ELSEVIER

Polymer 42 (2001) 3195–3203

polymer

www.elsevier.nl/locate/polymer

Kinetics of the molar mass decrease in a polyurethane melt: a rheological study

T. Hentschel[1], H. Münstedt*

Institute of Polymer Materials, Department of Materials Science, University of Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany

Received 12 July 1999; received in revised form 23 May 2000; accepted 13 June 2000

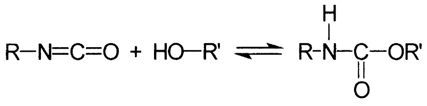
Abstract

Dynamic melt viscometry was used to study the kinetics of molar mass decrease in the molten liquid state of a polyurethane elastomer based on 4,4′-diphenyl-methane diisocyanate and 1,4-butanediol. It was found that at constant temperatures chosen between 180 and 220°C the molar mass of the polyurethane melt decreased continuously until a thermal equilibrium was reached. The rates as well as the degree of decrease strongly depend on temperature and time. Based on a kinetic model, the temperature dependence of the zero shear viscosity was shown to be controlled not only by the molecular mobility but also by the change in molar mass. The true activation energy of flow (131 kJ/mol) could be calculated after separation of the molar mass contribution. The rate constants and the activation energies of urethane formation and dissociation were also determined. © 2001 Published by Elsevier Science Ltd.

Keywords: Thermoplastic polyurethane elastomers; Molar mass decrease; Dissociation kinetics

1. Introduction

Most thermoplastic polyurethanes are synthesised by a polyaddition reaction of diisocyanates, polyols and short chain diols. The isocyanate and hydroxyl end groups form the characteristic urethane linkages that are stable in the solid state of the polymer. However, in the molten liquid state the addition reaction is reversible. Above the stability temperature, urethane bonds dissociate and reassociate simultaneously.



$$R{-}N{=}C{=}O + HO{-}R' \rightleftharpoons R{-}\overset{H}{\overset{|}{N}}{-}\underset{O}{\underset{\|}{C}}{-}OR'$$

This process affects the hard segment sequence length distribution, a phenomenon that is known as "transurethanisation" [1–5]. For example, the strictly monodisperse hard segment length distribution of a model compound becomes polydisperse. The dissociation of urethane bonds also causes a considerable molar mass decrease because the equilibrium reaction is shifted towards the free end-groups. As a consequence of transurethanisation and change in molar mass, any thermal treatment of thermoplastic polyurethane elastomers beyond a critical temperature, in particular measurements and processing in the molten liquid state, can change viscosity, crystallisation behaviour and even mechanical properties significantly.

According to Eisenbach and co-workers [2], an alternative transurethanisation mechanism occurs in polyurethanes with hard segments based on 4,4′-diphenyl-methane diisocyanate (MDI) and 1,4-butanediol (BDO): a four-centre type reaction with simultaneous breaking and reforming of urethane bonds. This mechanism, however, does not contribute to the change in molar mass since no free end-groups are formed.

The present study deals with the thermally induced molar mass decrease of a commercial polyetherurethane elastomer with hard segments produced from MDI and BDO. Bayer [6] reported an upper stability temperature of approximately 200°C for the urethane group of this type of polyurethane. Several authors investigated model compounds with MDI/BDO hard segments and reported that the dissociation of the urethane bond to free isocyanate and hydroxyl end-groups was the primary degradation mechanism: Grassie and Zulfiqar [7] found that below 240°C no reaction products other than isocyanates and alcohols were formed; Montaudo et al. [8] reported that even at 330°C essentially MDI and BDO appeared as degradation products; Yang et al. [3] observed on model urethane oligomers the existence of free isocyanate above 150°C and significant degradation above 200°C; Martin et al. [5] concluded from annealing

---

* Corresponding author.

[1] Present address: VAW Aluminium AG, Georg-von-Boeselager-Str. 25, D-53117 Bonn, Germany.

0032-3861/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0032-3861(00)00489-4

experiments that urethane linkages dissociated and reassociated at temperatures above 150°C. It was indicated by Koberstein et al. [4] that crystallinity appeared to stabilise the urethane bond: isocyanate formation was detected only in the melting range above 215°C.

Endres [9] has proposed a model for the quantitative description of the kinetics of molar mass decrease in polyurethanes. Assuming first order kinetics, he introduces rate constants k_f and k_d for the formation and dissociation of the urethane bond, respectively, and obtains a rate equation:

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t} = -k_\mathrm{d}[\mathrm{U}] + k_\mathrm{f}[\mathrm{NCO}][\mathrm{OH}], \tag{1}$$

where [U] is the urethane group concentration, and [NCO] and [OH] are the isocyanate and hydroxyl group concentrations, respectively. A function $u_\mathrm{r}(t)$ is derived that describes the residual urethane bond concentration as a function of time:

$$u_\mathrm{r}(t) = \frac{k_\mathrm{d} + 2k_\mathrm{f}(1 + [\mathrm{E}])}{2k_\mathrm{f}} + \frac{A}{2k_\mathrm{f}}\frac{1 + B\mathrm{e}^{At}}{1 - B\mathrm{e}^{At}}, \tag{2}$$

$$A \equiv \sqrt{k_\mathrm{d}^2 + 4k_\mathrm{d}k_\mathrm{f}(1 + [\mathrm{E}])} > 0, \tag{3}$$

$$B \equiv \frac{(k_\mathrm{d} + 2k_\mathrm{f}[\mathrm{E}]) + A}{(k_\mathrm{d} + 2k_\mathrm{f}[\mathrm{E}]) - A} < 0. \tag{4}$$

The values of A and B depend on the rate constants k_f and k_d and on the initial end-group concentration [E] that is related to the initial degree of polymerisation, P_n, by $[\mathrm{E}] = (P_n - 1)^{-1}$. A is the rate of decrease. It has to be noted that the rate constants k_f and k_d are *apparent* since the four-centre type reaction and the diffusivity of the reactants may affect the kinetics.

Starting with $u_\mathrm{r}(t = 0) = 1$, the function drops exponentially and asymptotically approaches a constant concentration $u_\mathrm{r}(t \to \infty) = \mathrm{const} > 0$. The model was shown to be in reasonable agreement with experimental data gained from isocyanate concentration measurements after defined heat treatments of a technical MDI/BDO-based polyurethane elastomer. The rate constants could be determined.

In this paper, an experimental technique for on-line monitoring of the thermally induced molar mass decrease of a technical polyurethane elastomer is presented. Dynamic viscometry was employed to characterise the kinetics of the decrease as a function of time and temperature. By extending Endres' model, the degree of molar mass decrease, the apparent rate constants and the activation energies of urethane formation and dissociation were determined from the time-dependent behaviour of the zero shear viscosity.

2. Experimental

2.1. Materials

The polyurethane under investigation is a medical-grade product that is employed for intracorporal applications such as catheters. The material contains approximately 34% by weight of MDI/BDO hard segments. The soft segments are composed of polytetramethylene ether glycole (PTMEG) with a molar mass of approximately 800 g/mol. With the molar masses of MDI and BDO being 250 and 90 g/mol, respectively, a stoichiometry of MDI/BDO/PTMEG ≈ 1.5:0.5:1 can be concluded. The average monomer molar mass amounts to $m_\mathrm{n} = \frac{1}{3}1220\ \mathrm{g/mol} \approx 400\ \mathrm{g/mol}$.

2.2. Differential scanning calorimetry

A DSC 2920, TA Instruments, was used to determine the melting range. 10–20 mg of the sample was placed in an aluminium pan under nitrogen gas atmosphere. The thermogram was obtained at a scan rate of 10 K/min. Isothermal annealing at 90 and 170°C was performed. Enthalpy calibration was carried out with an indium standard. The DSC temperature was calibrated with indium, lead and tin standards.

2.3. Dynamic melt viscometry

Dynamic viscosity measurements were performed in oscillation on a stress-controlled rheometer (Bohlin Instruments). The as-received polyurethane resins were dried for 3 h at 90°C in a vacuum oven and immediately transferred to a hydraulic press. Samples with a thickness of 0.8 mm and a diameter of 25 mm were pressed at 170°C under a load of 5000 kg. Immediately prior to measurement the samples were dried again under the same conditions as the resins. They were placed in a cone and plate arrangement with 2.5° cone angle under nitrogen gas atmosphere. Data recording was started 3 min after mounting. Frequencies were chosen in such a way that the melt was in the linear viscoelastic region, which was 0.01 Hz at 180°C, 0.05 Hz at 190°C and 0.1 Hz between 200 and 220°C, as has been shown in a previous study [10].

To obtain reliable stability information by means of dynamic viscometry, there must be no crystalline or other ordered domains left in the sample. This was assured by calorimetric characterisation. Also, the temperature must be equalised prior to data recording. It was assured by heating-up experiments on a high melting reference sample with three built-in thermocouples, where 3 min after mounting the desired temperature was reached within ±0.5°C. It could be also shown that only 30 s after mounting the temperature deviation was not more than 5°C. For this reason, the thermally induced molar mass decrease was assumed to start 30 s after mounting.

At each temperature chosen, one sample was removed from the rheometer in the molten liquid state and quenched in liquid nitrogen. These samples were dissolved in tetrahydrofuran and analysed by GPC.

2.4. Gel permeation chromatography

A four-columns GPC with a refractive index detector was used to determine the molar mass distribution (MMD) of the as-received material, the pressed samples and the samples heat-treated in the rheometer. The samples were prepared in tetrahydrofuran (THF) at 10 mg/ml. The mobile phase was THF at a rate of 0.5 ml/min and the column temperature was maintained at 25°C. A polystyrene calibration curve was used to determine the number and mass averaged molar masses M_n and M_w, respectively. For calculations performed in this paper, the approximate degree of polymerisation of the initial state is required. For this reason the absolute molar mass of the as-received polyurethane was determined by means of Ubbelohde dilution viscometry.

2.5. Ubbelohde dilution viscometry

The viscosity average molar mass M_v was measured in an Ubbelohde viscometer at 25°C. The solvent was dimethylformamide (DMF). All solutions were filtered prior to measurement. Four dilutions with different concentrations were measured. The intrinsic viscosity was obtained by extrapolating the relative and the specific viscosity to zero concentration. The Mark–Houwink constants used for molar mass calculation are $a = 0.636$ and $K = 8.52 \times 10^{-5}$ ($[\eta]$ in l/g and M_v in g/mol) [9]. Assuming a log-normal molar mass distribution, the mass and number average molar masses can be calculated when the Mark–Houwink parameter K is transformed according to $K_n = K(M_w/M_n)^{0.5a(a+1)}$ and $K_w = K(M_w/M_n)^{0.5a(a-1)}$. The polydispersity M_w/M_n was obtained from GPC analysis.

3. Results and discussion

3.1. Initial molar mass distribution

GPC measurements of the polyurethane samples as prepared for the dynamic melt rheometer yielded $M_w/M_n = 2.75$. The intrinsic viscosity was $[\eta] = 0.089$ l/g, resulting in $M_v \approx 56,000$ g/mol, and $M_n \approx 24,000$ g/mol. Hence, the degree of polymerisation amounts to $P_n = M_n/m_n \approx 24,000 : 400 = 60$.

By means of GPC the pressing procedure required for specimen preparation was shown to cause a molar mass decrease of 8%, but no significant change in polydispersity. Therefore the degree of polymerisation of the untreated polyurethane is $P_n \approx 70$.

3.2. DSC analysis

The thermograms of polyurethane samples exposed to two different heat treatments are shown in Fig. 1. One sample was annealed at 90°C for 2 h, as 90°C is the drying temperature of the rheometer specimens. As the thermogram (a) shows, the sample does exhibit a very broad endotherm extending from 90 to 175°C. This endotherm is due to mixing of the initially separated hard and soft phases, and, simultaneously, disordering of the paracrystalline hard phase [4,11,12]. True crystallinity is generally not observed on polyurethane elastomers with DSC endotherms below 200°C [13,14]. The endothermal peak at 110°C is due to annealing. Annealing peaks of polyurethane elastomers containing 40% by weight of MDI/BDO hard segments were shown to occur typically 20°C above the annealing temperature [5]. It is important to note that above 175°C no microstructural order is left. It can be assumed that at temperatures above 180°C where our rheological experiments are performed no ordered domains remain in the polymer melt.

The annealing behaviour of polyurethane elastomers has been thoroughly investigated and it is known that annealing at high temperatures can induce the formation of crystallites with higher melting temperature [2,5,15]. It must be ruled out that this effect occurs during the measurements in the rheometer where the material is maintained at temperatures above 180°C. For this reason another sample was annealed at 180°C for 30 min. This treatment does not extend the endotherm to higher temperatures, as can be seen in thermogram (b). It can be concluded that at temperatures ≥180°C no ordered domains are formed in the polymer melt.

3.3. Molar mass decrease

Dynamic viscometry is a common technique to characterise the thermal stability of molten polymers. It is a sensitive probe for molecular degradation because of the empirical equation relating the zero shear viscosity η_0 and the mass average molar mass

$$\eta_0 = K M_w^{3.4}, \quad (5)$$

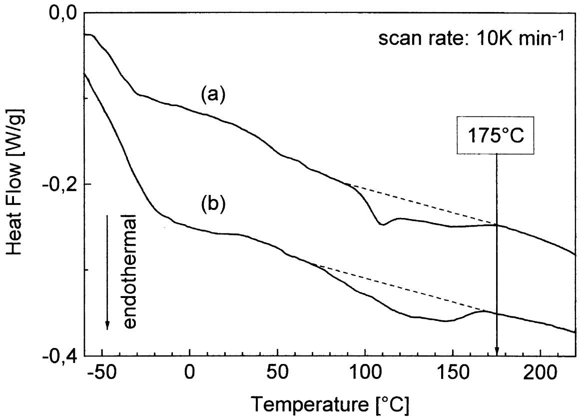


Fig. 1. DSC results obtained at a scan rate of 10 K/min under nitrogen gas atmosphere: (a) annealed at 90°C for 2 h; (b) annealed at 180°C for 30 min. No transformations occur above 175°C.

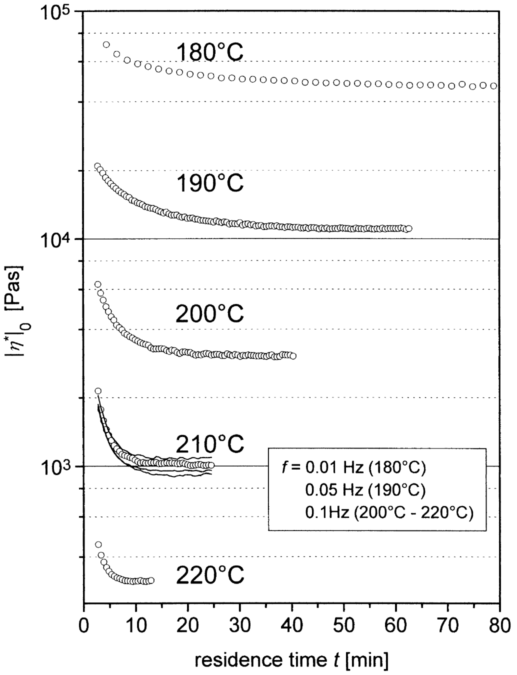


Fig. 2. Dynamic zero shear viscosity as a function of residence time in the rheometer at different temperatures. To demonstrate the reproducibility, four measurements performed at 210°C are shown.

which has been proven to hold for most linear polymers beyond a critical molar mass M_c. For a polyurethane elastomer, Endres verified the validity of this relation and found an exponent of approximately 3.5 [9]. This value will be used in further calculations.

According to the Cox–Merz relation, the magnitude of the complex viscosity $|\eta^*(\omega)|$ at the angular frequency ω is identical with the steady shear viscosity $\eta(\dot{\gamma})$ at the shear rate $\dot{\gamma}$, if $\omega = \dot{\gamma}$. Fig. 2 shows the behaviour of $|\eta^*|_0$ at different temperatures for residence times $t > 3$ min after mounting. The curves were shifted by $\Delta t = 30$ s towards shorter times because this is the estimated heating-up period, as has been discussed in Section 2. The reproducibility is shown by plotting additional viscosity curves obtained at 210°C. At a given residence time, the viscosities did not deviate more than $\pm 10\%$ from the average value when the measurements were repeated. This is a satisfying experimental correctness considering that the reaction of polyurethane to the preparation and drying conditions is extremely sensitive.

It is obvious that the viscosities decrease continuously and approach equilibrium values. The higher the temperature, the faster the equilibrium is established. Furthermore, a very strong dependence of the viscosity on temperature can be noticed.

The viscosity decrease is interpreted in terms of a thermally induced molar mass decrease. This is most likely because melting of crystallites could be ruled out by thermal analysis (cf. Fig. 1). Consequently, the viscosity equilibrium is associated with a molar mass equilibrium. This is in agreement with the reaction equilibrium expected from the reversal of the urethane formation reaction.

Other thermal degradation reactions known for polyurethanes [7,16] include the dissociation of the urethane group to amine, carbon dioxide and olefin, and the dissociation to secondary amine and carbon dioxide. Additionally, free isocyanate groups can form carbodiimide and carbon dioxide or can bind to water molecules. The ether linkages in the soft segments can also undergo chain scission. To make sure that none of these reactions does contribute in our case, it was made use of the fact that they are *not* reversible. An as-received sample was kept in the DSC at 200°C for 45 min and subsequently cooled down at a low rate of 1 K/min, so as to give time for thermal equilibration. GPC analysis revealed that the molar mass distribution did not change during the heat treatment (apart from a slight molar mass increase due to crosslinking), indicating that no permanent molar mass loss (i.e. no true degradation) occurred. The thermally induced molar mass decrease is completely reversible. Such behaviour can be understood only in terms of shifting a thermodynamic equilibrium state.

To characterise the equilibrium state at each temperature chosen, samples were removed once the equilibrium viscosity was reached, and quenched in liquid nitrogen for GPC analysis. The GPC results are displayed in Fig. 3. It is evident that the heat treatment decreases the molar mass to a value that depends on the temperature of the melt. The higher the temperature, the lower is the resulting equilibrium molar mass. This observation indicates that the strong dependence of the equilibrium viscosities on temperature (cf. Fig. 2) does not only reflect the change in molecular mobility but also the change in molar mass. For this reason a true activation energy of flow cannot be determined unless the molar mass contribution is separated. This problem is discussed in detail in the following section. The polydispersity drops slightly from 2.75 to values close to

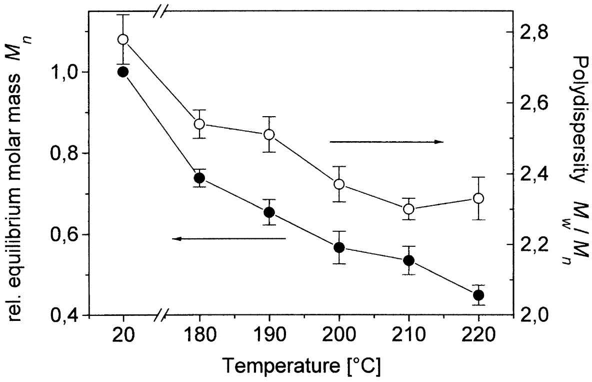


Fig. 3. GPC results of samples kept at different heating temperatures in the dynamic viscometer until the equilibrium viscosity was reached. The number average molar mass decreases at 220°C to less than half of the initial value, the polydispersity decreases slightly and approaches a value of 2.3. The molar mass is normalised with respect to the initial value of the as-received polyurethane.

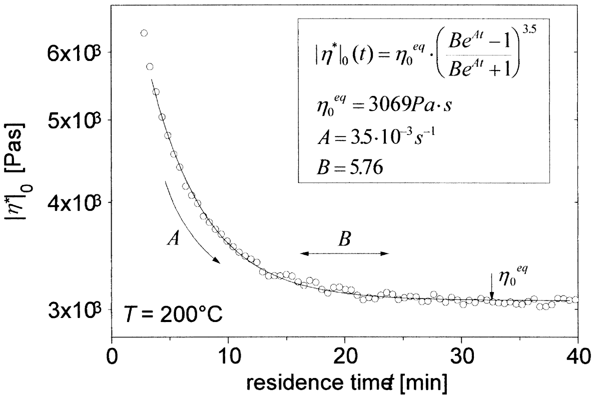


Fig. 4. Zero shear viscosity at 200°C as a function of time fitted with the analytical function (9).

2.3, indicating that the MMD approaches a most probable distribution.

3.4. Kinetics of the molar mass decrease from dynamic viscometry

A quantitative treatment of the kinetics of molar mass decrease requires a physically based function to fit the corresponding viscosity curve. Such a fitting function can be derived from the model proposed by Endres. The residual urethane concentration u_r can be written as

$$u_r(t) \approx 1 + \frac{m_n}{M_n(0)} - \frac{m_n}{M_n(t)}, \tag{6}$$

where m_n is the number average molar mass of the monomers and $M_n(t)$ the number average molar mass of the polymer at time t. The approximation is good if $M_n \gg m_n$, which is true for all polymers. The comparison of the time-dependent terms in Eqs. (2) and (6) yields the time dependence of the molar mass:

$$M_n(t) = m_n \frac{2k_f}{A} \frac{Be^{At} - 1}{Be^{At} + 1}. \tag{7}$$

If the polydispersity is assumed not to change considerably during the measurement, which has been proven in our case by means of GPC (cf. Fig. 3), one can rewrite Eq. (5) as

$$\eta_0(t) = K(M_w(t))^{3.5} \equiv K_n(M_n(t))^{3.5}. \tag{8}$$

By substituting $M_n(t)$ with the right-hand side of Eq. (7) one obtains

$$\eta_0(t) = \eta_0^{eq} \left(\frac{Be^{At} - 1}{Be^{At} + 1} \right)^{3.5}, \tag{9}$$

$$\eta_0^{eq} \equiv K_n(M_n^{eq})^{3.5}, \tag{10}$$

$$M_n^{eq} \equiv m_n \frac{2k_f}{A}. \tag{11}$$

This equation contains A, B and η_0^{eq} as fitting parameters. η_0^{eq} is to be understood as the equilibrium zero shear viscosity and M_n^{eq} as the equilibrium number average molar mass.

The fit of a viscosity curve measured at 200°C is shown in Fig. 4. The analytical function fits the experimental data well. The arrows indicate the influence of the fitting parameters on the position and shape of the curve. Parameter A controls the slope of the curve and thus can be interpreted as the *rate of decrease*. Since the dissociation constant k_d is small compared to the formation constant k_f [9], and the initial end-group concentration [E] is small compared to unity for all polymers, Eq. (3) can be approximated as

$$A = \sqrt{k_d^2 + 4k_d k_f(1 + [E])} \approx 2\sqrt{k_d k_f}, \qquad k_d \ll k_f, \quad [E] \ll 1. \tag{12}$$

This implicates that an increase either in dissociation or in formation velocity accelerates the resulting thermal rate of decrease. This appears to be reasonable considering that the rate of the molar mass decrease is related to the time required to establish the equilibrium state. At a high dissociation rate the equilibrium is reached quickly, and at a high formation rate as well.

Parameter B shifts the curve in horizontal direction. Its value is related to the ratio of initial and equilibrium viscosity,

$$\frac{\eta_0(t = 0)}{\eta_0^{eq}} = \left(\frac{B - 1}{B + 1} \right)^{3.5} \tag{13}$$

as can be easily derived from Eq. (9). From Eq. (8) it follows that

$$\frac{M_n(t = 0)}{M_n^{eq}} = \frac{B - 1}{B + 1}. \tag{14}$$

Thus, B is a measure of the *degree of decrease*.

Parameter η_0^{eq} represents the equilibrium viscosity. By introducing the chemical equilibrium constant $K_{eq} = k_d/k_f$,

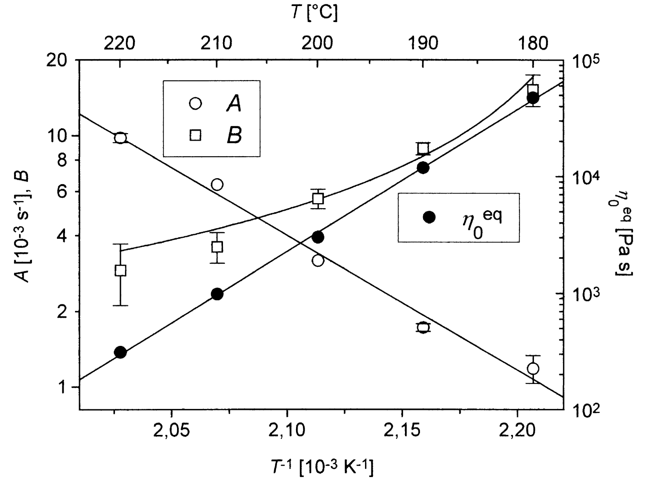


Fig. 5. Arrhenius plot of the fitting parameters A, B and η_0^{eq}. The rate of decrease of A and the equilibrium zero shear viscosity η_0^{eq} obey an Arrhenius law. The data of B are fitted with the function (20).

and exploiting the approximation in (12), Eq. (10) can be rewritten as

$$\eta_0^{\mathrm{eq}} \approx K_{\mathrm{n}}\left(\frac{m_{\mathrm{n}}}{\sqrt{K_{\mathrm{eq}}}}\right)^{3.5}. \tag{15}$$

In this form, the equation demonstrates clearly that the equilibrium in viscosity is directly related to the chemical equilibrium of urethane dissociation and formation.

The parameters obtained from fitting the viscosity curves in Fig. 2 are exhibited in the Arrhenius plot in Fig. 5. The straight-line fits indicate that A and η_0^{eq} obey the Arrhenius law. In fact, it can be deduced from theoretical considerations that A and η_0^{eq} are thermally activated quantities. To show this, it is assumed that urethane dissociation and formation are thermally activated which is reasonable for a chemical reaction. It follows that

$$k_{\mathrm{d}} \propto \exp\left(-\frac{E_{\mathrm{d}}}{\mathrm{R}T}\right), \qquad k_{\mathrm{f}} \propto \exp\left(-\frac{E_{\mathrm{f}}}{\mathrm{R}T}\right) \tag{16}$$

where E_{d} and E_{f} are the activation energies of dissociation and formation, respectively. Substituting these exponential terms for k_{d} and k_{f} in Eq. (12) gives

$$A \propto \exp\left(-\frac{E_{\mathrm{d}} + E_{\mathrm{f}}}{2\mathrm{R}T}\right) \tag{17}$$

implicating that A is thermally activated. The temperature dependence of η_0^{eq} is more complex. In Eq. (15) two temperature-dependent quantities appear, K_{n} and K_{eq}. K_{n} is expected to show an Arrhenius behaviour, $K_{\mathrm{n}} \propto \exp(E_0/\mathrm{R}T)$, with E_0, the activation energy of flow, because the melt temperature in our experiments is much higher than the glass transition temperatures of ≈ -50°C (soft phase) and ≈ 80°C (hard phase). $K_{\mathrm{eq}} = k_{\mathrm{d}}/k_{\mathrm{f}}$ can be substituted by the exponential terms in (16), and one obtains

$$\eta_0^{\mathrm{eq}} \propto \exp\left(\frac{E_0}{\mathrm{R}T}\right)\exp\left(\frac{3.5(E_{\mathrm{d}} - E_{\mathrm{f}})}{2\mathrm{R}T}\right). \tag{18}$$

The first exponential factor describes the explicit temperature dependence of the viscosity that is due to the higher mobility of the polymer chains at higher temperatures. The second factor does express the temperature dependence of the molar mass as can be seen from Eq. (10). If the difference of the activation energies, $E_{\mathrm{d}} - E_{\mathrm{f}}$, is positive, a temperature increase will result in an *additional viscosity decrease* due to a molar mass decrease. Eq. (18) states that the explicit and the implicit temperature dependence are separable, i.e.

$$\eta_0^{\mathrm{eq}} = \eta_0^{\mathrm{eq}}(T, M_{\mathrm{n}}^{\mathrm{eq}}(T)) = K_{\mathrm{n}}(T)(M_{\mathrm{n}}^{\mathrm{eq}}(T))^{3.5}. \tag{19}$$

From the Arrhenius behaviour of η_0^{eq} and from Eq. (13) it follows that B cannot show an Arrhenius behaviour. It can be deduced from Eq. (13) that the function $B(1/T)$ has the form

$$B\left(\frac{1}{T}\right) = \frac{C\exp(E/\mathrm{R}T) + 1}{C\exp(E/\mathrm{R}T) - 1} \tag{20}$$

with an activation energy $E \equiv (1/3.5)E_0 + (1/2)(E_{\mathrm{d}} - E_{\mathrm{f}})$ and a constant C. This function is convex. As shown in Fig. 5, it fits the experimental data of B well.

As a major consequence of Eq. (18), the true activation energy of flow, E_0, can be determined by plotting K_{n} vs. T^{-1}. Similarly, the activation energy of urethane dissociation, E_{d}, can be determined by plotting k_{d} vs. T^{-1}, and the activation energy of formation, E_{f}, by plotting k_{f} vs. T^{-1}. This procedure requires the calculation of K_{n}, k_{d} and k_{f}.

3.5. Rate constants and activation energies

The rate constants k_{d} and k_{f} can be obtained easily by solving Eqs. (3) and (4). Since the exact solutions are complicated expressions that might conceal the physical background, we will discuss approximate solutions. The complete solutions and the derivation of the approximations are given in the Appendix. It could be shown that the approximate solutions did not deviate more than 1% from the exact ones. The approximate solutions are

$$k_{\mathrm{d}} \approx \frac{A[\mathrm{E}]}{2}\frac{B-1}{B+1}, \tag{21}$$

$$k_{\mathrm{f}} \approx \frac{A}{2[\mathrm{E}]}\frac{B+1}{B-1}, \tag{22}$$

$$K_{\mathrm{eq}} = \frac{k_{\mathrm{d}}}{k_{\mathrm{f}}} \approx \left([\mathrm{E}]\frac{B-1}{B+1}\right)^2. \tag{23}$$

Multiplication of k_{d} and k_{f} in this form gives approximation (12) again, a proof of consistency. The physical interpretation of Eqs. (21)–(23) is as follows. If the rate constant of dissociation, k_{d}, increases, the rate A will increase like $A \propto \sqrt{k_{\mathrm{d}}}$, as can be deduced from approximation (12). Consequently, $(B-1)/(B+1)$ also varies with the square root of k_{d}. From Eq. (14) it follows that $M_{\mathrm{n}}^{\mathrm{eq}} \propto 1/\sqrt{k_{\mathrm{d}}}$, that is, the faster the dissociation takes place, the higher is the degree of the molar mass decrease and the smaller is the equilibrium molar mass. The inverse effect will occur if k_{f} is increased. The ratio of k_{d} and k_{f} controls the degree of decrease, but does not influence the rate.

The rate constants can now easily be determined from the experimental fit parameters. The initial end-group concentration is known to be $[\mathrm{E}] = (P_n - 1)^{-1} \approx 1/70$. Subsequently, K_{n} can be obtained from Eq. (15), with the average monomer molar mass $m_{\mathrm{n}} \approx 400$ g/mol.

From an Arrhenius plot of K_{n} one obtains an activation energy of flow that amounts to $E_0 = 131$ kJ/mol. This value is still large compared to the activation energies of other semicrystalline polymers such as polyethylene, polypropylene and polyamid that typically range from 30 to 60 kJ/mol. It is, however, significantly smaller than apparent activation energies of flow determined directly from the equilibrium viscosities. From the Arrhenius plot of η_0^{eq} in Fig. 5, one obtains an apparent activation energy of 233 kJ/mol that is in agreement with the apparent activation energies of flow,

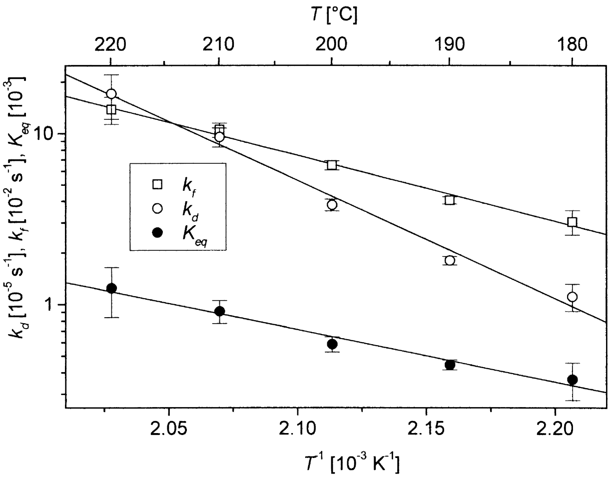


Fig. 6. Arrhenius plot of calculated constants k_d, k_f and K_{eq}. The linear fits of the K_{eq} and k_d values determine the activation energies of degradation, $E_d - E_f$, and urethane dissociation, E_d.

170–330 kJ/mol, reported in literature [9]. Comparison of the true and the apparent activation energy, 131 and 233 kJ/mol, indicates that a considerable amount of the viscosity decrease with increasing temperature is caused by molar mass decrease. For example, in the range between 180 and 220°C the change in molar mass contributes a factor of

$$\exp\left(\frac{(233 - 131)\ \text{kJ/mol}}{R}\left(\frac{1}{453\ \text{K}} - \frac{1}{493\ \text{K}}\right)\right) \approx 9$$

to the viscosity change, that is, almost an order of magnitude while the total change comprises two orders of magnitude (cf. Fig. 5).

Fig. 6 shows the equilibrium constant K_{eq} and the rate constants k_d and k_f as functions of the reciprocal temperature. The formation constants are three to four orders of magnitude larger than the dissociation constants. The k_d values range from $1 \times 10^{-5}\ \text{s}^{-1}$ at 180°C to $17 \times 10^{-5}\ \text{s}^{-1}$ at 220°C, in good agreement with the result of Endres who obtained $22 \times 10^{-5}\ \text{s}^{-1}$ at 235°C for a polyurethane with comparable molar mass. The formation constants range from $3 \times 10^{-2}\ \text{s}^{-1}$ at 180°C to $16 \times 10^{-2}\ \text{s}^{-1}$ at 220°C, while Endres reported $70 \times 10^{-2}\ \text{s}^{-1}$ at 235°C [9]. The overall agreement is remarkable, regarding that our investigation and that of Endres differ at least in three aspects: (1) the polyurethane investigated by Endres had a higher hard segment content than ours and contained a chemically different soft segment; (2) Endres processed the polyurethane melt in an extruder prior to measurements, thus exposing it to a thermomechanical treatment, whereas the mechanical stress in the rheometer at low shear rates and small amplitudes can be neglected; (3) Performing isocyanate concentration measurements, Endres employed a chemical technique to monitor the molar mass decrease, in contrast to our rheological technique.

From the straight regression lines in Fig. 6 one obtains the activation energy of urethane formation, $E_f = 74$ kJ/mol, and the activation energy of urethane dissociation, $E_d = 132$ kJ/mol. The difference that amounts to $E_d - E_f = 58$ kJ/mol accounts for the increasing molar mass loss when the temperature rises. The value is close to the range given by Endres, 60–65 kJ/mol [9].

The formation constants and the activation energy of urethane formation determined in the high viscous polymer melt could be compared to data given for the formation of polyurethane in low viscous momomer/oligomer melts. Wright and Cumming [17] report rate constants for the reaction of MDI with polytetramethylene glycole (PTMG). They found 3.4×10^{-3} l/(mol s) at 100°C and 10.6×10^{-3} l/(mol s) at 130°C, with an activation energy of 32 kJ/mol. The values are plotted in the Arrhenius diagram in Fig. 7.

To obtain formation constants in dimensions of l/(mol s), the initial urethane concentration $u_r(t = 0)$ that has been set equal to unity in our model has to be given in mol/l. With the polyurethane melt density of $\rho \approx 1000$ g/l and the monomer mass being $m_n \approx 400$ g/mol, the concentration of urethane bonds is approximately 2.5 mol/l. Division of the calculated constants k_f by this quantity yields the values shown in Fig. 8. They are in the order of magnitude expected from the extrapolation of the rate constants in low viscous melts. However, the activation energy is more than twice as large. The reason for this is likely the enormous change in viscosity in the range between 180 and 200°C. The increase in molecular mobility contributes to the increase in reaction velocity. This suggests that the activation energy of formation in the melt consists of a "chemical" and a "mobility" contribution. In low viscous melts, the mobility contribution is likely to be small.

The knowledge of K_n also enables us to describe the complete process of the molar mass decrease $M_n(t)$ by applying Eq. (8) to the $\eta_0(t)$-fitting curves. Fig. 8 shows that both the temperature and the residence time of the polyurethane melt strongly affect the degree of the molar mass decrease. While the molar mass decreases by only 5%

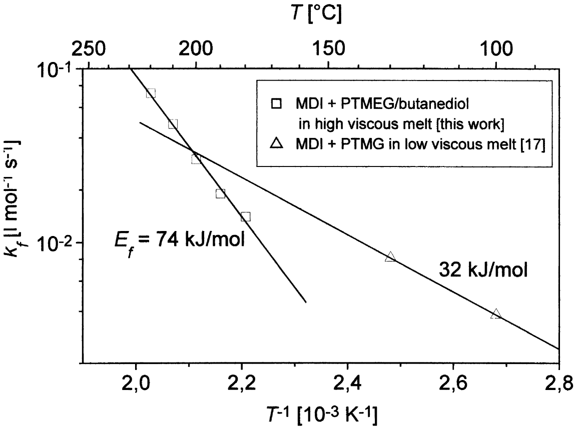


Fig. 7. Arrhenius plot of urethane formation constants in a high viscous polyurethane melt (this work) and in a low viscous oligourethane melt [17].

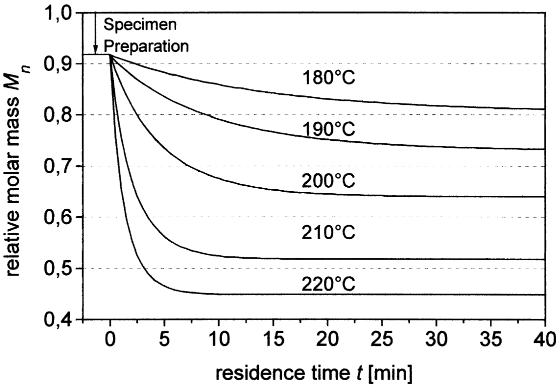


Fig. 8. Molar mass degradation as a function of residence time in the rheometer, calculated from the zero shear viscosity curves in Fig. 2, using Eq. (8). The molar mass is normalised with respect to the initial value of the as-received polyurethane.

after 5 min at 180°C, it decreases by 50% after 5 min at 220°C.

It has to be noticed that the molar mass at $t = 0$ is that of the pressed rheometer specimen and is reduced by 8% compared to the molar mass of the as-received product, due to pressing at 170°C. Further studies will have to improve specimen preparation in such a way that thermal degradation prior to measurement will be minimised.

3.6. Critical temperature of urethane dissociation

According to Eq. (10), the equilibrium molar mass M_n^{eq} is a thermally activated quantity because η_0^{eq} and K_n have been shown to obey an Arrhenius law. Hence the threshold temperature of urethane dissociation can be determined from a $M_n^{eq}(T)$ vs. T^{-1} Arrhenius plot by linear extrapolation to the initial molar mass. In Fig. 9 this was done for the rheological and for the GPC results. The values are normalised to the molar mass of the as-received polyurethane. The results are in good agreement within the statistical errors.

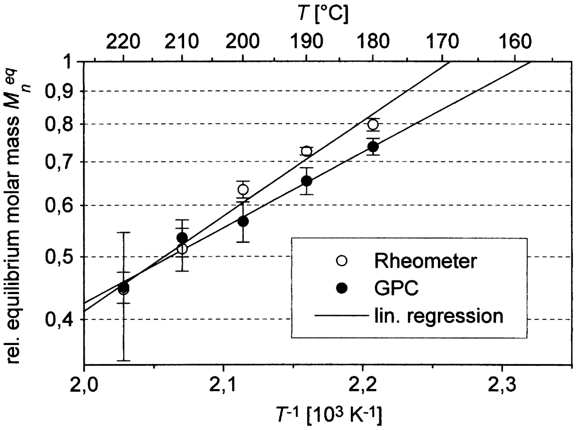


Fig. 9. Arrhenius plot of relative equilibrium molar masses determined by means of viscometry and GPC. Normalisation was done with respect to the initial value of the as-received polyurethane.

The critical temperatures obtained are 169°C from the rheological and 159°C from the GPC data. Both values are in reasonable agreement with IR spectroscopic results reported in literature: Schmid [18] investigated a MDI/ethylene diamine based polyurethane elastomer containing only 21% by weight of hard segments. He observed the occurrence of an isocyanate absorbance band above 150°C. In contrast, Koberstein et al. [4] found the isocyanate band only above 215°C when analysing a material with 70% by weight of MDI/BDO hard segments. The polyurethane investigated in the present study contains 37% by weight of hard segments. Since the volume fraction of the ordered hard phase (crystalline or paracrystalline) and the melting temperature in polyurethanes generally increase with increasing hard segment content [5], our result suggests that the more ordered the microstructure of a polyurethane is, the higher is its critical temperature of urethane dissociation. This supports the observation of Koberstein et al. that crystallisation stabilises the urethane bond.

4. Summary and conclusions

Polyurethanes synthesised from 4,4′-diphenyl-methane diisocyanate, 1,4-butanediol and polytetramethylene ether glycol undergo a thermally induced molar mass decrease at temperatures above $T \approx 160°C$ and approach a thermal equilibrium. The rate and the degree of the molar mass decrease increase with temperature. At 210°C the molar mass decreases to half of the initial value.

The molar mass decrease is reflected in the decrease of the zero shear viscosity that can be measured as a function of time. Assuming dissociation to the polyaddition reactants, the time dependence of the viscosity can be described by a model based on first order reaction kinetics.

The model allows for the separation of the explicit temperature dependence of the viscosity (due to the molecular mobility) from the implicit temperature dependence that is related to the temperature dependence of the molar mass. As a consequence, the true activation energy of flow can be obtained, also the activation energies of urethane formation and dissociation.

The activation energy of flow, $E_0 = 131$ kJ/mol, is significantly smaller than the values reported in literature so far. The reason is that the molar mass decrease contributes to the viscosity change by means of an Arrhenius-like factor, $\exp(3.5(E_d - E_f)/2RT)$, that decreases the viscosity by almost one order of magnitude within a 40 K temperature range.

The rate constants of urethane formation in the high viscous polymer melt are in the range that is expected from the extrapolation of rate constants in low viscous melts at lower temperatures. The activation energy in the polymer melt is larger what is likely due to the enormous change in viscosity with increasing temperature.

The decrease of M_n calculated from the zero shear viscosity curves does reasonably agree with the corresponding GPC results. From the point of view of the manufacturer who processes polyurethane elastomers it is important to note that both the processing temperature and the residence time of the polymer in the molten liquid state strongly affect the degree of the molar mass decrease. However, it has to be taken into consideration that the molar mass decrease is to some extent reversible.

Acknowledgements

The authors gratefully acknowledge the financial support of this project by the Bavarian Research Foundation (Bayerische Forschungsstiftung).

Appendix

Eqs. (3) and (4) can be resolved for k_d and k_f. The complete solutions are:

$$k_d = \pm\sqrt{X^2 - Y^2} + X, \qquad X \equiv A\frac{B+1}{B-1}\frac{1+[E]}{2+[E]}, \qquad Y^2 \equiv \frac{A^2[E]}{2+[E]}, \tag{A1}$$

$$k_f = \frac{1}{2[E]}\left(A\frac{B+1}{B-1} - k_d\right). \tag{A2}$$

The solution " + " can be ruled out for physical reasons because it yields values for k_d and k_f in the same order of magnitude. This would correspond to half of all urethane bonds being broken, that is, an average degree of polymerisation of 2, which is far from any experimental evidence. The approximate solutions (21) and (22) discussed in this paper are derived as follows. The square root in (A1) can be expanded to the first order in Y^2/X^2 provided that $Y^2 \ll X^2$ or, equivalently,

$$[E] \ll \left(\frac{B+1}{B-1}\right)^2. \tag{A3}$$

This condition is satisfied because the molar mass loss does not exceed 55% (cf. Figs. 8 and 9), thus $[M_n^{eq}/M_n(t=0)]^2 = [(B+1)/(B-1)]^2 \geq (0.45)^2 \gg 1/70 \approx [E]$. One obtains

$$k_d \approx \frac{Y^2}{2X} = \frac{1}{2X}\frac{A^2[E]}{2+[E]} \approx \frac{A^2[E]}{4X} \approx \frac{A[E]}{2}\frac{B-1}{B+1}, \tag{A4}$$

where $[E] \ll 1$ was also used. Substituting this approximation for k_d in Eq. (A2) and exploiting (A3) gives

$$k_f \approx \frac{A}{2}\left(\frac{1}{[E]}\frac{B+1}{B-1} - \frac{1}{2}\frac{B-1}{B+1}\right) \approx \frac{A}{2[E]}\frac{B+1}{B-1}. \tag{A5}$$

References

[1] Eisenbach CD, Günter C, Baumgartner M, Struth U. Makromolekulares Kolloquium, Freiburg, February 1984.
[2] Eisenbach CD, Baumgartner M, Günther C. In: Lal J, Mark JE, editors. Advances in elastomers and rubber elasticity. New York: Plenum, 1986. p. 51–97.
[3] Yang WP, Macosko CW, Wellinghoff ST. Polymer 1986;27: 1235–40.
[4] Koberstein JT, Gancarz I, Clark TC. J Polym Sci, Polym Phys 1986;24:2487–98.
[5] Martin DJ, Meijs GF, Gunatillake PA, McCarthy SJ, Renwick GM. J Appl Polym Sci 1997;64:803–17.
[6] Bayer O. Das Diisocyanat-Polyadditions-Verfahren. München: Carl Hanser, 1963.
[7] Grassie N, Zulfiqar M. J Polym Sci, Polym Chem Ed 1978;16: 1563–74.
[8] Montaudo G, Puglisi C, Scamporrino E, Vitalini D. Macromolecules 1984;17:1605–14.
[9] Endres W. PhD thesis, University of Osnabrück, 1994.
[10] Karl H. Diploma thesis, University of Erlangen-Nürnberg, 1998.
[11] Strazielle C, Benoit H, Vogl O. Eur Polym J 1978;14:331.
[12] Janardhan R, Ramamurthy K, Anand JS. Polym Testing 1994;13: 397–404.
[13] Koberstein JT, Russell TP. Macromolecules 1986;19:714–20.
[14] Ryan AJ, Macosko CW, Bras W. Macromolecules 1992;25:6277–83.
[15] Bonart R, Morbitzer L, Hentze G. J Macromol Sci — Phys 1969;B3:337–56.
[16] Koberstein JT, Stein RS. J Polym Sci, Polym Phys Ed 1983;21: 1439–72.
[17] Goyert W, Hespe H. Kunststoffe 1978;68:819–25.
[18] Schmid J. PhD thesis, University of Regensburg, 1990.