperscript{33} are indicated with symbols.
From the gel conversion onward, the post-gel properties can be calculated. The mass fraction of the sol, pending and elastic effective phase are also given in Figure VIII-3. At the conversion of 50.0% the \( w_{fs} \) starts at a value of one, meaning that the whole system is in the sol phase. As the conversion increases the sol fraction \( w_{fs} \) gradually decreases, reaching zero at full conversion. The pending fraction \( w_{fp} \) starts at zero at the gel conversion and increases to a maximum value of 0.5 at a conversion 66.6%, after which \( w_{fp} \) decreases to a value of zero at full conversion. The elastic effective fraction \( w_{fe} \) starts at zero at the gel conversion and increases continuously as the conversion increases, reaching a value of one at full conversion, meaning that at full conversion all monomers are part of the network and that no pending chains are left in the reactive mixture. This is an ideal, theoretical situation as due spatial or practical topological limitations some of the remaining functional groups will never be able meet and therefore full cure is never reached, with a portion of the chains remaining pendant chains.

4.3 Structure development with urethane formation

To illustrate the formation of a urethane network (eq. VIII-98), the reaction of a stoichiometric mixture of HDI and PETO will be investigated. The solutions of the average molar masses and post-gel properties for the system are shown in Figure VIII-4. \( M_w \) and \( M_z \) become infinite at reaction conversion of 57.7%, corresponding with the gel conversion. The results agree with those calculated by Shiau, as seen in Figure VIII-4.

Before the gel conversion the whole mixture is in a liquid state, thus sol mass fraction is one, while the pending and elastic effective mass fractions are zero. From the gel point onwards \( w_{fs} \) starts to decline and both \( w_{fp} \) and \( w_{fe} \) start to rise, with \( w_{fp} \) quickly increasing to a maximum of 0.453 at a conversion of 67.3%, after which it declines back to zero at full conversion. As the system is stoichiometric, no dangling or pending chains are observed at full conversion, thus \( w_{fe} \) steadily increases to a value of one at full conversion. Comparing the \( w_{fs} \) calculation
with results published by Miller\(^4\), the two coincide (Figure VIII-4). Branching point of order three and order four are observed in this network. A branching point of order three and four corresponds with a PETO monomer that has reacted three and four times, respectively. At the start the branching points of order three rise more quickly than the branching points of order four, reaching a maximum at a conversion of 75.0% after which all of these branching points are converted into branching points of order four, and its concentration declines to zero at full conversion. The branching points of order four reach a maximum of at full conversion when all branching points of order three are converted into branching points of order four. The crosslinks of order three and four correspond with the monomer PETO linking three and four times to the infinite network, respectively. Note that before the gel conversion the concentration of the crosslinks is zero as there is no infinite network yet. After gelation the concentration of order three crosslinks rises quickly to a maximum at a conversion of 87.3%, after which it declines to a concentration of zero as more and more crosslinks of order three are converted into crosslinks of order four. The crosslinks of order four will steadily increase after gelation reaching a maximum at full conversion. The likelihood of branching of order three and four were compared to literature\(^4\) values to validate the algorithm.

4.3.1 Effects of the molecular structure on the properties

To investigate the effect of substitution on the network formation, the urethane formation of HDI and PTO is investigated. The molar mass of PETO and PTO is the same but their structures are different (Table VIII-2). PETO has four primary alcohol groups, which have the same reactivity. PTO has two geminal diol functional groups. The stability of these functional groups is very low and are given here just as a theoretical example to illustrate some complexities that can arise using the recursive algorithm. The reactivity of the alcohol groups of one of the geminal diol functional groups will be influenced by whether the other alcohol group has reacted. In order to simulate this substitution effect, the reaction mechanism has to be changed. In a first reaction, one of the (OH)\(_2\) reacts with an isocyanate group forming a urethane bond with one alcohol function remaining next to the urethane (UROH). The rate constant corresponding with this reaction is \(k_{UROH}\). In a second step, the alcohol of the UROH group can react again with an isocyanate group forming a (UR)\(_2\), having a rate constant \(k_{(UR)2}\). The linking scheme corresponding to this reaction mechanism is represented in the linking scheme:

\[
1 \text{(OH)}_2 + 1 \text{NCO} \xrightarrow{k_{UROH}} \text{UROH} \quad \text{(eq. VIII-100)}
\]

\[
1 \text{UROH} + 1 \text{NCO} \xrightarrow{k_{(UR)2}} (\text{UR})_2 \quad \text{(eq. VIII-101)}
\]

As a first simulation, the reactivity of \(k_{UROH}\) and \(k_{(UR)2}\) is chosen in a way that the reactivity is the same as \(k_{UR}\) of the HDMI - PETO system and thus no effect of substitution would be present. When comparing the two results in the pre-gel phase, the molar mass build-up of \(M_n, M_w\) and \(M_z\) are identical and both systems gel at the same conversion.
In the post-gel phase, the $wfs$ are the same, while the $wfp$ are slightly higher for the HDI – PTO system compared to the HDMI-PETO system (Figure VIII-5). Because $wfe$ depends both on $wfs$ and $wfp$, their values will also differ. The reason why the two $wfps$ are slightly different, comes from its definition. Recall that a polymer chain is pending if it has exactly one connection to the infinite network.

This can be more clearly explained using Figure VIII-6. In the figure the different configurations of the PETO (left) and PTO (right) monomers are represented, with their connections to the infinite network represented by the ground symbol (the three vertical lines). At the top no connections with the infinite network are made, while at the bottom all four connections are made, and the intermediate stages are put in between those. If no connections are made with the infinite network, the monomer and all what is attached to it is part of the sol fractions. As the reactivities were chosen in a way that the OH consumption of both the PETO and PTO system are the same, the mass fractions of these monomers should be the same, as is shown in Figure VIII-5. When one of the OH is connected to the infinite network, the monomer is part of the pending mass fraction. For both the PETO and PTO system with one connection, the same amount is present. The situation changes if two connections are made to the infinite network. For the PETO system, when two of the alcohol groups have linked to the infinite network, the monomer has two links to the infinite network and thus is part of the elastic fraction. For the PTO system there are two configurations. The first (left) is when two alcohol groups link to the infinite network through one (UR)$_2$ group. When looking outwards from within the PTO monomer, from its two (OH)$_2$ function groups, one of them linked to the infinite network, while the other one is finite. Therefore the monomer has only one connection to the infinite network and by definition it is part of the pending fraction. The second configuration (right) is that one of the alcohol groups of each of the (OH)$_2$ functional groups has connected to the infinite network. When looking outwards from within the PTO monomer, two links to the infinite network are observed and by definition the PTO monomer is part of the elastic fraction. Due to the different configurations that are possible for the PTO system, the pending and elastic
effective mass fractions differ between PETO and PTO, with PETO having a higher elastic mass fraction and a lower pending fraction compared to the PTO system, as can be seen in Figure VIII-5. For the configurations with three and four connections to the infinite network, the evaluation for PETO and PTO is again the same.

4.3.2 Effects of the kinetics on the properties

To simulate this substitution effect on the molar mass buildup, the reaction rate of the second alcohol \( k_{(UR)2} \) is changed, while the reaction rate of the first alcohol \( k_{UROH} \) has been left unchanged. The reactivity ratio of the original \( k_{(UR)2} \) and changed \( k'_{(UR)2} \) is called \( r_k \). Three different reactivity ratios have been chosen: 1, 2 and 10. The result of the molar mass build up is shown in Figure VIII-7. The results show that up until gelation \( M_n \) is the same and thus independent of the reaction rate of the \( k'_{(UR)2} \). The way \( M_w \) increases is different: the higher the reactivity ratio and thus reactivity of the \( k'_{(UR)2} \), the higher \( M_w \) for the same extent of reaction. The higher reactivity ratios will lead to a lower gel conversion, with ratio 1, 2 and 10 corresponding to a gel conversion of 0.577, 0.596 and 0.618, respectively.

Figure VIII-6. The different configurations of the monomer PETO (left) and PTO (right) with the infinite network schematically represented. The connections with the infinite network are represented by the ground symbol (three vertical lines). The top schematic has no connectivity with the infinite network, the one below has one connection. This continues to the bottom schematic with all four alcohol groups connected to the infinite network. The different permutations of the schematics are not represented.
4.4 Using the generalized algorithm by combination of urethane and isocyanurate formation

To illustrate the capabilities of the algorithm developed in this work, the combination of urethane and isocyanurate network formation will be investigated. Two monomers will be used in this study: HDO and HDI (Table VIII-2). Three different ratios are investigated, and the compositions of these mixtures are given in Table VIII-3. The concentrations of urethane and isocyanurate groups are presented as a function of the extent of reaction for the different ratios in Figure VIII-8. The extent of the reaction is here defined as the relative consumption of the isocyanate groups. Molar ratio $r_1$ corresponds with an equimolar ratio of alcohol and isocyanate groups and would lead to full urethane conversion if no isocyanurate would form. As some isocyanurate will be formed, some alcohol groups will remain unreacted. This can be seen in Figure VIII-8 where the final conversion to isocyanurate is not zero but $8.5\%$, while $91.5\%$ was reacted to urethanes. Molar ratio $r_3$ is pure HDI and will lead to full isocyanurate conversion. The $r_2$ mixing ratio is chosen in a way that when all isocyanates are consumed the concentration of urethane and isocyanurate are equal, as can be seen in Figure VIII-8.

Table VIII-3. Mixing ratios of polyurethane – polyisocyanurate

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Mass fraction</th>
<th>Mass fraction</th>
<th>Initial concentration [OH] / mol.kg$^{-1}$</th>
<th>Initial concentration [NCO] / mol.kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDO</td>
<td>HDI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_1$</td>
<td>41.26%</td>
<td>58.74%</td>
<td>6.99</td>
<td>6.99</td>
</tr>
<tr>
<td>$r_2$</td>
<td>14.94%</td>
<td>85.06%</td>
<td>2.53</td>
<td>10.13</td>
</tr>
<tr>
<td>$r_3$</td>
<td>0%</td>
<td>100%</td>
<td>0</td>
<td>11.90</td>
</tr>
</tbody>
</table>

Figure VIII-7. $M_n$ and $M_w$ fraction as a function of the extent of reaction for a HDI-PTO system with reactivity ratio $r_\gamma=k_2/k_2'$ equal to: $r_\gamma=1$ (solid), $r_\gamma=2$ (dot dash) and $r_\gamma=10$ (dash).
Chapter VIII

The average molar mass buildup for the different mixing ratios can be seen in Figure VIII-8. Both $M_n$ and $M_w$ gradually increase, going to an infinite value when all isocyanates are consumed. The $r_1$ mixture actually gels before reaching full conversion, at an extent of reaction of 99.6%, due to the unavoidable formation of isocyanurate.

5 Conclusions

A generalized algorithm for calculating weight average molar masses for step-growth polymerization reactions was developed, inspired by the Macosko and Miller. The ideas behind the molar mass increase and network formation during step-growth polymerization with their mathematical derivation were shown. This approach can also be used for calculating higher order average molar masses and the solution for z-average molar mass was given. The techniques used in the pre-gel phase could also be used in the post-gel phase, leading to the calculation of sol-, pending- and elastic effective mass fractions and the crosslink density.

Example simulations based on the polyurethane/isocyanurate chemistry were given and the results were compared with literature models to validate the algorithm developed. The capabilities of the algorithm to calculate the effects of substitution and unequal reactive functional groups where shown. Finally, an example of the combined parallel and competing formation of urethane and isocyanurate, leading to the formation of a complex polymer structure was calculated. Without the newly developed approach, the average molar masses, gel conversion and post-gel properties of these formed networks could not be calculated, while these are the parameters needed to estimate the mechanical properties of polymer networks. In the next chapter, the kinetic model developed in the previous chapters will be applied to model the molar mass evolutions and viscosity evolutions during reaction and at full conversion.
6 References


CHAPTER IX

MOLAR MASS AND VISCOSITY

1 Introduction

The goal of this final chapter is to use the gained in-depth knowledge and insight in the reaction kinetics of polyurethane resins and to link them to the changing rheological properties, consequently gaining insight in the use of these resins to produce composite materials.

Composite materials are often used in automotive and aerospace industry because of their high strength and light weight, which leads to a decrease in fuel consumption. In the larger framework of global warming, this makes composite materials and their processing methods of increasing importance.

To produce composite materials, resin transfer molding (RTM) is a technique increasingly employed due its ability to produce big composite parts of complex shape at high production rate and relatively low cost. In the RTM process, a reactive resin first flows through a fiber bed in a closed mold, and subsequently reacts to a fiber reinforced thermoset due to an increase in temperature. The fiber impregnation and mold filling process can fail due to, for example, insufficient wetting, air encapsulation and shape complexity, leading to reduced mechanical properties. Therefore, knowledge on the evolving rheological behavior of the resin, which is temperature and reaction conversion dependent, is essential.

The polyurethane reaction mechanism and the associated reaction kinetics were investigated for MDI polymerized with aliphatic polyols in Chapters IV to VII, resulting in a mechanistic kinetic model allowing to calculate and predict the concentrations of all relevant functional groups. In Chapter VIII, a recursive algorithm based on the work of Macosko and Miller\textsuperscript{1,2} was developed, allowing the calculation of the average molar masses and the post-gel properties. This algorithm was evaluated with literature simulation data. In this chapter, the polyurethane reaction kinetics model will be applied together with the recursive algorithm to calculate several structure property relations. The results of the model will be compared to measured properties.

First, the molar mass distribution and the corresponding viscous behavior is studied experimentally for fully cured, linear polyurethane samples. The molar mass and viscosity are varied by adding controlled amounts of end-cappers into the reactive mixture, thus reducing the molar mass. The advantage of working with fully cured samples is that these are time independent, so that the polyurethane kinetics will only influence the final molecular structure. The obtained experimental results will be compared with the calculated properties.

Next, a fully cured, network-forming polymer is tested by adding crosslinker to the reactive mixture. By controlling the amount of crosslinker, the crosslink density and the resulting
mechanical properties are changed. Finally, after discussing properties of properties for fully cured materials, the evolving properties as a result of the polyurethane cure are investigated by following the viscosity evolution as function of time and extent of reaction. This is a required step needed to model and later improve industrial processes.

2 Experimental

2.1 Materials

Linear polyurethanes with different average molar mass were synthesized by adding cyclohexanol as a monofunctional alcohol end-capper to a PPG-425 with 0.04 w% of DABCO catalyst. The end-capper was added as 0.1 w%, 1 w% and 10 w% of the amount of PPG-425. Next, these premixes and a PPG-425 with 0.04 w% catalyst were mixed in with MDI in a stoichiometric ratio at ambient temperature and kept at 21 °C for about three hours. After this, the samples were kept in an oven at 75 °C for a week in order to cure them to nearly full cure. Next, samples were taken out of the oven and left to cool to ambient temperature.

Five network-forming samples with varying crosslink density were made using PPG-425 and Daltolac 251 as crosslinker. First a certain amount of the crosslinker was put into a tarred vial. Next, the correct amount of PPG-425 with 1 w% catalyst was added to the crosslinker, in order to obtain a catalyst concentration to alcohol concentration ratio of $7.5 \times 10^{-4}$ that is the same ratio as for PPG-425 with 0.04 w% catalyst. Next, the remaining PPG-425 is added to obtain the required ratio of crosslinker and PPG-425. Once the polyol mixtures are prepared, polyurethane samples are made by adding MDI to a tarred vial, and the polyol is added to obtain a stoichiometric mixture of about 3 g. This mixture is mixed vigorously (about 2000 rpm) for two minutes using a mechanical mixer, before being poured into a 55.0 mm by 55.0 mm by 3.5 mm Teflon mold. The mixture was cured in an oven at 85 °C for a week to cure them. Next, the solid samples were removed from the mold and cut into a rectangular shape of 20.0 mm by 5.6 mm with a sample thickness 1.3 mm before measuring them in DMA.

2.2 Gel permeation chromatography

The molar mass distribution of the linear PU samples was measured using gel permeation chromatography (GPC), performed by VITO (Mol, Belgium). The GPC setup used had three columns and a UV and a refractive index (RI) detector. Tetrahydrofuran (THF) was used as eluent. The instrument was calibrated using 17 monodisperse polystyrene reference materials with average molar masses varying between 370 and 956000 g.mol$^{-1}$. A small amount of fully cured material was taken from the sample and dissolved into THF.
2.3 Dynamic rheometry

Measurements were performed on a TA Instruments Discovery hybrid rheometer (DHR-2) using 25 mm aluminum disposable parallel plates. Prior to the measurement, the instrument inertia calibration and rotational mapping were performed (see Chapter III). The sample was loaded on to the lower plate at the starting temperature of the measurement.

2.3.1 Frequency sweeps on fully cured polymers

A frequency sweep of the fully cured material was done at different isothermal temperatures. This was done by first heating the oven to the isothermal temperature of the measurement. A period of 10 minutes was taken upon reaching isothermal temperature, making sure that thermal equilibrium was reached. A strain of 0.01% was applied and the response was measured for frequencies between $10^{-3}$ and 100 Hz, with points logarithmically distributed having (5 per decade).

2.3.2 Isothermal viscosity evolution

The polyurethane reactive mixture was prepared in the same way as was for DSC and TAM measurements (see Chapter III). Once the reactive mixture is prepared, about 0.5 g of (liquid) sample is put in the middle of the bottom plate of the rheometer. The top plate is then lowered manually in different stages while rotating it. This is done to completely fill the space between the two plates with the sample. When this is achieved, the (potential) excess material is removed and the measurement is started. The measurement comprises an isothermal multifrequency measurement with five frequencies logarithmically distributed between 1 and 10 Hz. The initial strain applied is 10%. Once a complex viscosity of 10 Pa.s is obtained, the stain is lowered to 1%. When the complex viscosity has reached a value of 1000 Pa.s, the stain is lowered again to a value of 0.1%.

2.4 Dynamic mechanical analyzer (DMA)

The dynamical mechanical analyzer used is a Q800 DMA of TA instruments. A thin film tension setup was used to measure the viscoelastic behavior of the samples.
Chapter IX

3 Results and discussion

3.1 Full cure properties of linear polymers

Properties of fully cured linear polyurethanes will be investigated first, making the measurements independent of time, and avoiding the complexity of studying highly reactive materials. The system investigated is MDI – PPG-425 with 0.04 w% catalyst, forming a linear polymer. The molar mass was varied by introducing a certain amount of monofunctional alcohol (cyclohexanol) end-capper, ranging from 0.1 w%, 1 w% and 10 w% of the total polyol mixture.

3.1.1 Molar mass distribution

First, the molar mass distribution of the fully cured linear polyurethane samples was measured with GPC. The molar mass distribution for MDI – PPG-425 with 1 w% end-capper and the molar mass averages $M_n$, $M_w$ and $M_z$ are shown in Figure IX-1. On the logarithmic molar mass scale, the distribution looks very symmetrical around the peak maximum and has a small tail around the lower molar mass compounds. The values of $M_n$, $M_w$ and $M_z$ obtained with the UV detector are 11.0, 26.0 and 45.2 kg.mol$^{-1}$, respectively, leading to a polydispersity of 2.36.

![Normalized molar mass distribution measured by GPC for fully cured MDI – PPG 425 with 1 w% end-capper: UV and RI. The molar mass averages of the UV detector are indicated. (left) linear, (right) logarithmic scale for molar mass.](image)

3.1.2 Modelling the molar mass averages

Combining the ionic mechanism developed in Chapter VII and the recursive algorithm developed in Chapter VIII, the final molar masses averages were calculated by simulating the reaction and structure build-up for the temperature program described, above starting from the initial concentrations. The molar mass averages measured in GPC and those calculated with the model are compared in Figure IX-2. The simulated molar mass averages for the systems with 0 w%, 0.1 w% and 1 w% end-capper strongly overestimated the final molar mass averages. The biggest difference between the measured and the simulated results is observed with the 0 w%...
system. This is expected as this is the result of an idealized simulation, assuming that mixing errors did not occur, and that the kinetics remain valid up to very high conversions. As the amount of end-capper is increased, the difference between the measured and the simulated molar masses is decreased, resulting in a good correspondence at 10 w% of end-capper. The lower experimental molar mass could be due to small errors in the mixing ratio, or small amounts of monofunctional polymer in the polyol or MDI. A good correspondence was obtained by assuming that a 0.25 w% of monofunctional polyol (end-capper) was added to the PPG-425 with 0.04 w% catalyst. This small amount of end-capper can be justified by assuming that small amounts of water was present at the start of reaction, the presence of monofunctional alcohols in the polyol, or by a deviation of the kinetic model at high conversions. With the additional added end-capper, the simulated and measured molar masses are close to one another.

Figure IX-2. Molar mass averages measured by GPC: experimental average from SPD-20A UV and RID-10A (red), and averages calculated by the recursive algorithm: no additional end-capper and with 0.25 w% of additional end-capper.

3.1.3  Modeling the molar mass distributions

In GPC, a molar mass distribution is measured, while the modelling approach supplies molar mass averages. As the higher order averages contain information about the shape of the distribution, an approach was developed to derive the distribution from the calculated averages. There are several theoretical models that are often used to describe the molar mass distributions
of linear polymers. When plotting the measured distribution on a logarithmic mass scale, a symmetric curve around the peak maximum is observed. A first model that is symmetric is a log normal distribution. This means the logarithm of the stochastic variable is normally distributed.

The log normal distribution is given by following formula:

$$W(x) = \frac{1}{\sqrt{2\pi}\sigma x} \exp \left( -\frac{(\ln(x) - \mu)^2}{2\sigma^2} \right)$$  \hspace{1cm} (eq. IX-1)

Where \(\mu\) and \(\sigma\) are the mean and the standard deviation of the natural logarithm of the variable \(x\). The mean \(\mu_W\) and the standard deviation \(\sigma_W\) of the log normal distribution are given by (eq. IX-2) and (eq. IX-3), respectively.

$$\mu_W = \exp(\mu + \sigma^2)$$  \hspace{1cm} (eq. IX-2)

$$\sigma_W^2 = (\exp(\sigma^2) - 1) \exp(2\mu + \sigma^2)$$  \hspace{1cm} (eq. IX-3)

\(\mu_W\) is by definition equal to \(M_w\):

$$\mu_W = \mathbb{E}[W] = M_w$$  \hspace{1cm} (eq. IX-4)

Applying the definition of the standard deviation leads to (eq. IX-5).

$$\sigma_W^2 = \mathbb{E}[(W - \mathbb{E}[W])^2]$$  \hspace{1cm} (eq. IX-5)

$$\sigma_W^2 = \mathbb{E}[W^2] - \mathbb{E}[W]^2$$  \hspace{1cm} (eq. IX-6)

\(\mathbb{E}[W^2]\) can be calculated using (eq. VIII-24), resulting in (eq. IX-7). Substituting (eq. IX-4) and (eq. IX-7) into (eq. IX-6) results in (eq. IX-8).

$$\mathbb{E}[W^2] = M_w M_z$$  \hspace{1cm} (eq. IX-7)

$$\sigma_W^2 = M_w M_z - M_w^2$$  \hspace{1cm} (eq. IX-8)

This means that from the molar mass averages \(M_w\) and \(M_z\), the corresponding log normal distribution can be calculated, using the parameters \(\mu\) and \(\sigma\) calculated using \(\mu_W\) and \(\sigma_W\) derived from the experimental \(M_w\) and \(M_z\). The calculated parameters are given in Table IX-1.

The measured and the calculated distribution are given in Figure IX-3. One of the distributions was calculated using the molar mass averages derived by the recursive algorithm without accounting for the additional end-capper, the other with the 0.25 w\% additional end-capper (Figure IX-2). While the log normal distribution is perfectly symmetrical around its average, the measured distribution (in black) is not perfectly symmetrical, having a small tail at lower molar masses.
Table IX-1 Calculated mean $\mu_W$, standard deviation $\sigma_W$, mean $\mu$ and standard deviation $\sigma$

<table>
<thead>
<tr>
<th></th>
<th>$\mu_W$ kg.mol$^{-1}$</th>
<th>$\sigma_W$ kg.mol$^{-1}$</th>
<th>$\mu$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>no additional</td>
<td>0 w%</td>
<td>440</td>
<td>312</td>
<td>12.6</td>
</tr>
<tr>
<td>end-capper</td>
<td>0.1 w%</td>
<td>250</td>
<td>177</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>1 w%</td>
<td>49.0</td>
<td>34.7</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>10 %</td>
<td>5.12</td>
<td>3.62</td>
<td>8.13</td>
</tr>
<tr>
<td></td>
<td>with 0 w%</td>
<td>63.7</td>
<td>45.1</td>
<td>10.7</td>
</tr>
<tr>
<td>0.25 w%</td>
<td>0.1 w%</td>
<td>56.9</td>
<td>40.3</td>
<td>10.5</td>
</tr>
<tr>
<td>additional</td>
<td>1 w%</td>
<td>28.5</td>
<td>20.2</td>
<td>9.85</td>
</tr>
<tr>
<td>end-capper</td>
<td>10 %</td>
<td>4.77</td>
<td>3.38</td>
<td>8.06</td>
</tr>
</tbody>
</table>

For the experiments with 0.1 w%, 1 w% and 10 w% plus 0.25 w% of additional end-capper (dashed, colored curves) the peak position and width of the distributions match those of the measured distribution fairly well. For 0 w% of end-capper, the simulation with additional end-capper underestimates the peak position. As the measured distribution is not symmetrical, the log normal distribution is not the best model to predict the distribution.

Figure IX-3. Comparison of experimental and calculated molar mass distributions: (dashed black) distribution measured by GPC using the UV detector, (coloured) the log normal distributions calculated from the molar mass averages predicted by the recursive algorithm without additional end-capper (full) and with 0.25 w% added end-capper (dashed).
Chapter IX

By assuming equal reactivity of all functional groups and the absence of intermolecular reactions, Flory derived a distribution for A-A + B-B or A_2+B_2 type step-growth polymerization. This distribution, called the most probable or Flory – Schulz distribution, is given by following formula:

\[ W(x) = a^2 x(1 - a)^{x-1} \]  \hspace{1cm} (eq. IX-9)

With parameter \( a \) between zero and one. The mean of this distribution is given by (eq. IX-10).

\[ \mu_W = \frac{2}{a} - 1 \]  \hspace{1cm} (eq. IX-10)

Using (eq. IX-10) and (eq. IX-4) the parameter \( a \) can be calculated and the corresponding distribution curve drawn. The Flory – Schulz distribution based on the molar mass averages predicted by the recursive algorithm for the systems with end-cappers are compared with the distribution measured in GPC in Figure IX-4. In contrast with the log normal distribution, the Flory – Schulz distribution is not symmetrical. A tail towards the lower molar mass compound can be seen, which is in agreement with the measured GPC results.

![Figure IX-4](image_url)

Figure IX-4. Comparison of experimental and calculated molar mass distributions: (dashed black) distribution measured by GPC using the UV detector, (coloured) the Flory-Schulz distribution calculated from the molar mass averages predicted by the recursive algorithm without additional end-capper (full) and with 0.25 w% added end-capper (dashed).
3.1.4 Prediction of the viscosity

The temperature and frequency dependence of the complex viscosity $\eta^*$ of a full cured MDI – PPG-425 sample was measured on a dynamic rheometer using frequency sweeps at different temperatures (Figure IX-5). The viscosity at the lowest frequency (0.001 Hz) increases as the temperature decreases. At a temperature of 130 °C, the complex viscosity is independent of frequency when the frequency is below 10 Hz, indicating the first Newtonian plateau. From 10 Hz onwards, the viscosity decreases as the frequency increases as result of shear-thinning and a power law regime is followed. At lower temperatures, the start of the shear-thinning behavior moves to lower frequencies. At 50 °C the Newtonian plateau is no longer observed within the applied frequency range.

![Figure IX-5. Complex viscosity as function of frequency for a full cured MDI – PPG-425 system without added end-capper, measured at 50, 60, 70, 80, 90, 100, 110, 120 and 130 °C.](image)

Using the time-temperature-superposition (TTS) principle\(^4,5\), a master curve can be constructed by applying a shift factor $a_T$ on the applied frequencies and the measured viscosities:

$$a_T = f(T_r)/f(T) \quad (eq. \ IX-11)$$

$$a_T = \eta^*(f, T)/\eta^*(f, T_r) \quad (eq. \ IX-12)$$

With $T_r$ being the reference temperature, which is chosen to be 50 °C. Starting from the curve measured at 50 °C, the curves measured at other temperatures are shifted (vertically and horizontally) individually in such a way that a continuous curve is obtained (Figure IX-6 (left)). Using this approach, the response of the material can be predicted over a large frequency range: from $10^{-7}$ Hz up to $10^5$ Hz or 9 orders of magnitude.
Figure IX-6. (left) Master curve constructed by TTS using the measured viscosities from (Figure IX-5), shifted with a shift factor in order to obtain a continuous curve at a reference temperature of $50 \, ^\circ\text{C}$. (right) Shift factors plotted as a function of temperature ($x$) and WLF function (eq. IX-13) fitted on data (dashed black curve).

When plotting the shift factors as function of the temperature a WLF behavior $^6$ (eq. IX-13) fits the data well, as can be seen in Figure IX-6 (right).

$$\ln(a_T) = -\frac{C_1(T - T_r)}{C_2 + T - T_r}$$  \hspace{1cm} (eq. IX-13)

The resulting values of the WLF parameters $C_1$ and $C_2$ are 9.9 and 126 K, respectively.

The frequency sweeps were also measured for the systems with 0.1 w%, 1 w% and 10 w% end-capper. The TTS master curves for the different mixtures can be found in Figure IX-7. The mixture without end-capper has the highest plateau viscosity $\eta_0$. By adding end-capper, the plateau viscosity is reduced, which is attributed to the reduced molar mass at full cure. In the power law region, the curves with 0 w%, 0.1 w% and 1 w% converge to single line at high frequencies. For 10 w%, only the onset of the shear-thinning behavior is observed.

Figure IX-7. Master curves constructed using the TTS at a reference temperature of $50 \, ^\circ\text{C}$ for full cured MDI – PPG-425 with 0 w%, 0.1 w%, 1 w% and 10 w% added end-capper. Cross model (eq. IX-14) applied for the different polymers is shown in dashed lines.
Molar mass and Viscosity

The evolution of the steady shear viscosity with the shear rate can be described with a Cross model:

\[ \eta(\dot{\gamma}) = \frac{\eta_0}{1 + (K_C \dot{\gamma})^{1-n}} \]  

(eq. IX-14)

Where \( \eta_0 \) is the zero-shear viscosity, \( K_C \) a time constant, and \( n \) the power law index. Using the Cox-Merz rule, it is reasonable to use this equation for dynamic measurements, replacing \( \eta \) by \( \eta^* \) and the shear rate by the frequency \( f \). The model fits the data for the different mixtures quite well (black dashed lines in Figure IX-7). The Cross parameters for the different mixtures can be found in Table IX-2. The value of the power law index \( n \) was found to be 0.32 by fitting the samples with 0 w% up to 1 w% of end-capper. The time constant \( K_C \) indicates the position of the transition between zero shear and the power law behavior, which shifts to lower values for lower molar masses (more end-capper).

**Table IX-2** Cross model parameters resulting in the dashed curves (Figure IX-7) for MDI-PPG-425 mixtures with different amounts of added end-capper.

<table>
<thead>
<tr>
<th>MDI - PPG-425 with end-capper</th>
<th>( \eta_0 ) Pa.s</th>
<th>( K_C ) s</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 w%</td>
<td>1.08 ( 10^6 )</td>
<td>86.4</td>
<td>0.32</td>
</tr>
<tr>
<td>0.1 w%</td>
<td>3.84 ( 10^5 )</td>
<td>23.7</td>
<td>0.32</td>
</tr>
<tr>
<td>1 w%</td>
<td>1.46 ( 10^5 )</td>
<td>6.05</td>
<td>0.32</td>
</tr>
<tr>
<td>10 w%</td>
<td>1.47 ( 10^3 )</td>
<td>8.10 ( 10^{-3} )</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Figure IX-8.** (left) Zero-shear viscosity \( \eta_0 \) and (right) time constant \( K_C \) of the Cross model (Table IX-2) as a function of the mass average molar mass for MDI – PPG-425 with 0 w%, 0.1 w%, 1 w% and 10 w% added end-capper.

When plotting the logarithm of the zero-shear viscosity \( \eta_0 \) as a function of the logarithm of the mass average molar mass, a linear relationship is found (Figure IX-8 (left)). By taking the logarithm of (eq II – 16), the equation can be linearized, resulting in (eq. IX-15).

\[ \log \eta_0(M_w) = \alpha \log M_w + \log K \]  

(eq. IX-15)

The linearized equation (eq. IX-15) was fitted through the measured datapoints, leading to a value of 2.67 for \( \alpha \) and -6.57 for \( \log K \). The value of \( \alpha \) according to theoretical models is 1 when
the molar mass is below the critical molar mass $M_C$, and 3.4 when the molar mass is larger than $M_C$. This $M_C$ is closely related with the entanglement molar mass $M_e$ of the polymer and for many polymers $M_C$ is double the value of $M_e$. The entanglement molar mass of a polyethylene oxide (PEO) is $1.6 \times 10^3$ g.mol$^{-1}$ leading to an estimated $M_e$ of $3 \times 10^3$ g.mol$^{-1}$. The $M_C$ of the linear polyurethane is assumed to be around same value. This is a thought to be a reasonable approximation, as $M_C$ is mainly determined by the chain flexibility. For the linear polyurethane the PPG-425 monomer has a structure similar to PEO, thus a similar $M_C$ can be assumed.

A similar behavior is found for the time constant $K_C$ and $M_w$, resulting in following equation:

$$\log K_C(M_w) = \beta \log M_w + C \quad \text{(eq. IX-16)}$$

Knowing the relation between the zero-shear viscosity (eq. IX-15) and time constant (eq. IX-16) as function of the mass average molar mass, (eq. IX-14) can be transformed to:

$$\eta(\dot{\gamma}, M_w) = \frac{\eta_0(M_w)}{1 + (K_C(M_w)\dot{\gamma})^{1-n}} \quad \text{(eq. IX-17)}$$

This equation describes the viscosity evolution, including the shear thinning behavior, as a function of the shear rate and the mass average molar mass. This model (eq. IX-17) was applied and compared to the measured results in Figure IX-9. The model can predict the viscosity evolution quite well. The largest difference is observed for the zero-shear viscosity of the system with 0.1w% end capper, which is underestimated by a factor of 0.66. The advantage of this approach is that evolution of the viscosity can be predicted from a model-estimated average molar mass as function of shear rate (eq. IX-17) and this for different temperatures using TTS (eq. IX-13) and is valid for an MDI – PPG-425 system. With this model predictions can be made for industrial processes that will run at higher temperatures and different shear rates.

Figure IX-9. Master curves constructed using the TTS at a reference temperature of 50 °C for full cured MDI – PPG-425 with 0 w%, 0.1 w%, 1 w% and 10 w% added end-capper compared to the adapted Cross model (eq. IX-17) (dashed).
3.1.5 Glass transition temperature

The molar mass of the polymer also affects its glass transition temperature. The glass transition temperatures of linear polyurethane samples with added end-capper, measured with DSC in a non-isothermal HCH experiment at 5 K.min\(^{-1}\) (not shown), are plotted versus the inverse experimental number average molar mass in Figure IX-10. Using the Flory-Fox\(^{11}\) relationship, the effect of the molar mass on the glass transition temperature can be modelled (eq. II-13). The Flory-Fox equation fits the experimental data nicely. The obtained parameters are 22 °C for \(T_{g\infty}\) and 69 kg.mol\(^{-1}\) for \(B\).

![Graph showing the relationship between glass transition temperature and molar mass](image)

*Figure IX-10. Glass transition temperature for MDI – PPG-425 mixtures with 0 w%, 0.1 w%, 1 w% and 10 w% added end-capper plotted as a function of the inverse of \(M_n\) as measured by GPC with the UV detector. Dashed line represents the Flory – Fox equation fitted to the data.*

A reduction in the glass transition temperature at full cure is also observed when an off-stoichiometric mixing ratio of MDI and DPG was used (see Chapter VI section 3.1.3), which is attributed to the reduction in number average molar mass. Using the recursive algorithm and the kinetic model, the number average molar masses at full cure can be estimated. The measured \(T_g\)’s are plotted as a function of the inverse of the calculated \(M_n\) in Figure IX-11 (left). Also in this case, a linear behavior is observed, with the parameters of the Flory-Fox relationship being 97 °C and 47 kg.mol\(^{-1}\) for \(T_{g\infty}\) and \(B\), respectively. In Figure IX-11 (right) the \(T_g\) is given as function of \(M_n\). For molar masses below \(B\), the \(T_g\) changes rapidly, but once this value is reached the \(T_g\) becomes nearly constant at the value of \(T_{g\infty}\).

Thus, using the Flory-Fox equation in combination with the kinetic and recursive model, it would be possible to estimate the \(T_g\) of full cured polymers for stoichiometric and off-stoichiometric conditions, taking the effect of end-cappers into account.
3.2 Modulus of fully cured network polymers

The mechanical properties of a network forming PU were tested by combining a crosslinking monomer Daltolac 251, which has three OH groups, with bifunctional PPG-425 in a stoichiometric ratio with MDI. The amount of crosslinker was varied from 0% to 100% crosslinker (expressed as a mass fraction of the polyol). The effect of the crosslinker on \( T_g \) of the fully cured material is given in Figure IX-12 (left). The \( T_g \) was measured in a non-isothermal DSC measurement at 5 K min\(^{-1}\) (not shown). The mixture without crosslinker has a \( T_g \) of 20 °C, which increases to 80 °C when only crosslinker is used.

The rubber modulus of a polymer network can be estimated using the recursive algorithm (see Chapter VIII section 3). The modulus was measured in DMA for the different compositions at 120 °C (Figure IX-12 (right)). This temperature was chosen as it is above well the highest measured \( T_g \), as is needed to measure the rubber modulus. For a mixture without crosslinker, a linear polymer is formed and the sample will behave as a liquid if heated well above its glass transition temperature (100 K in this case) and as a consequence no mechanical properties can be measured. The modulus of a mixture with 20 w% crosslinker has a modulus around 2 MPa, which increases up to a maximum of 8 MPa as the amount of crosslinker is increased at 100 w%.

Using the affine deformation model, the modulus was estimated using the recursive algorithm (eq. VIII-90). A good match between the measured and the modelled results is observed, except at 100 w% crosslinker, for which the measured modulus is 1.5 time higher than the modelled modulus. A possible explanation for this it that the temperature (120 °C) is too close to the glass transition temperature (80 °C) and therefore the measured modulus is an overestimation of the rubber modulus for this composition. Overall, the combination of kinetic and structural models developed in this work can be used for quite reliable estimations of the rubber modulus.
3.3 Properties as a function of the cure

3.3.1 Evolution of the molar mass

Knowing that the kinetic and structural models permit good estimations of full cure properties, the estimation of polyurethane properties will also be evaluated as a function of the extent of reaction. A stoichiometric mixture of MDI – PPG-425 with 0.04 w% catalyst is used for this study. The reaction kinetics of this system at 40 °C are well modelled and are therefore best suited for the study (see Chapter VII). For the full cure molar mass averages, it was observed that by adding small amount of 0.25 w% end-capper the modelled and measured averages matched better. Therefore, the same (small) amount of end-capper is added to the mixture for the simulations in this section. The result of the simulation of the evolution of the extent of reaction and the molar mass averages with reaction time can be found in Figure IX-13. All molar mass averages increase as function of the time, with $M_n$ increasing more slowly than the $M_w$ and even more than $M_z$. At the start of the reaction, the molar mass averages increase rapidly as function of the time, while from two hours onwards they increase more gradually. The molar mass evolutions are a direct result of the increasing conversion of the reaction, which is fast at the start of the reaction and slows down as the reaction continues, in correspondence with higher order reaction kinetics.

When looking at the average molar mass increase as function of the extent of reaction (Figure IX-13 (bottom left)), the increase of the averages is more gradually at the start of the reaction, with a more rapid increase when the extent of reaction approaches full cure. The polydispersity (PDI) is given as a function of the extent of reaction in Figure IX-13 (bottom right). At the start of the reaction, the PDI is close to one – it would be exactly equal one if all monomers would have the same molar mass. As the extent of reaction progresses, the PDI increases as a direct consequence of the difference in growing rates of $M_n$ and $M_w$. Once an extent of conversion of
0.85 is reached, the PDI increase accelerates. In the idealized case, where two bifunctional monomers of the same molar mass react with one another, the PDI will reach a value of two at full cure (eq. II-45). However, the growth of $M_n$ is reduced by introducing small amounts of end-capper, causing the PDI to increase rapidly near full cure.

![Figure IX-13. Simulations for the reaction at 40 °C of an MDI – PPG-425 system with 0.04 w% added catalyst, assuming 0.25w% end-capper (top left) the extent of reaction and (top right) the molar mass averages $M_n$, $M_w$, and $M_z$ derived using the recursive algorithm, plotted as a function of the reaction time. (bottom left) Molar mass averages and (bottom right) polydispersity (PDI) as a function of the extent of reaction.](image)

The distribution evolution as a function of the time can be estimated from the calculated molar mass averages by applying the models used in section 3.1.3. The evolution of the molar mass distribution using the Flory-Schulz distribution is given in Figure IX-14. The evolution of the molar mass averages $M_n$, $M_w$ and $M_z$ are also shown on the graph. The distribution at the start of the reaction is not shown as applying the distribution for the monomer mixture is not useful. It can be seen that molar mass distribution evolves to higher molar masses as the reaction progresses as function of time. Although harder to see, the distribution also becomes broader as a function of time.
Figure IX-14. Estimated evolution of the Flory-Schulz molar mass distribution as a function of the reaction time, calculated using the molar mass averages $M_n$, $M_w$, and $M_z$ (Figure IX-13) obtained using the recursive algorithm for the reaction of an MDI – PPG-425 system with 0.04 w% catalyst at 40 °C.

3.3.2 Evolution of the viscosity

The rheological changes of a curing stoichiometric mixture MDI - PPG-425 with 0.04 w% catalyst was measured by dynamic rheometry at 40 °C for frequencies from 1.0 to 10 Hz (Figure IX-15). First, the viscosity is analyzed (Figure IX-15 (top)). At start of the measurement, the viscosity of the sample is at its lowest and below the detection limit of the rheometer for the setup and conditions used. As a result, the initially measured torque is the result of the inertia of the rotor, which gives the highest contribution for the measurement at the highest frequency of 10 Hz. From 0.5 hours onwards, the curves for the different frequencies coincide with one another, and the viscosity is correctly measured. As prior to 0.5 hours, the data is not well recorded, it is not shown for the storage and loss modulus in (Figure IX-15 (middle)), nor for the phase angle (Figure IX-15 (bottom)).

After 0.5 hours, the increase in viscosity is the result of an increase of the molar mass caused by the polyurethane reaction. After 2.8 hours the viscosity is increased to about 1000 Pa.s. In the time window between 0.5 and 2.8 h, the phase angle is around 90°, which corresponds with a Newtonian liquid behavior. From 2.8 h, onwards the phase angle begins to go down with the curve for 10 Hz going down the fastest. As the phase angle becomes lower than 90°, the sample starts behaving as a visco-elastic material. This can also be observed in the storage modulus, which becomes higher. At the same time, the viscosity measured at the different frequencies starts to diverge from one another. At the highest frequency, the lowest viscosity is measured, which corresponds with a shear-thinning behavior.
Figure IX-15. Results of a dynamic rheometry experiment for MDI-PPG-425 with 0.04 w% catalyst at 40°C, measured in multifrequency mode at 1.00, 1.58, 2.51, 3.98, 6.30 and 10.0 Hz: (top) viscosity, (middle) storage ($G'$) and loss ($G''$) modulus, and (bottom) phase angle $\delta$ as a function of time.
The viscosity evolution was also measured in dynamic rheometry for polyurethane samples where cyclohexanol end-capper (0.1 w% and 1 w%) was added to the mixture Figure IX-16 (left). At the start of the measurement, the viscosity increases in a similar way for all measured samples. When they start deviating, the viscosity increases the fastest for the sample without added end-capper, the slowest for 0.1 w% end-capper. This is explained by the slower increase of the molar mass in samples with end-capper. The mass average molar mass evolution of these samples calculated with the recursive algorithm is shown in (Figure IX-16 (right)). Like for the fully cured samples and additional 0.25w% end-capper was accounted for in these simulations. The increase in molar mass has a similar shape as the viscosity evolution.

The measured viscosity is plotted as a function of the calculated $M_w$ for the different materials in Figure IX-17 (left). Plotting both axes on a logarithmic scale, a nearly linear behavior is observed, nearly coinciding for the different materials, indicating a single power law relation could be used to describe all data. Fitting a linear line through these data, the resulting values for $\alpha$ and $\log K$ of (eq. IX-15) are obtained. The value of 3.63 for $\alpha$ is slightly higher than the expected theoretical value of 3.4 for a polymer system above the critical molar mass $M_c$. With these obtained parameters, the evolution of the viscosity can be predicted based on the average molar mass evolution (Figure IX-17 (right)). A good match between the model and the experiment is found for the system with 0.1 w% end-capper. The model underestimates the viscosity for the system with 0% end-capper, while it overestimates the viscosity for the system with 1w% end-capper. The error is the highest at higher conversions. These errors indicate a systematic error in describing viscosity evolution as function of the mass average molar mass.
Figure IX-17 (left) Viscosity as a function of simulated mass average molar mass for the reaction at 40 °C of MDI – PPG-425 with 0.04 w% catalyst and added end-capper: 0 w%, 0.1 w% and 1 w%. Viscosity data were measured in dynamic rheometry at 40 °C and 1 Hz and are given for viscous behavior only (δ = 90°). The simulated mass average molar mass was calculated using the kinetic model and the recursive algorithm. (right) The evolution of the viscosity (full) compared to the prediction (dashed) using (eq. IX-15) with the parameters of the left figure, the curves are shifted in one-hour intervals between one another for clarity.

Nevertheless, the model can describe the evolution quite well at the start of the reaction for the lower viscosities. Knowing the desired maximum viscosity used in industrial processes like resin transfer molding is about 10 Pa. s⁻¹, this model could be applied for evaluating the application of an MDI - PPG-425 system in these processes.¹²

Although the progressing reaction kinetics and the viscosity evolution directly influence one another, they were measured independently with DSC and TAM and with dynamic rheometry. A problem with this approach is that linking the two measurements is not always evident. Possible discrepancies will occur due to, for example, the use of different reactive mixtures with inherently slightly different concentrations, having not exactly the same temperature programs (during sample preparation and during the measurements: the temperature is much better controlled in DSC and TAM compared to rheometry). A solution for these problems is using a device that simultaneously measures the reaction kinetics and the viscous properties. Such a device, called a rheoDSC, was developed by FYSC at VUB together with SMART at KUL.¹³–¹⁶ This device is constructed by combining a DSC and a rheometer (Figure IX-18). For this setup, a hole is made in the lid of the DSC cell for a specially designed rotor of the rheometer to be inserted. An insert was designed to place on top of the DSC sensors, having two parallel plates cover the sample and the reference side. The sample is than placed on the sample side plate, indirectly making contact with the DSC sensor, and the rotor is placed on top of the sample to measure the rheological behavior.
The advantage with this setup is that both a heat flow and rheological properties can be measured simultaneously on a single sample with the temperature being well-controlled. The technique has important drawbacks for studying the fast polyurethane reactions, however. A first drawback is that due to the less well controlled thermal environment in the DSC cell, the heat flow signal is more prone to noise and the baseline curvature and drift are more pronounced. Another drawback is that to apply the sample into the device takes about 5-10 minutes. The longer sample preparation coupled with the less accurately measured heat flow are the major reasons why the rheoDSC was not used to study the coupled viscosity and kinetics evolutions of the polyurethanes, which show their highest reactivity at the start of the experiment and a very long reaction tail due to their high order reaction kinetics.
Chapter IX

4 Conclusion

The aim of this PhD was to build models that were able to predict the polyurethane properties as function of the progressing reaction. The recursive algorithm developed in Chapter VIII was applied for the polyurethane system using the ionic kinetic model to obtain the structure parameters (molar mass averages, crosslink density,…). With the recursive algorithm, the average molar masses could be predicted quite well by accounting for a small amount of additional end-capper, possibly related to the presence of small amounts of water or monofunctional alcohols or isocyanates. By applying some simple models, the molar mass distribution developed during the reaction can be estimated, using the calculated average molar masses as parameters in the distribution.

Using dynamic rheometry over a broad frequency range at different temperature, the viscosity and the shear-thinning behavior of the full cured polymers was measured and transformed in a master curve using TTS. The power law index in the shear-thinning region was found to be the same for materials having different molar masses.

The modulus of crosslinking systems was measured with DMA and a good match between measured and predicted values was observed for materials with different crosslink densities. The Flory – Fox model could be applied on the linear polyurethanes to fit the evolution of the glass transition temperature of the materials, which is one of the major properties determining the viscous and mechanical behavior of amorphous polymers.

Describing the evolution of the viscous behavior as function of the progressing polymerization of linear polyurethanes was possible up to a certain extent and was limited by the shear-thinning behavior of the polymer at higher molar masses. A further investigation of network-forming polymers is needed in order to apply and validate the models, a necessary step to be taken in order to predict and improve industrial processes. Finite element methods are used for the prediction industrial processes. To do these simulations well, correlations between the flow, temperature and kinetics of the system must be made, making them very complicated and time consuming to calculate and often approximations are made to reduce the complexity and the recursive algorithm together with the viscosity models can aid in simplifying these systems.
5 References

CHAPTER X

CONCLUSION

The aim of this PhD research project was to gain insight in the chemorheological behavior of curing polyurethane systems, with goal to obtain models able to predict their behavior. The development of these models was established in several steps: investigating the kinetics, linking the kinetics to a molecular architecture build-up, and using it to predict viscosity and mechanical properties.

The polyurethane system has some inherent difficulties making it challenging to study. It was found that the urethane formation has a high order reaction kinetics, meaning that the reaction rate is fastest at the start of the reaction and slows down rapidly as the reaction progresses, leading to very long reaction tails. Additionally, the system is reactive at room temperature. As a result of the high order kinetic and the reactivity at room temperature, the samples preparation is required to be fast in order to measure the effect of the start of the reaction. The kinetics were investigated using thermal analysis techniques in isothermal and non-isothermal conditions. Due to the high order kinetics resulting in long reaction tails, obtaining the reaction heat flow in DSC becomes difficult as the baseline of the measurement is hard to determine. In contrast microcalorimetry in the TAM can record the tail of the reaction with high accuracy but, due to its design, cannot measure the fast evolution of the reaction at the start of the measurement. The two techniques were combined by using the fast response of the DSC at the start of the reaction and the stability of the TAM for the tail of the reaction (Chapter IV).

With the aid of the developed measuring methods, the kinetics of the urethane formation was first investigated by combining MDI with monofunctional alcohols in the absence of a catalyst (Chapter V), resulting in short oligomers, and this to obtain a kinetic mechanism able to describe the urethane formation. The total kinetic order of the urethane formation in stoichiometric conditions was experimentally determined to vary between three at the start of the reaction and two near full cure. The conversion rate in off-stoichiometric conditions is higher for both excess alcohol and isocyanate, meaning that the partial reaction order for both isocyanate and alcohol is more than one. Additionally, if ether groups are present in the reactive mixture a slowing down of the reaction was observed. Several literature mechanisms were tried, but none of the investigated mechanism resulted in a satisfactory result, able to describe the reaction heat flow over all investigated conditions. An ionic mechanism with the formation of a reactive alkoxide ion was developed in order to model the urethane formation. This mechanism also included non-reactive complex formations between the ether and alcohol groups present in the reactive mixture.
Chapter X

The kinetics of the formation of linear urethane polymers were investigated by combining MDI with dipropylene glycol (Chapter VI) and polypropylene glycols (Chapter VII). When MDI is mixed with DPG in a stoichiometric ratio, the resulting polymer has a glass transition temperature of 97 °C at full cure. Curing the polymer below this glass transition temperature results in diffusion limited conditions, reducing the reaction rate. The diffusion effects on the kinetics cannot be modelled solely with a mechanistic model. In this work, the focus remained on studying the reactions in conditions without diffusion limitations. In earlier work, curing epoxy-amine systems could be modelled by introducing a diffusion factor and this approach could also be used for the urethane reaction.

By increasing the length of the alcohol monomer from a dipropylene glycol to a polypropylene glycol, the full cure glass transition temperature could be reduced. However, when increasing the length of the polyl to PPG-1000 reaction-induced phase separation was observed, making it difficult to study the kinetics. No phase separation was observed with the shorter polyl PPG-425 and the final polymer had a glass transition temperature of 20 °C at full cure. The urethane polymerization kinetics of MDI with PPG-425 were investigated in the presence of a catalyst (DABCO). The catalyzing effect of DABCO is due to two ternary amine groups, which react with alcohol groups resulting in the formation of alkoxide ions. To take the effect of the catalyst into account, the uncatalyzed ionic reaction mechanism was extended with an equilibrium reaction between the catalyst and the alcohol group. A good correspondence between the experiment and the model was observed for stoichiometric mixing ratios for both the isothermal and non-isothermal conditions. The model was however less successful in modeling the kinetics in conditions with an excess of isocyanate.

In the next step, an approach for predicting the molecular structure build-up was needed. A generalized recursive algorithm was developed, based on the ideas presented in the papers of Macosko and Miller from 1976, which can model the creation of the molecular structure of step-growth polymers (Chapter VIII). This generalized algorithm is able to describe the evolution of the molar mass averages ($M_n, M_w, M_z$) in the pre-gel phase as well as the crosslink density and the different fractions (sol, pending and elastic effective) in the gelled state as a function of the extent of reaction. The strength of this algorithm is that it functions for any combination of monomers with multiple functional groups and functionalities and that the linking functional groups can be built out of different functional groups with two or more functional groups. The developed algorithm was confronted with literature values describing specific cases and was able to describe them well.

The recursive algorithm and the ionic mechanism were used to predict the average molar masses of the linear polyurethanes created by MDI and PPG-425 and compared with experimental results (Chapter IX). A good match between the experiments and the model was found if a small amount (0.25 w%) of extra end-capper was presumed to be present, which might be explained by small amounts of water or kinetic deviations at near full cure. Using this approach, the
evolution of the average molar mass and its impact on the viscosity evolution could be described, which was the goal of this PhD work.

The development of the ionic model and the recursive algorithm could not be established without the development of a software package. The software and its development was only briefly discussed in this work (Chapter III) but has taken quite some effort and was developed from scratch during the PhD. The software was made user friendly so it can be, and was already, used by other researchers. With the aid of the software, developments in self-healing materials based on Diels-Alder polymer network are being made. The structure development capabilities of the software will be used in the near future for the further development of self-healing materials including reversible covalent networks and vitrimers.
List of publications and disseminations

Publications in peer reviewed journals


Invited talks


Talks

“Kinetics and network formation in polyurethanes”, Verhelle R. R. and Van Assche G., BPG annual meeting (2019), Houffalize, Belgium

“Modelling polyurethane reactions by combining differential scanning calorimetry and microcalorimetry”, Verhelle R. R. and Van Assche G, CEEC-TAC 5, Rome, Italy

Publications in preparation

