

A Kinetic Investigation of Polyurethane Polymerization for Reactive Extrusion Purposes

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ABSTRACT: The effects of the reaction conditions on the kinetics of two different polyurethane systems were investigated. To do so, three different kinetic methods were compared: adiabatic temperature rise (ATR), measurement kneader, and high-temperature measurements. For the first polyurethane system, consisting of 4,4-diphenylmethane diisocyanate (4,4-MDI), butane diol, and a polyester polyol, the reaction conditions did not seem to matter; a kinetically controlled reaction was implicated for all reaction conditions. The reaction was second order in isocyanate concentration and 0.5th order in catalyst concentration and had an activation energy of 52 kJ/mol. The second polyurethane system consisted of a mixture of 2,4-diphenylmethane diisocyanate and 4,4-MDI, methyl propane diol, and a polyester polyol. For this system, each of the three measurement

methods showed different behavior. Only at a low catalyst concentration did the ATR experiments show catalyst dependence; at higher catalyst levels and for the other two measurement methods, no catalyst dependence was present. Furthermore, the ATR experiments proceeded much faster. Presumably, for this system, the rapid diffusion interfacial of the species present was hindered by the presence of bulky oligomer molecules. The result was a diffusion limitation reaction at low conversions and an inhomogeneous distribution of species at higher conversions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 370–382, 2006

Key words: extrusion; interfaces; kinetics (polym.); mixing; polyurethanes

INTRODUCTION

Fair numbers of publications have considered the kinetics of polyurethane polymerization.^{1–4} In these investigations, several techniques have been used for the acquisition of kinetic data. Commonly used methods include titration, Fourier transform infrared spectroscopy, adiabatic temperature rise (ATR) experiments, and size exclusion chromatography (SEC). Unfortunately, the method applied often poses limits to the reaction conditions. In general, the reaction cannot be too fast for all of these methods. Therefore, it is often necessary to keep the temperature and catalyst level low for the kinetic measurements. This restrains the predictive window of the kinetic investigation.

Apart from these limitations, the reaction mechanism has to be universal for all reaction conditions to extend the model prediction to any situation. For polyurethane polymerization, this uniformity of mechanism cannot always be assumed. Several phenomena may cause the reaction to be nonuniform. First, the complex reaction mechanism is still not understood

completely. Several reaction steps, each with its own activation energy (E_A) and equilibrium constant, occur during the formation of a urethane bond. The overall reaction E_A may, therefore, change with temperature, depending on which step is rate-limiting. Also, the composition of the reaction mass changes tremendously during the reaction. Initially, low-viscous immiscible monomers react into a highly viscous and more or less homogeneous reaction mass. This change in composition may have a profound influence on the reaction. Finally, the reaction conditions also affect the side reactions. Also, the type of catalyst, the stoichiometric ratio of monomers, and the temperature influence the side reactions. Although the effect of side reactions is often negligible in a kinetic investigation, the effect of side reactions on the product properties can be considerable.

To study the kinetics of polyurethane formation for reactive extrusion the previously discussed reasoning must be kept in mind. In the extrusion process for polyurethane polymerization, the monomers are fed to the extruder at a temperature of 60–80°C. The temperature of the reaction mass increases rapidly in the first part of the extruder, mainly due to the fast exothermic reaction. Heat transfer through the wall and viscous dissipation are still of minor importance. For this part of the reaction, the reaction conditions more or less mimic ATR measurements, although no

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mixing is present during ATR experiments. However, the situation changes as soon as high-molecular-weight material appears. At that moment, the reaction velocity slows considerably (due to the second-order nature of the reaction), and hardly any reaction heat will be generated. Furthermore, the temperature of the reaction mass will be well over 160°C. In this regime, ATR experiments will give a poor prediction of the reaction kinetics because hardly any reaction heat is produced (which will give a large error in the ATR measurements). Methods based on molecular weight measurements, such as SEC or rheology, are more apt in this situation.

With the previous arguments in mind, two different measurement methods are necessary to establish the kinetics for the modeling of polyurethane polymerization in an extruder. However, only a single kinetic measurement method has been applied in the few studies on thermoplastic polyurethane extrusion that are present in the literature.⁵⁻⁹ Either ATR measurements or SEC were used in these studies; this inevitably led to descriptive errors. The importance of these errors were investigated experimentally in this study. The different methods were compared with respect to the Arrhenius behavior, the influence of the catalyst, and the effect of mixing. Three different methods were surveyed: ATR, SEC, and kneader measurements. Two different thermoplastic polyurethane systems were investigated to further validate our assumptions concerning the necessity of additional kinetic measurement methods for polyurethane polymerization.

THEORY: REACTION KINETICS

To understand why the different measurement methods may lead to different results, a better understanding of the bulk polyurethane polymerization reaction is necessary. We briefly discuss a few key phenomena: the reaction mechanism, the miscibility of the monomers, and the effect of long molecules on the reactivity of the end groups. The catalyzed urethane reaction gets all the attention in this discussion because this is by far the most frequently occurring reaction in bulk. The influences of the uncatalyzed reaction, the autocatalyzed reaction (by the urethane group), and the acid-catalyzed reaction are neglected.

Reaction mechanism

The reaction mechanism for the metal carboxylate catalyzed polyurethane polymerization reaction is still not completely understood. The catalyzed reaction takes place through several intermediate (equilibrium) steps. Which steps actually occur and which of these steps is rate-determining are still not clear. A few general mechanisms for the polyurethane reaction are proposed,^{1,10} but no conclusive evidence has yet been

presented. The rate equations proposed are based on a mechanism where the catalyst forms a complex with an isocyanate group. Subsequently, this complex reacts with an alcohol group. If the complex formation is considered an equilibrium reaction, this mechanism will result in a hyperbolic rate equation. A second approach that is often used to describe the polyurethane formation uses an n th-order rate equation [eq. (2)]. This model is adapted in this research because the n th-order model needs fewer parameters than the hyperbolic model and fits the reaction equally well.¹¹

Miscibility of the monomers

A second aspect of the bulk polyurethane polymerization that has to be considered is the miscibility of the isocyanate and the polyol. Because of their incompatibility, the reaction will take place on and near the interface, and interfacial effects will influence the reaction. These interfacial aspects of polyurethane polymerization have been investigated in several studies.¹²⁻¹⁴ The starting point of these investigations was the effect of impingement mixing because many polyurethane products are made through a reactive injection-molding processes where generally impingement mixing is an important process step. Kolodziej et al.¹⁵ found that impingement mixing gave a dispersion with droplets that were still quite large ($>100 \mu\text{m}$). An increase in the Reynolds number above 200 did not seem to decrease the droplet size any further. This droplet diameter was far too high to result in a kinetic controlled reaction. A second process was necessary to overcome these limitations. This second (fast) mixing process seemed to be related to surface instabilities. Machuga et al.¹⁶ confirmed the observation of other authors that the polyol at the boundary layer diffuses spontaneously and rapidly ($<1 \text{ s}$) in the isocyanate to form a well-mixed intermaterial phase. They found that the dimers that are formed on the boundary layer of the isocyanate and the polyol play an important role in this process. Probably, the urethane groups of these dimers undergo H-bond interactions with the isocyanate molecules across the border, resulting in strong surface destabilizing forces. It seemed that the initial growth of the intermaterial area was independent of the monomers used. However, further growth of the intermaterial area appeared to depend on the viscosities of the species that were present in the intermaterial area. Rigid oligomer molecules, a fast reaction, or the use of a crosslinking system limited the growth of the intermaterial zone, which result in a diffusion controlled reaction. The effect of catalyst on the interfacial process was ambivalent. Wickert et al.¹⁴ observed a much finer dispersion with catalyst than without, whereas Machuga et al.¹⁶ detected no difference between catalyzed and uncatalyzed experiments.

Concept of the functional group reactivity independent of molecule size

A third concept that can have an effect on the polyurethane reaction is the concept of functional group reactivity independent of molecule size. For condensation polymerization reactions, it is expected that the reaction rate constant (k) and the reaction mechanism are constant for the entire reaction.¹⁷ The size of the molecules attached to a reactive group has no influence on the reaction rate. In other words, possible diffusion limitations will have no effect. A reactive group will be in two alternating states: colliding with a different reactive group and diffusing to the next reactive group. If a lengthy molecule is attached to the reactive group, the diffusion time is longer, but the collision time is also longer. A reactive group will switch many times between these states before it reacts; therefore, the length of a molecule will not have a net effect on the reaction velocity. This hypothesis is applied successfully in many cases. However, the theory does have a limitation: it does not hold for very long molecules or for very fast reactions. The theory has been verified with rather slowly reacting systems (reaction time > 100 min). The polyurethane reaction is much faster, especially at higher temperatures. Whether this will result in a reaction that is diffusion-limited can be verified experimentally.

EXPERIMENTAL

Chemicals

Two different polyurethane systems were used in this investigation. The difference in both systems regards the type of chain extender and the type of isocyanate used. Both systems have the same number of hard segments (24.0%) and use the same catalyst (bismuth octoate). For all experiments, the pretreatment of the monomers was the same. Before usage, the polyol was dried *in vacuo* at 110°C for 2 h; the chain extender was dried at 80°C *in vacuo*. Subsequently, molecular sieves (0.4 nm) were added to remove any moisture that still might have been present. The isocyanate was used as received. The isocyanate was used at 50°C, whereas the polyol fraction was used at 80°C.

System 1 was composed of a polyester polyol of monoethylene glycol, diethylene glycol, and adipic acid [weight-average molecular weight (M_w) = 2200 g/mol, $f = 2$]; 1,4-butanediol ($M_w = 90.1$ g/mol, $f = 2$); and 4,4-diphenylmethane diisocyanate (4,4-MDI; $M_w = 250.3$ g/mol, $f = 2$).

System 2 was composed of a polyester polyol of monoethylene glycol, diethylene glycol, and adipic acid ($M_w = 2200$ g/mol, $f = 2$); methyl propane diol ($M_w = 90.1$ g/mol, $f = 2$); and a eutectic mixture (50/50) of 2,4-diphenylmethane diisocyanate (2,4-MDI) and 4,4-MDI. ($M_w = 250.3$ g/mol, $f = 2$).

Although the difference is not very large in the chemicals used in both systems, the differences that do exist may well have resulted in a different reaction pattern. The following properties are affected:

- The polyol and diol are more compatible in system 2 than in system 1; therefore, the chain extender dissolved at a lower temperature in system 2.
- The hard segments in system 1 will crystallize more readily. The differences in both the chain extender and the isocyanate contribute to this property. In system 2, a methyl group on the chain extender will hinder the formation of a layered structure of hard segments. In addition, the nonlinear 2,4-MDI that is present in system 2 will also be obstacle for the crystallization of the hard segments.
- The compatibility of hard and soft segments in system 2 is also different than that of system 1. The use of methyl propane diol as the chain extender in system 2 may influence the solubility of the hard and soft segments in a positive way.
- The polymer molecules formed are generally assumed to adapt a different conformation, depending on the system. Although system 1 produces a completely linear molecule, the polymer molecules in system 2 will adopt a more staggered/coiled structure because of the presence of nonlinear 2,4-MDI.
- The reactivity of the end groups of both systems may differ. We expect that the isocyanate group of 2,4-MDI that is placed in the ortho position has a comparable reactivity to that of an isocyanate group in the para position. However, the approachability of the isocyanate group in the ortho position will be less because of steric hindrance. Therefore, the reactivity of the ortho-positioned isocyanate group may be lower than of the para-positioned isocyanate group. This difference in reactivity may lead to a lower overall reaction velocity.

ATR experiments

ATR is a common method for measuring the kinetics for polyurethane polymerization. With this method, the polyurethane kinetics at relatively low conversions and relatively low temperatures can be investigated. Many authors have described the experimental procedure for ATR measurements.¹ The operating procedure for the experiments is identical to ref. 1. The adiabatic reactor consisted of a paper cup (diameter = 5 cm) surrounded by a layer of urethane foam for insulation. The reactor could be closed with a lid. The lid was equipped with a thin Copper Constantine thermocouple that stuck in the middle of the reaction

mass when the lid was closed. The reaction mass was stirred with a turbine stirrer with a diameter of 4 cm. We used 200 g ($\pm 1\%$) of material per experiment. To start each experiment, the necessary amounts of polyol and diol were weighed in the reactor and mixed for 60 s with a turbine stirrer at 600 rpm. Care was taken to keep the temperature of the mixture above 60°C because demixing would take place at lower temperatures. The proper amount of catalyst was added with a syringe, and the polyol mixture was stirred for another 30 s. Finally, the proper amount of isocyanate was added with a syringe, and the reaction mass was stirred at 1500 rpm for 15 s. The cover was put on top of the reactor, and the measurement was started.

Analysis of ATR results

To derive kinetic data from the ATR experiments, a simplified heat balance [eq. (1)] and rate equation [eq. (2)] were solved simultaneously.^{3,11} For the heat balance, quasi-adiabatic conditions were assumed because the reactor was not completely adiabatic for the time period under investigation. Depending on the reaction time, up to 4% of the total reaction heat generated during the reaction was lost to the surroundings. We obtained the overall heat-transfer coefficient (h^*) by fitting the cooling curves of several experiments with eq. (1). We took the density (ρ) and the specific heat to be constant over the whole measurement range. Although both the specific heat and ρ were somewhat dependent on the temperature, the temperature effects of both constants counteracted so that the net effect was negligible (<5%). A nonlinear regression method (error controlled Runge–Kutta) was used to solve the differential equations. With a least-squares routine, the difference between the model and the measurement was minimized. The calculations were performed with the software program Scientist (Micromath, St. Louis, MO):

$$V\rho C_p \frac{dT}{dt} = V\rho R_{\text{NCO}}\Delta H_R - hA(T - T_{\text{room}}) \quad \text{or} \quad C_p \frac{dT}{dt} = R_{\text{NCO}}\Delta H_R - h^*(T - T_{\text{room}}) \quad \text{with } h^* = \frac{hA}{V\rho} \quad (1)$$

$$R_{\text{NCO}} = \frac{d[\text{NCO}]}{dt} = R_{\text{NCO,Unecat}} + R_{\text{NCO,Cat}} = -A_{0,\text{Unecat}} e^{-\frac{E_{A,\text{Unecat}}}{RT}} [\text{NCO}]^n - A_0 [\text{Cat}]^m e^{-\frac{E_A}{RT}} [\text{NCO}]^n \quad (2)$$

where V is the volume of the adiabatic temperature rise reactor, C_p is the heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$), T is the temperature (K), T_{room} is the room temperature (K), R_{NCO} is the rate of isocyanate conversion (mol

$\text{kg}^{-1} \text{s}^{-1}$), ΔH_R is the heat of the reaction (J/mol), h is the heat-transfer coefficient ($\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$), A is the surface area of the adiabatic temperature rise reactor (m^2), A_0 is the preexponential reaction constant ($\text{mol kg}^{-1} \text{s}^{-1}$), R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), $[\text{NCO}]$ is the concentration of isocyanate groups (mol/kg), n is the reaction order, $[\text{Cat}]$ is the catalyst concentration (mg/g), and m is the catalyst order.

The fit procedure was as follows. Data obtained from the uncatalyzed runs on $E_{A,\text{Unecat}}$ and $A_{0,\text{Unecat}}$ were used as input parameters for the fit of the catalyzed runs. All of the catalyst dependence runs were fitted simultaneously, with the values for E_A , m , and A_0 . ΔH_R was taken from the experiment that gave the largest temperature rise.

Representation of ATR results

Often, the results of ATR measurements are plotted straightforwardly as the temperature versus the time. These plots give a clear view on the value of the adiabatic temperature rise (ΔT_{ad}) and a global idea of the reaction velocity. A different method of plotting the results is to translate the temperature versus time plot into an Arrhenius plot. Although it is much harder to visualize ΔT_{ad} in such a graph, these plots give more information on the course of the reaction. E_A and the actual reaction velocity constants are better illustrated. Furthermore, the effect of the catalyst on the reaction velocity is clearly perceptible in these graphs. For an Arrhenius plot, k must be known as a function of temperature. k for an n th-order reaction can be calculated from an ATR experiment according to Richter and Macosko:¹⁸

$$k_f = \frac{\rho C_p}{-\Delta H_R [\text{NCO}]_0^n} \left(\frac{\Delta T_{\text{ad}}}{\Delta T_{\text{ad}} + T_{t=0} - T} \right)^n \frac{dT}{dt} \quad (3)$$

where k_f is the forward reaction rate constant ($\text{kg mol}^{-1} \text{s}^{-1}$) and $T_{t=0}$ is the temperature at time = 0 (K).

To account for the nonadiabatic conditions in our ATR reactor, the temperature versus time curve that was obtained in the ATR experiment was modified. This modified curve then served as the basis for the calculation of k [eq. (3)]. To modify the curve, the amount of heat lost (ΔT_{loss}) had to be calculated for every time interval, starting at a time of $t = 0$ [eq. (4)]:

$$\Delta T_{\text{loss}} = \frac{h^*}{C_p} \Delta t (T - T_{\text{room}}) \quad (4)$$

where Δt is the time interval (s).

ΔT_{loss} was added to the measured temperature at that time interval. In this way, a modified ATR curve was constructed.

High-temperature measurements

A method for following the conversion of a polyurethane polymerization at higher temperatures and conversions was described by Ando.¹⁹ In contrast to ATR experiments, this method is based on isothermal measurements. Small reaction flasks filled with premixed monomers are kept in a thermostated oil bath. The polymer in the flasks is allowed to react for a certain time period. Subsequently, the reaction is quenched, and the samples are analyzed with SEC. The kinetic constants are then derived from a plot of the number-average molecular weight (M_n) versus time.

Two important conditions must be met to get meaningful results from this method. First, it is important that the reaction flasks reach the oil-bath temperature much faster than in the characteristic reaction time. For our experiments, an analysis based on the Fourier number revealed that this condition was met if the reaction time was longer than 15 min. This analysis did not take into account the reaction heat generated in the flasks. However, the reaction heat released only helped the reaction reach the oil-bath temperature sooner. During the relevant part of the measurement, hardly any heat was generated.

A second condition that must be met to obtain relevant results is related to the analytical method. The molecular weight that is measured must represent the real molecular weight of the sample. Because our SEC equipment was calibrated with polystyrene samples, this requirement was not obvious. To check for this requirement, the samples of one experiment were analyzed on a second SEC system. This second system was equipped with a triple detection system so that the real molecular weight could be determined. A comparison of the results of the two systems revealed that the polystyrene calibrated system underestimated the M_w 's by 10–20%. The difference in M_n was about 10%. These errors were acceptable, which meant that the results obtained on the polystyrene calibrated column could be used for our kinetic investigations.

Experimental procedure

The premixing procedure for these experiments was similar to that of the ATR experiments. However, the premixing time was extended to 40 s to ensure optimal mixing. After premixing, a part of the reaction mass was transferred to small 1.5-mL reaction vials with a syringe. Subsequently, submerging of the flasks in liquid nitrogen quenched the reaction temporarily. The total premix, fill, and quench cycle took about 2 min. In the next step, the flasks were capped while they were still frozen; the capping was carried out in a nitrogen atmosphere to prevent the intrusion of moisture. The flasks were then submerged in a heated oil bath to restart the reaction. After the desired reac-

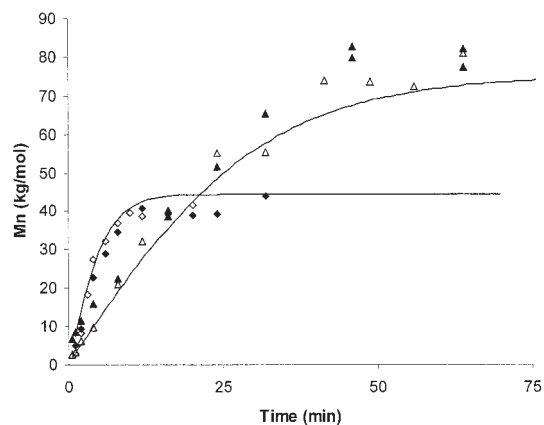


Figure 1 M_n versus time for the high-temperature experiments for system 2: experimental results and model prediction: (▲) 150°C, (△) 150°C replicate, (◆) 200°C, and (◇) 200°C replicate. The points in the gray areas were used to determine the equilibrium molecular weight.

tion time, a flask was transferred quickly into a beaker filled with liquid nitrogen. The flasks were broken, and the content was dissolved in a 5% solution of dibutyl amine in tetrahydrofuran. Subsequently, the tetrahydrofuran was evaporated. The samples obtained in this way were analyzed through SEC. The SEC procedure was described in a previous publication.²⁰ The experiments for system 1 were performed at five different temperatures (150, 160, 170, 180, and 200°C). The effect of [Cat] was investigated at 150°C. Furthermore, three different catalyst levels were investigated (0.005, 0.015, and 0.05 mg/g). The experiments for system 2 were performed at seven different temperatures (150, 160, 170, 180, 190, 200, and 210°C). Every experiment was replicated at least once. The effect of [Cat] was investigated at 180°C. Three different catalyst levels were investigated (0.1, 0.17, and 0.3 mg/g).

Analysis of experiments

The result of a high-temperature experiment consisted of a plot of M_n versus time; an example is shown in Figure 1. M_n was taken as a measure of the conversion in these plots because this average represented the number of molecules present. For a second-order step-polymerization reaction, M_n increases linearly in time:²¹

$$M_n = M_0 \{1 + [\text{NCO}]_0 k_f(T, [\text{Cat}]) t\} \quad (5)$$

where M_0 is the average weight of the repeating unit (g/mol).

Strictly speaking, eq. (5) is only valid for step-growth homopolymerizations with an A–B type of monomer. For the terpolymerization that we investi-

gated, large deviations of this equation could have occurred, especially if the reactivities of the chain extender and the polyol were different.²² However, for the conversion range we investigated (>95%), the differences were negligible, and therefore, eq. (5) was suitable.

To derive k from an experiment, the initial slope of the curve has to be determined. A least-squares routine was used to establish this slope for every experiment. As follows from eq. (5), the initial slope relates to k according to

$$k_f(T, [\text{Cat}]) = \frac{dM_n}{dt} \frac{1}{M_0[\text{NCO}]_0} = \text{Slope} \times \frac{1}{M_0[\text{NCO}]_0} \quad (6)$$

In this way, k values could be obtained at different temperatures. The initial slope was used to derive k because the M_n did not increase endlessly in time. Polyurethane formation is an equilibrium process, and because the experiments were performed at high temperatures, the reverse reaction limited the maximum conversion. Because of depolymerization, the molecular weight did not increase any further after a certain reaction time. At that time, the forward reaction rate was equal to the reverse reaction rate. The equilibrium constant and the reverse reaction rate were related to the equilibrium M_n according to

$$K = \frac{k_f}{k_r} = \frac{[U]_{\text{Eq}}}{[\text{NCO}]_{\text{Eq}}^2} = \frac{M_n(M_n - M_0)}{M_0^2[\text{NCO}]_0} = A_{0,\text{Eq}} e^{\frac{E_{A,\text{Eq}}}{RT}} \quad (\text{kg/mol}) \quad (7)$$

where K is the equilibrium constant (kg/mol), k_r is the reverse reaction rate constant (1/k) and $[U]$ is the concentration of urethane bonds (mol/kg).

For every temperature, the equilibrium molecular weight could be established. This value could then be used to calculate the equilibrium constant and the reverse reaction rate at that temperature. The experimental graphs (e.g., Fig. 1) show that there was some scatter in the value for the equilibrium molecular weight. Therefore, an average equilibrium molecular weight was taken for every temperature. In Figure 1, the shaded areas indicate which part of the curve was considered to be in equilibrium.

Kneader experiments

The third method for measuring the kinetics of polyurethane polymerizations makes use of a measurement kneader. A measurement kneader is a batch reactor that consists of two counterrotating nonintermeshing paddles that rotate in a closely fitted barrel. The barrel of the kneader is provided with a

thermostated heating system; therefore, experiments up to 300°C can be performed. The torque the paddles experience is measured, and because the conversion is related to the measured torque (through the viscosity), the polymerization reaction can be followed. However, a calibration procedure is necessary to relate torque to conversion. For the calibration procedure, samples must be analyzed on molecular weight. The experimental setup and method of analysis were described for system 2 by Verhoeven et al.²⁰ Experiments were performed at four different temperatures (125, 150, 175, and 200°C). The effect of $[\text{Cat}]$ was investigated at 175°C. Four different catalyst levels were used (0.25, 0.40, 0.75, and 1.30 mg/g). For systems 1 and 2, the same experiments were performed. All experiments were replicated three times. The results of these experiments are discussed in the Results section.

The kneader experiments were comparable to the high-temperature measurements because, in both cases, the kinetics were measured under isothermal conditions and at high temperatures. Therefore, the method of representing and obtaining the data was the same. Naturally, when we compared both methods, there were also differences. The most obvious difference was the mixing situation; in contrast to the high-temperature experiments, the material in the kneader underwent large deformations. Moreover, it was possible to distill rheological data from the kneader experiments. However, the kneader experiments tended to be less accurate because the reaction was followed indirectly, and the reaction mass was not protected completely from its surroundings. Notwithstanding, a comparison of the results of both methods gave useful information on the effect of mixing on polyurethane formation.

RESULTS

This section is split into different parts. The results of each measurement method are discussed separately, and for each method, the two different urethane systems are compared. Subsequently, the measurement methods are compared for every system to see if they really resulted in different kinetic data.

ATR measurements

Typical graph

As discussed in the Experimental section, the ATR results are shown in an Arrhenius plot. Figure 2 shows the results of a duplicate experiment for systems 1 and 2. The same catalyst level was used for both systems. A second-order reaction rate equation was adopted to construct Figure 2. This assumption seemed to be valid for both systems. When we compared both

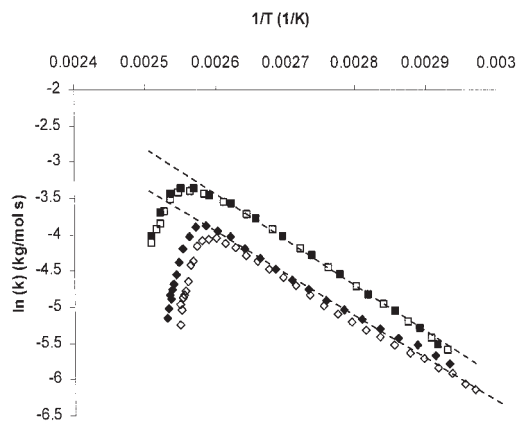


Figure 2 Replicate ATR experiments. [Cat] = 0.075 mg/g: systems (■/□) 1 and (◆/◇) 2.

graphs, it was clear that system 1 reacted about one and a half times faster than system 2. As expected, the reaction rate did not rise to infinity; the reaction slowed considerably at a certain conversion. Surprisingly, the conversion at that point was still quite low for both systems, between 65 and 70%. A comparison of all experiments showed that regardless of the catalyst level, the decrease in reaction velocity started between 65 and 70% for both systems. The reaction did proceed after that point, but k continued to decrease at higher conversions. The reason for the decrease in k was not immediately clear. The decrease was too large to attribute it to a change in n . As explained in the Theory: Reaction Kinetics section, the reaction may have slowed due to diffusion effects. However, the average degree of substitution at 70% conversion was about equal to 3, which was too low to give rise to a large diffusion resistance. Therefore, a phase separation of hard and soft segments was the more probable cause for the drop in reaction velocity. Because of the clustering of the hard segments, the mobility of the molecules decreased considerably; this could have decreased the observed reaction velocity.²³ Blake et al.²³ showed that for fast ATR experiments, the onset of the phase separation is dependent on the initial temperature, catalyst level, and hard-segment percentage. They found that phase separation occurred between 66 and 90% conversion, which was in agreement with our observations. In contrast to Blake et al.,²³ we did not see an effect of [Cat] on the position of the onset point. This could be explained by the fact that our experiments were much slower. In that case, the phase separation kinetics were much faster than the reaction kinetics, regardless of the catalyst level. In other words, in our case, the phase separation was never delayed by a faster reaction. Surprisingly, the chemical composition also seemed to have no influence on the onset point because both systems showed the same effect at the same conversion. Possibly, the

structure of the hard segments did not differ largely for our systems, despite the difference in the chain extender and isocyanate.

The effect of phase separation on the reaction velocity has not been observed in many other ATR investigations. However, these investigations have often used a higher hard-segment percentage, which increased the conversion at which the phase separation took place.²³ Because, at higher conversions, the reaction becomes difficult to follow (because of the decrease in heat generation at high conversions), the effect of phase separation may be less visible, which would explain the lack of data. For ATR investigations in which crosslinking polyurethane systems were used, a decrease in reaction velocity has been observed at higher conversions (3/4).²⁴ In contrast to phase-separating systems, the mobility of the molecules for these systems was limited due to crosslinking at higher conversions, instead of the clustering of the hard segments. Crosslinking already took place around 70% conversion, which made the effect more perceptible.

Comparison of different catalyst levels

In Figures 3 and 4, the experiments with different catalyst levels are shown. The zero-catalyst experiments were much slower than the runs with the lowest catalyst level (3–6 times for system 1 and 2–4 times for system 2).

However, the reaction path of the uncatalyzed runs could hardly be compared with that of the catalyzed runs. As mentioned in the theoretical section, the isocyanate droplets may disperse much more finely in the presence of catalyst. When the catalyst is absent, the then-occurring larger droplets result in a more

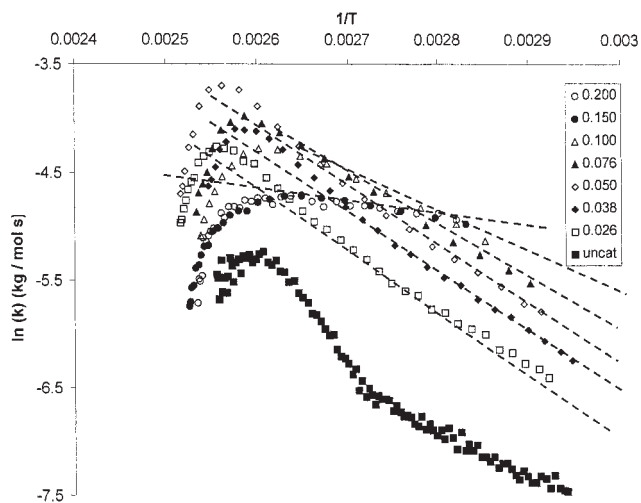


Figure 3 ATR experiments: catalyst dependence of system 2.

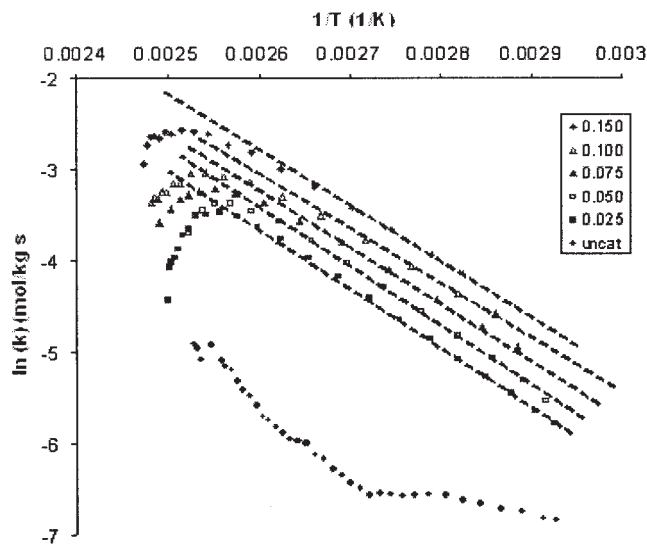


Figure 4 ATR experiments: catalyst dependence of system 1.

pronounced diffusion limitation for the initial part of the reaction. This probably explains the low initial E_A of the uncatalyzed runs (20 kJ/mol for system 1 and 35 kJ/mol for system 2). Nevertheless, at a certain conversion, the oligomers formed were likely to compatibilize the reaction mass, which resulted in a less diffusion-limited reaction and a higher E_A (± 100 kJ/mol for system 1, 75 kJ/mol for system 2). This explained the sudden increase in E_A , as shown in Figures 3 and 4. An autocatalytic process might also have been responsible for the sudden increase in the reaction velocity. However, replicate experiments showed that the uncatalyzed runs were very mixing sensitive, which supported the mixing hypothesis. A model fit of the uncatalyzed runs would have been imprecise because of this mixing sensitivity, especially because the E_A increased suddenly during the reaction. Still, a fit of the uncatalyzed runs was used in this kinetic study because the effect of the uncatalyzed reaction could not be ignored.

Now, if we look at the catalyzed runs, the experiments for system 2 showed noteworthy behavior. Normally, one would expect the reaction velocity to increase with increasing catalyst level with E_A remaining the same. However, if we look at Figure 3, it seems that the E_A decreased with increasing catalyst level, whereas the initial reaction velocity increased with catalyst level, as expected. For system 1, this behavior did not occur (Fig. 4). Therefore, the cause of this phenomenon had to be found in the structure of the monomers of system 2. The 2,4-MDI in system 2 resulted in staggered oligomer and polymer molecules (see the theoretical section). Staggered or rigid molecules hindered the formation of a broad intermaterial layer of isocyanate and polyol. This broad layer was

necessary to produce a kinetically limited reaction. According to Machuga et al.,¹⁶ the intermaterial layer will grow initially the same for all catalyst levels. In this case, the reaction velocity depends on [Cat] in this interfacial zone, which results in an initial reaction velocity that is catalyst-dependent. However, at higher catalyst levels, the growth rate of the intermaterial zone decreases or even stops because of the faster formation of large viscous molecules. Therefore, the combination of staggered molecules and a high catalyst level may result in the incomplete micromixing of the reactants. The resulting diffusion limitation is observable in an Arrhenius plot as a decrease in E_A with increasing catalyst level. As shown in Figure 3, E_A continued to decrease with higher [Cat] until a maximum reaction velocity was reached at high catalyst levels (0.15 and 0.20 mg/g).

As a result, we needed to determine two different sets of kinetic parameters for system 2. The lowest four catalyst level runs (0.025–0.075 mg/g) were used to establish the kinetic constants for the experiments with low catalyst levels. The fitting procedure can be found in the Experimental section. However, because of the inconsistency in E_A in system 2, a second set of parameters seemed to be necessary to model the reaction at high catalyst levels. Therefore, the highest two catalyst level runs were used to establish a catalyst-independent rate equation because these experiments seemed to be equally fast, regardless of [Cat]. The results are shown in Table I.

In contrast to system 2, the Arrhenius plot for system 1 (Fig. 4) showed regular behavior. With a higher catalyst level, E_A remained constant while k increased, indicating that no diffusion limitations occurred, as was observed for system 2. With Figure 4, a fit was executed according to the fitting procedure as described in the Experimental section. The resulting model parameters are also shown in Table I.

High-conversion experiments

A typical graph for a high-conversion experiment is shown in Figure 1. Two experiments and their replicates are shown. System 2 was used for these experiments. The solid lines represent the model predictions; the model predictions were based on a fit of all of the high-temperature experiments performed in this research. The resulting kinetic data are shown in Table I. As expected, the molecular weight increased with time. Initially, the rise was linear. This part of the curve was used to determine the initial slope. At longer reaction times, the molecular weight leveled off because of depolymerization. For both temperatures, the reproducibility of the experiments was reasonable.

The procedure used to derive the kinetic data was described in the Experimental section. This procedure was used to obtain the forward and reverse reaction

TABLE I
Kinetic Parameters for Systems 1 and 2

	ATR		High-temperature experiments	Kneader experiments
	Low [cat]	High [cat]		
System 1				
$A_{0,Uncat}$ (kg/mol s)	169.1			
$E_{A,Uncat}$ (kJ/mol)	35.3			
A_0 (kg/mol s) \times (g/mg)m	1.25×10^6		2.69×10^6	5.13×10^5
m	0.61		0.5	0.57
E_A (kJ/mol)	50.5		53.6	52.0
System 2				
$A_{0,Uncat}$ (kg/mol s)	5.37×10^3			
$E_{A,Uncat}$ (kJ/mol)	45.8			
A_0 (kg/mol s) \times (g/mg)m	1.09×10^5	0.208	1.49×10^7	2.18×10^6
m	0.92	0	0	0
E_A (kJ/mol)	42.5	9.9	71.9	61.3

rates for every temperature under investigation. In Figure 5, an Arrhenius plot of the forward reaction rate is shown for all of the experiments performed with systems 1 and 2. At lower temperatures, both systems exhibited a linear relationship between $\ln k$ and $1/T$, which confirmed the second-order rate assumption. However, for system 2, a deviation from linearity turned up at higher temperatures (200°C, 210°C). This was due to the fact that the slopes of these curves were determined largely during the first 15 min of the reaction when the flasks were still warming up (as explained in the theoretical section). Therefore, the effective flask temperature was lower than the oil-bath temperature, which explained the downward curvature in Figure 5. For this reason, the experiments at 200 and 210°C were not used to determine the Arrhenius parameters for system 2. However, the runs at 200 and 210°C could still be used to determine the kinetics of the depolymerization reaction. The equilibrium molecular weights were determined at reaction times longer than 15 min, which ensured that the flasks had

reached the oil-bath temperature. In Figure 6, the Arrhenius plot for the depolymerization reaction is shown for systems 1 and 2. The equilibrium constant for every temperature was calculated by the substitution of the equilibrium molecular weight in eq. (7). The plot showed that even at 150°C, the effect of depolymerization was noticeable. The resulting parameters for the depolymerization reaction are presented in Table II. In addition to the effect of depolymerization, the effect of [Cat] was also investigated through high-conversion experiments. For system 2, the catalyst level did not have an effect on k , at least not for the relatively high catalyst levels that were chosen. For system 1, the reaction rate was about proportional to the square root of [Cat] (Table I).

Kneader experiments

The results of the kneader experiments for system 2 were discussed in a previous publication.²⁰ However, in this experiment, only one catalyst level was used. Therefore, additional experiments were performed to

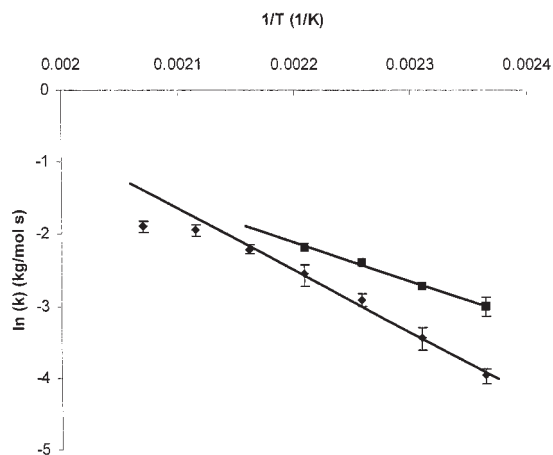


Figure 5 k_f as a function of temperature for the high-temperature experiments: systems (■) 1 and (◆) 2.

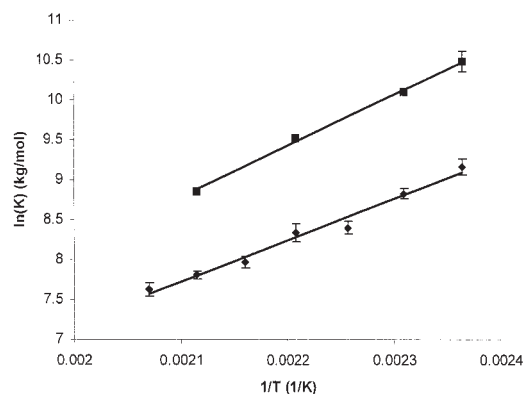


Figure 6 Equilibrium constant as a function of temperature for the high-temperature experiments: systems (■) 1 and (◆) 2.

TABLE II
Equilibrium Parameters for Systems 1 and 2

	System 1	System 2
A_{EQ} (kg/mol)	0.0110	0.0393
$E_{A,\text{EQ}}$ (kJ/mol)	52.7	43.4

establish the catalyst dependence for both systems. The resulting plots of the reaction rate versus [Cat] are shown in Figure 7. For system 2, the experiments with the highest catalyst level were a little faster than the other three experiments, indicating that there was a slight effect of [Cat] on the reaction velocity. Because this influence was very small and because the other three catalyst levels did not show any effect of the catalyst, the reaction velocity was considered independent of [Cat]. For system 1, the catalyst dependence was obvious; the dependency factor m , shown in eq. (2), was equal to 0.57. More discussion on the effect catalyst follows in the next sections.

Furthermore, Figure 7 shows that system 1 reacted faster than system 2 for all catalyst levels. As explained in the theoretical section, the 2,4-MDI that was used in system 2 may have caused this slower reaction. The effect of the temperature on the reaction velocity for system 1 is shown in Figure 8. In analogy to system 2,²⁰ the model predictions and the experimental curves are shown. The kinetic constants were obtained in a similar way as the constants for system 2.²⁰

Comparison of the different measurement methods: System 1

Table I shows a comparison of all the kinetic data obtained for system 1. In addition to the catalyst dependence, E_A seemed to agree fairly well for all of the experimental methods. This observation indicated

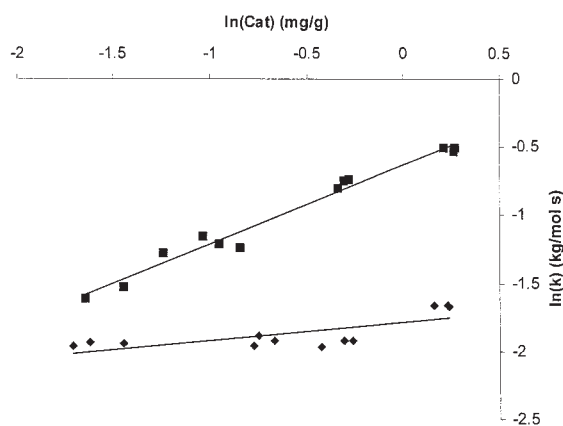


Figure 7 Dependence of the Arrhenius preexponential constant on the catalyst level: systems (■) 1 and (◆) 2.

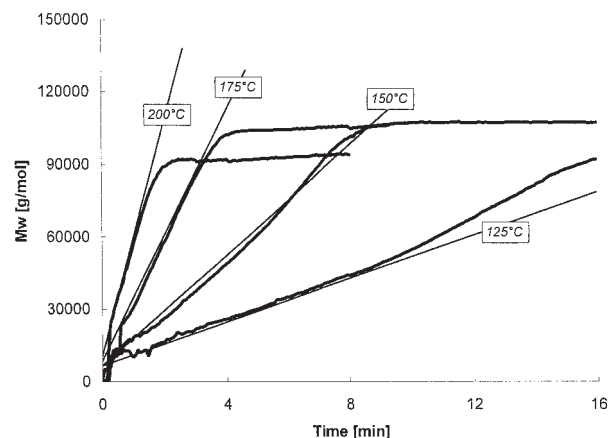


Figure 8 M_w versus time for the kneader experiments for system 1 (80 rpm): model predictions and experimental results.

that for all of the measurement methods used, the reaction developed identically for system 1. Neither E_A nor the catalyst dependence changed considerably with the temperature range or conversion range of the measurement method. The simplified second-order assumption seemed to hold for all measurement conditions. When we looked at the catalyzed urethane reaction, the reaction developed through several equilibrium steps, all related to the catalytic center. Naturally, these equilibria shifted with temperature, which may have changed n and the catalyst dependence. Surprisingly, both n and the catalyst dependence remained constant for the temperature range under investigation. The order of catalyst dependence (≈ 0.5) fell within the limits reported by other authors (0.5–1). A possible explanation for the value of 0.5 for the order of catalyst dependence was given by Richter et al.¹⁸ They related this value to a simple reaction mechanism. In the first step of this mechanism, the catalyst dissociates, and in a second step, the cationic catalytic center forms a complex with an isocyanate group. If both steps are thermodynamically unfavorable, $n = 0.5$.

The effect of the different measurement methods on k is shown in Figure 9. Figure 9 shows that the ATR experiments were as fast as the high-temperature experiments. Within the experimental error for these two types of measurements, the method did not seem to have any influence on the observed reaction velocity. *A priori*, one would expect the kneader experiments to be equally fast or even faster than the high-temperature experiments. However, the kneader experiments showed k values that were 3–4 times lower. No feasible explanation was present for this result. The mysterious drop in the reaction velocity may have been due to the materials used. The differences between the kneader experiments and the other two experiments were the batches of polyol and chain

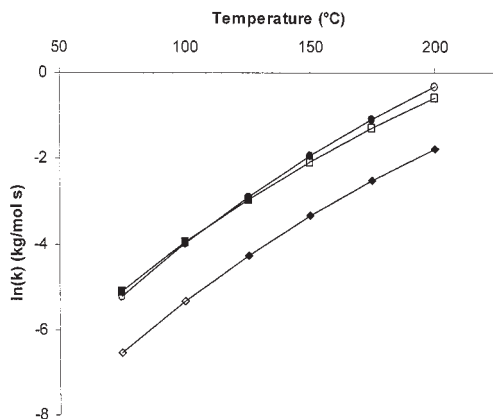


Figure 9 Model k versus temperature for the different measurement methods for system 1. The open symbols are extrapolations to areas where no measurements were carried out: (◆) ATR, (■) kneader, and (●) high-temperature experiments.

extender used. The acidity and OH value, which had an effect on the reaction rate, may have changed per batch of polyol. No corrections were made for these changes.

Because of the use of a different polyol batch, no valid comparison could be made between the kneader experiments and the other two types of experiments. However, the other two experiments do give important information on the polyurethane reaction. The observation that the reaction velocity did not depend on the measurement method deployed implied that the theory of functional group reactivity independent of chain length is also valid for polyurethanes. Moreover, it strengthens the vision that, for ATR and high-temperature experiments, no (initial) diffusion limitations occur because the reaction velocity, n , and catalyst dependence is the same for both types of experiments. For extruder applications, the result means that the most convenient measurement method can be chosen to obtain the proper kinetic data, at least for this polyurethane system. The advantage of ATR experiments is the ease of effectuation; on the other hand, the high-temperature experiments gave valuable information on the depolymerization reaction.

Comparison of the different measurement methods: System 2

Like system 1, two batches of materials were used for the experiments of system 2. The ATR experiments for system 2 were performed with the same batch of polyol as the ATR experiments and high-temperature experiments of system 1. The kneader and the high-temperature experiments were performed with the other batch of polyol, which was also used for the kneader experiments of system 1. In Table I, the deviating batches are shown in italics. The inconsistency in

batches again complicated comparison of the different experiments. Moreover, the specific diffusion limitations that were observed for the ATR experiments made comparison of this method with the other two methods even harder. These diffusion limitations were specific for the ATR method (and for the polyurethane system used) and resulted in a catalyst-independent reaction velocity at higher catalyst levels and a decrease in E_A . For the high-conversion experiments, a lack of catalyst dependence was also observed at higher catalyst levels, but E_A was much higher for these experiments. Therefore, the cause of the catalyst independence for these experiments must have been different. An obvious explanation was not available; possibly, the functional groups of the polymer molecules experienced a diffusion limitation that was noticeable at higher catalyst levels. In this case, the catalyst level did not make any difference above a certain threshold concentration. This explanation is not completely satisfactory. First, this type of diffusion limitation did not occur for system 1. However, the difference in monomers for the two systems might have produced a difference in the polymer structure and, therefore, in the diffusion behavior. The staggered 2,4-MDI groups in system 2 may have resulted in a more coiled polymer molecule, which subsequently resulted in a more entangled polymer melt in which diffusion limitation occurred more readily. Still, a second question remains. The E_A values that were found for the high-conversion experiments were rather high for a diffusion-limited reaction (60–70 kJ/mol). The flow E_A for system 2, which could be considered the E_A of diffusion, was much lower, at 43 kJ/mol.²⁰ The reason for this difference was not clear.

Now, if we look at the difference between the two different high-conversion methods, mixing seemed to have an influence. Both experiments were performed with the same batch of polyol; therefore, a comparison could be made. The kneader experiments showed a much higher k than the high-temperature experiments (Fig. 10). This observation may support the assumption that the reaction for system 2 was subject to diffusion limitations. Mixing in that case alleviated the diffusion limitation and resulted in a faster reaction.

CONCLUSIONS

The objective of this study was to study the reaction kinetics of polyurethane polymerization. In particular, the need for different measurement methods for reactive extrusion purposes was investigated. If we look at the commercial polyurethane system (system 1), the study showed that ATR as high-temperature measurements also produced the same kinetic constants. Because both methods differed greatly in reaction time, reaction temperature, and analytical method, it seems probable, therefore, that for this system, any kinetic

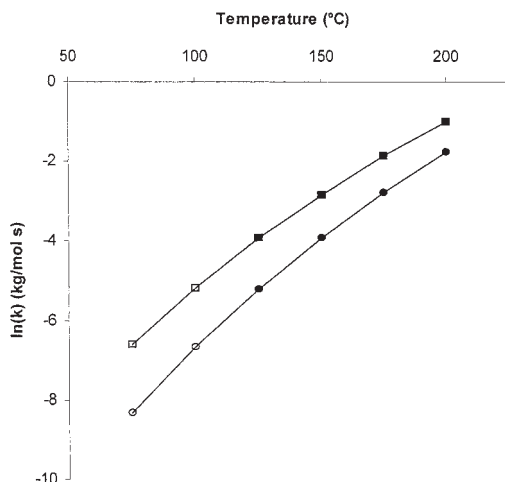


Figure 10 k versus temperature for the different measurement methods for system 2. The open symbols are extrapolations to areas where no measurements were carried out: (■) kneader and (●) high-temperature experiments.

measurement method could be applied. Unfortunately, an extra validation of this conclusion with a third method (kneader measurements) could not be used because a different batch of polyol was used for these last measurements. However, E_A , catalyst dependence, and n were alike for the kneader experiments, which strengthened the vision that any measurement method would yield the same kinetic equation for system 1. Therefore, it seemed probable that the reaction was kinetically controlled and that the reaction proceeded uniformly over a wide range of temperatures and conversions.

For a less common polyurethane system (system 2), a completely different result was obtained. The three different measurement methods each resulted in different kinetic equations, which indicated that for this system, a uniform reaction mechanism could not be adapted. For extrusion purposes, this signifies that a single kinetic measurement method did not suffice. At least two measurement methods seemed to be required: a low-temperature, low-conversion method (ATR experiments) and a high-temperature, high conversion method.

The cause of these inconsistencies may have resulted from the structure of the monomers used in system 2. As explained in the Results section, the presence of 2,4-MDI in system 2 may have hindered the expansion of surface instabilities that were indispensable for good micromixing and, therefore, for a kinetically controlled reaction for polyurethanes.¹⁶ However, because this hypothesis was only derived from kinetic measurements for this system, further validation would be necessary; for example, by following the reaction under a microscope.

NOMENCLATURE

A_0	Preexponential reaction constant ($\text{mol kg}^{-1} \text{s}^{-1}$)
A	Surface area of the adiabatic temperature rise reactor (m^2)
[Cat]	Catalyst concentration (mg/g)
C_p	Heat capacity ($\text{J kg}^{-1} \cdot \text{K}^{-1}$)
E_A	Activation energy (J/mol)
f	Functionality (-)
ΔH_R	Heat of the reaction (J/mol)
h	Heat-transfer coefficient ($\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$)
h^*	Overall heat-transfer coefficient ($\text{J kg}^{-1} \text{s}^{-1} \text{K}^{-1}$)
k_f	Forward reaction rate constant ($\text{kg mol}^{-1} \text{s}^{-1}$)
k_r	Reverse reaction rate constant ($1/\text{s}$)
m	Catalyst order
M_0	Average weight of the repeating unit (g/mol)
M_n	Number-average molecular weight (g/mol)
M_w	Weight-average molecular weight (g/mol)
n	Reaction order
[NCO]	Concentration of isocyanate groups (mol/kg)
$[\text{NCO}]_0$	Initial concentration of isocyanate groups (mol/kg)
ρ	Density (kg/m^3)
R	Gas constant (J/mol K)
R_{NCO}	Rate of isocyanate conversion ($\text{mol kg}^{-1} \text{s}^{-1}$)
T	Temperature (K)
ΔT_{ad}	Adiabatic temperature rise (K)
t	time (s)
[U]	Concentration of urethane bonds (mol/kg)
V	Volume of the adiabatic temperature rise reactor (m^3)

Subscripts

Cat	Catalyzed
Uncat	Uncatalyzed
Eq	Equilibrium

References

1. Macosko, C. W.; RIM: Fundamentals of Reaction Injection Molding; Hanser: Munich, 1989.
2. Cassagnau, P.; Méliis, F.; Michel, A. J Appl Polym Sci 1997, 65, 2395.
3. Sun, X. D.; Sung, C. S. P. Macromolecules 1996, 29, 3198.
4. Sun, X.; Toth, J.; Lee, L. J. Polym Eng Sci 1997, 37, 143.
5. Cassagnau, P.; Nietsch, T.; Michel, A. Int Polym Process 1999, 14, 144.
6. Hyun, M. E.; Kim, S. C. Polym Eng Sci 1988, 28, 743.
7. Bouilloux, A.; Macosko, C. W.; Kotnour, T. Ind Eng Chem Res 1991, 30, 2431.
8. Hoppe, S.; Grigis, S.; Pla, F. Chisa A 2002, 53, 586.

9. Lu, G.; Kalyon, D. M.; Yilgör, I.; Yilgör, E. *Polym Eng Sci* 2003, 43, 1863.
10. Petrus, A. *Int Chem Eng* 1971, 11, 314.
11. Steinle, E. C.; Critchfield, F. E.; Castro, J. M.; Macosko, C. W. *J Appl Polym Sci* 1980, 25, 2317.
12. Fields, S. D.; Thomas, E. L.; Ottino, J. M. *Polymer* 1986, 27, 1423.
13. Fields, S. D.; Ottino, J. M. *AIChE J* 1987, 33, 959.
14. Wickert, P. D.; Ranz, W. E.; Macosko, C. W. *Polymer* 1987, 28, 1105.
15. Kolodziej, O.; Macosko, C. W.; Ranz, W. E. *Polym Eng Sci* 1982, 22, 388.
16. Machuga, S. C.; Midje, H. L.; Peanasky, J. S.; Macosko, C. W.; Ranz, W. E. *AIChE J* 1988, 34, 1057.
17. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
18. Richter, E. B.; Macosko, C. W. *Polym Eng Sci* 1978, 18, 1012.
19. Ando, T. *Polym J* 1993, 11, 1207.
20. Verhoeven, V. W. A.; van Vondel, M.; Ganzeveld, K. J.; Janssen, L. P. B. M. *Polym Eng Sci* 2004, 44, 1648.
21. Odian, G. *Principles of Polymerization*; Wiley: New York, 1991.
22. Lopez-Serrano, F.; Castro, J. M.; Macosko, C. W.; Tirrell, M. *Polymer* 1980, 21, 263.
23. Blake, J. W.; Yang, W. P.; Anderson, R. D.; Macosko, C. W. *Polym Eng Sci* 1987, 27, 1237.
24. Chen, Y. T.; Macosko, C. W. *J Appl Polym Sci* 1996, 62, 567.