

Kinetics of Polyurethane Formation Between Glycidyl Azide Polymer and a Triisocyanate

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ABSTRACT: Kinetics of the polyurethane formation between glycidyl azide polymer (GAP) and a polyisocyanate, Desmodur N-100, were studied in the bulk state by using quantitative FTIR spectroscopy. The reaction was followed by monitoring the change in intensity of the absorption band at 2270 cm^{-1} for NCO stretching in the IR spectrum, and was shown to obey second-order kinetics up to 50% conversion. The activation parameters were obtained from the evaluation of kinetic data at different temperatures in the range of $50\text{--}80^\circ\text{C}$. The enthalpy and entropy of activation were found to be $\Delta H^\ddagger = 44.1 \pm 0.5\text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -196 \pm 2\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. Dibutyltin dilaurate (DBTDL) was used as the curing catalyst. The kinetic study of the polyurethane formation between GAP and Desmodur N-100 showed that the reaction is enormously speeded up in the presence of the catalyst, and the reaction obeys second-order kinetics, provided that the catalyst concentration is kept constant. An investigation on the rate of the catalysed reaction depending on the catalyst concentration provided the order of the reaction, with respect to the DBTDL catalyst concentration, and the rate constant for the catalytic pathway of the reaction. The rate constant for the catalytic pathway was established to be 4.37 at 60°C , while the uncatalyzed reaction has a rate constant of $3.88 \times 10^{-6}\text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ at the same temperature. A rate enhancement factor of 23 was achieved by using 50 ppm catalyst. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 918–923, 2001

Key words: GAP; glycidyl azide polymer; isocyanate; kinetics; polyurethane; dibutyltin dilaurate; FTIR spectroscopy

INTRODUCTION

Glycidyl azide polymers (GAP) are promising candidates for energetic binder in future composite solid propellants having minimum-smoke, reduced pollution, and low sensitivity.¹ In the development of energetic binders for solid propellant, GAP has to be transformed into long-chain

polyurethane by using a proper curing agent.² The choice of appropriate curing agent is of prime importance to meet the minimum strain, stress, and hardness levels of mechanical properties, which crucially affect the performance of the propellant.³ The preliminary results of the continuing effort on curing of GAP show that the traditional curing agents, polyisocyanates, can also be used in the polyurethane formation with GAP; however, the use of an effective catalyst is required to speed up the reaction to a reasonable rate level.⁴ Although there have been numerous studies on curing and thermal characterization of

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GAP,⁵ the kinetics of its polyurethane reaction has not been studied yet. The rate and extent of the polyurethane formation affect the rheological and mechanical properties of the propellant.⁶ Therefore, knowledge on the kinetics of polyurethane formation is essential for the design and preparation of propellants possessing mechanical, dynamical, and ballistic properties suitable for specific purposes. However, there have been only a few studies concerning the kinetics of this kind of polyurethane formation between hydroxyl-terminated polymeric chain and diisocyanate, in general, and those mostly performed in solutions.⁷ The solution reaction is known to be largely affected by the nature of the solvent.⁸ Therefore, the solution data would be pertinent to the processes in the bulk if only the solvent used could create a medium similar to the bulk. The lack of kinetic data in bulk can be attributed to the difficulty in following the polyurethane formation, which starts in a viscous liquid state and ends up with a rubbery material. Recently, we have shown that quantitative FTIR spectroscopy can easily be used in studying the kinetics of polyurethane formation not only in solution but also in solid state.⁹ Here we report the results of a kinetic study of the polyurethane formation between GAP-diol and a triisocyanate, Desmodur N-100, by using the same method in bulk. Furthermore, dibutyltin dilaurate (DBTDL) was used to speed up the polyurethane formation and the effect of the catalyst concentration on the reaction kinetics could be readily studied by means of quantitative FTIR spectroscopy.

EXPERIMENTAL

Materials

The following materials were used as purchased: Glycidyl azide polymer (GAP-diol, L-996, 3M, USA; Density: 1.3 g/mL, Hydroxyl Value: 0.83 mEq/g, Molecular Weight— MW_w : 2900 g/mol, Viscosity at 25°C: 5000 cps), biuret triisocyanate (Desmodur N-100, Functionality—5.208 milliequivalent per gram, Bayer, Leverkusen, Germany), dibutyltin dilaurate (DBTDL, Bayer, Leverkusen, Germany), and potassium bromide (Merck, Darmstadt, Germany).

Kinetic Measurements

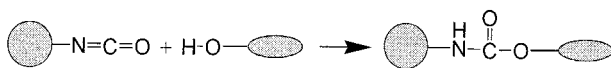
The polymerization reaction between GAP-diol and Desmodur N-100 was followed by monitoring

the changes in the IR absorption band for the NCO stretching vibration. Although the three isocyanate groups in Desmodur N-100 are not exactly equivalent in reactivity, our assay determines only the total amount of unreacted isocyanate, as three isocyanate groups in Desmodur N-100 give only one IR absorption band for the NCO stretching vibration and the peak position remains practically unaltered throughout the reaction. The infrared spectra of the bulk samples were recorded on a Nicolet 20SXB FTIR spectrophotometer using the OMNIC program. Samples studied contain equimolar amounts of hydroxyl and isocyanate groups from the glycidyl azide polymer (GAP-diol) and Desmodur N-100, respectively. Thus, the NCO/OH ratio of 1 remains constant through the reaction. About 50 mg of anhydrous crystalline potassium bromide was pressed into a self-supporting wafer with a diameter of 13 mm by applying a pressure of 10 tons/cm² for 60 s. GAP-diol and Desmodur N-100 were mixed at room temperature and a small amount of this mixture (1.6 ± 0.1 mg) was placed between two KBr pellets that were held together without applying any external force. For the catalytic reactions, GAP-diol containing DBTDL in a certain amount was mixed with Desmodur N-100 at room temperature, and samples were prepared in the same way. The sample assembly was heated in a vacuum oven to a preset temperature in the range of 50–80°C for the curing reaction between GAP-diol and Desmodur N-100. The reaction was followed by monitoring the changes in the intensity of the absorption band for NCO stretching at 2270 cm⁻¹ for Desmodur N-100 in the IR spectra of the sample wafer taken at a proper time interval depending on the curing temperature. The intensity of the absorption band for NCO stretching was calculated by taking the integral of the band between 2365 and 2233 cm⁻¹ and subtracting the integral value under the baseline in the same region by using Omnic E.S.P. Software (Nicolet). These resultant intensity values were divided by the intensity of the absorption band at 2930 cm⁻¹ for the CH stretching, which remains practically unaffected throughout the curing reaction, to ensure that the quantitative results are independent of the thickness of the sample film between two wafers. All the absorption values were then converted to the concentrations of NCO by using a calibration curve prepared from the standard samples, which contain known amount of Desmodur N-100 in GAP. The standard samples for calibration were prepared by mixing a known

amount of Desmodur N-100 in GAP at room temperature and the IR spectra were also taken at room temperature to assure that no reaction occurred between GAP and Desmodur N-100.

RESULTS AND DISCUSSION

At the final stage of composite propellant preparation, a curing agent, usually a polyisocyanate, is added to the heterogeneous mixture containing the prepolymer, fuel, oxidizer, and other ingredients. The prepolymer and polyisocyanate react with each other to form a polyurethane network that holds the fuel and oxidizer particulates in a composite matrix having mechanical and ballistic properties suitable for rocket applications. The polyurethane formation can be depicted in a simple manner.



The cure reaction between the prepolymer, GAP-diol (**1**), and the triisocyanate, Desmodur N-100 (**2**), can be followed by means of quantitative FTIR spectroscopy in bulk.

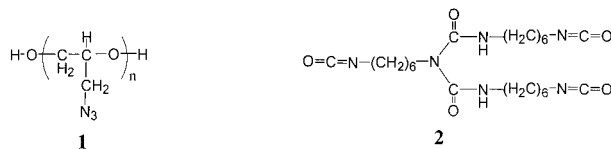


Figure 1 shows the IR spectra taken in the course of the polyurethane formation between GAP-diol and Desmodur N-100 at 60°C. A closer look at the spectra in the spectral region of 2400–1600 cm^{-1} reveals that the absorption band for NCO stretching at 2270 cm^{-1} gradually decreases as the reaction proceeds and ultimately disappears upon completion of the reaction. A new absorption feature grows in at 1726 cm^{-1} upon polyurethane formation. The new band is readily assigned to the CO stretching of the polyurethane carbonyl group. The azide stretching band at around 2100 cm^{-1} remains practically unaltered throughout the reaction. The diminution of the NCO stretching band at 2270 cm^{-1} and the growth of the C=O stretching band at 1726 cm^{-1} indicate the conversion of isocyanate to the polyurethane. The polyurethane formation between GAP-diol and Desmodur N-100 is followed by

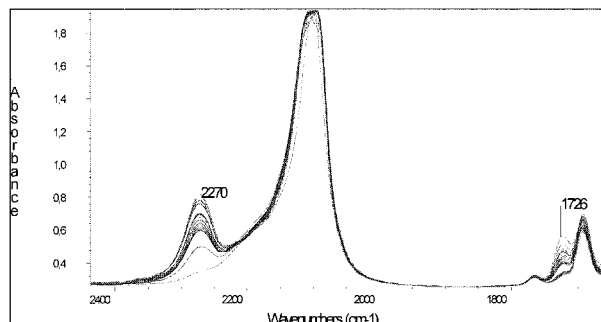


Figure 1 FTIR spectra taken during the course of the polyurethane formation between GAP-diol and Desmodur N-100 at 60°C from the film squeezed between two KBr pellets. The absorption band for NCO stretching at 2270 cm^{-1} gradually disappears while a new feature concomitantly grows in at 1726 cm^{-1} , which is readily assigned to the C=O stretching of urethane.

monitoring the changes in the intensity of the NCO stretching band at 2270 cm^{-1} relative to that of the C—H stretching band at 2930 cm^{-1} , which also remains unaltered throughout the reaction. The graph of concentration vs. time exhibits an exponential decay for the starting substances GAP-diol and Desmodur N-100 at all temperatures. However, the reciprocal concentration vs. time plot shows a straight line for the polyurethane formation between GAP-diol and Desmodur N-100 with equal initial concentrations up to about 50% conversion. This indicates that the polyurethane formation between GAP-diol and Desmodur N-100 obeys second-order kinetics. At higher conversion, one observes a deviation from linearity, which might be due to the prominent diffusion control after gelation. In many bulk polymerization systems the overall reaction rate is determined by both the reaction kinetics and the diffusion rates of monomers, and this competitive control is very dependent on the viscosity of the reaction media. In this work, both reactants are relatively viscous at room temperature. However, because the reactions are carried out at high temperatures, it can be assumed that the diffusion control is negligible until the starting of gelation, where the diffusion control would become prominent, which caused a deviation from second-order kinetics. Furthermore, the presence of the third NCO group in Desmodur N-100 molecule may have an effect of accelerating the crosslinking in the curing system. From the functionality, the gel point of GAP-diol is predicted to be at about 60% conversion. Therefore, the polyurethane formation between GAP-diol and Desmodur N-100 was followed up to about 50% conversion.

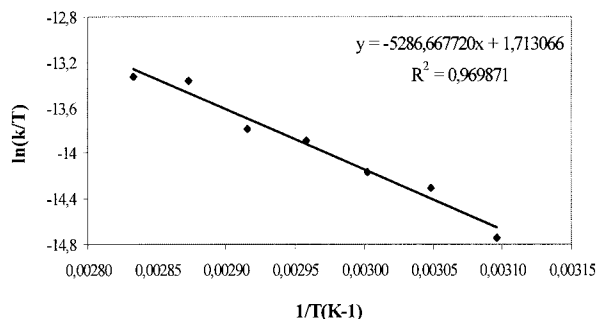


Figure 2 Eyring plot for the polyurethane formation between GAP-diol and Desmodur N-100 with an NCO/OH ratio of 1.

The rate law for the second order reaction is given in eq. (2).

$$\text{rate} = k[\text{OH}][\text{NCO}] \quad (2)$$

where [OH] and [NCO] stand for the concentrations of the hydroxyl groups in GAP-diol and isocyanate groups in Desmodur N-100, respectively, and k is the rate constant. Because the initial concentrations of hydroxyl and isocyanate groups are taken to be equal in this study ($[\text{OH}]_0 = [\text{NCO}]_0 = C_0$), the rate equation can be integrated to retrieve the concentration–time relationship.

$$\frac{1}{C} = kt + \frac{1}{C_0} \quad (3)$$

The slope of the straight line obtained by plotting the reciprocal concentration vs. time gives the rate constant for the second-order reaction. The polyurethane formation between GAP-diol and Desmodur N-100 was conducted at seven different temperatures in the range of 50–80°C to determine the activation parameters of the reaction. The rate constants for the second-order reaction could be obtained from the graphs of reciprocal concentration vs. time at all temperatures. The activation enthalpy and entropy for the thermal curing reaction between GAP-diol and Desmodur N-100 can be obtained from the evaluation of the Eyring plot illustrated in Figure 2. The activation enthalpy is found to be $\Delta H^\ddagger = 44.1 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$. This is comparable to the values given in the literature for polyurethane formation between alcohols and isocyanates.¹⁰ However, it is slightly greater than that for the polyurethane formation of hydroxyl-terminated polybutadiene

(HTPB) with diisocyanates ($\Delta H^\ddagger = 41.1 \pm 0.5 \text{ kJ/mol}$).⁹ This small difference in activation enthalpy values for two type of polyurethane formation implies that the curing reaction between GAP-diol and Desmodur N-100 is slower than that between HTPB and diisocyanate.

From the evaluation of the kinetic data in the Eyring plot (Fig. 2), the activation entropy can also be found to be $\Delta S^\ddagger = -196 \pm 2 \text{ J/K} \cdot \text{mol}$. The values of activation enthalpy and entropy can be used to understand the mechanism.¹¹ The large negative value obtained for the activation entropy is indicative of an associative mechanism in the transition states.¹² This is in agreement with the second-order rate law obtained for the polyurethane formation between GAP-diol and Desmodur N-100. Support for this assignment of an associated mechanism in the transition states for the polyurethane formation between GAP-diol and Desmodur N-100 comes from comparison of the activation enthalpies with the bond energies of the O—H and C=N bonds, which are broken in the reaction. The activation enthalpy is much smaller than the bond energy.¹³

This kinetic study shows that the polyurethane formation between GAP-diol and Desmodur N-100 is very slow compared to that of the system consisting of HTPB and diisocyanate. Therefore, the curing of GAP-diol needs to be speeded up for use as binder in energetic rocket propellants. Many organometallic compounds have been tested as a catalyst for the isocyanate-hydroxyl reaction.¹⁴ Among them, the organotin compounds are known to be the most suitable catalyst for the urethane formation between alcohols and isocyanates.¹⁵ Dibutyltin dilaurate (DBTDL) has been shown to be the most effective catalyst for many polyurethane formation reactions of the long-chain diols including glycidyl azide polymers.¹⁶ Dibutyltin dilaurate was selected to be used as a catalyst for the polyurethane formation between GAP-diol and Desmodur N-100.

The polyurethane formation between GAP-diol and Desmodur N-100 was carried out in the presence of a catalyst in different concentrations at 60°C. The reaction was found to be still of second-order when the catalyst concentration was kept constant. Thus, the reciprocal concentration versus time plots gave straight lines for all the blends of GAP-diol and Desmodur N-100 containing DBTDL as a catalyst in various concentrations (Fig. 3). At first glance, one observes an increase in the rate of the polyurethane formation with the increasing concentration of the catalyst,

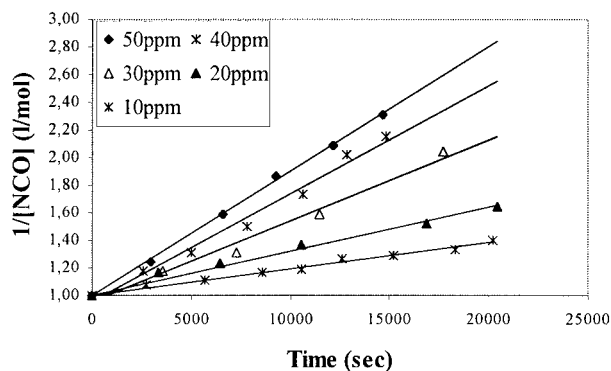


Figure 3 Reciprocal concentration vs. time plot for the catalyzed polyurethane formation between GAP-diol and Desmodur N-100 with an NCO/OH ratio of 1 but different catalyst concentrations at 60°C.

as expected. The reaction in the presence of the catalyst can proceed either through a catalytic pathway or via the uncatalyzed way as in the absence of the catalyst. The rate equation can be rearranged by taking the sum of two contributions:

$$\text{Rate} = k_u[\text{NCO}][\text{OH}] + k_c[\text{NCO}][\text{OH}][\text{Cat}]^\alpha \quad (4)$$

Here, k_u is the rate constant for the uncatalyzed reaction, k_c is the rate constant of the reaction through the catalytic pathway. Equation (4) can be rearranged:

$$\text{Rate} = (k_u + k_c[\text{Cat}]^\alpha)[\text{NCO}][\text{OH}] \quad (5)$$

Equation (5) shows that the reaction will still be of second-order provided that the catalyst concentration is constant. The overall rate constant for the catalyzed system has two contributions:

$$k = k_u + k_c[\text{Cat}]^\alpha \quad (6)$$

On taking the natural logarithm of both sides, eq. (6) gets a useful form:

$$\ln(k - k_u) = \ln k_c + \alpha \ln[\text{Cat}] \quad (7)$$

The values of the overall rate constant, k , were obtained from the slope of the lines given in Figure 3 for all the blends of GAP-diol and Desmodur N-100 containing DBTDL as a catalyst in various concentrations at 60°C. Because the rate constant for the uncatalyzed reaction at this temperature is known ($k_u = 3.88 \cdot 10^{-6} \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$ at 60°C),

the $\ln(k - k_u)$ values can be plotted against the catalyst concentration according to eq. (7). As shown in Figure 4, this gives a straight line and enables one to determine the rate constant for the catalytic pathway ($k_c = 4.38$) and the order of the reaction with respect to the catalyst concentration ($\alpha = 1.17$). The rate constant for the catalytic pathway is found to be extremely large compared to the rate constant for the uncatalyzed reaction ($k_c = 4.38$ and $k_u = 3.88 \cdot 10^{-6} \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$). This comparison might be misleading, because the contribution of the catalytic pathway to the overall rate constant is proportional to $k_c[\text{Cat}]^\alpha$. Nevertheless, a rate enhancement factor of 23 is achieved by using 50 ppm catalyst, which corresponds to the 0.04% of the weight of the polymeric mixture with an NCO/OH ratio of 1. This is a significant rate enhancement, and seems to be high enough to carry out the curing of GAP-diol within a reasonable time at the usual working temperature.

CONCLUSION

The kinetic study on the polyurethane formation reaction between glycidyl azide polymer (GAP) and a polyisocyanate, Desmodur N-100, in bulk by means of quantitative FTIR spectroscopy reveals the following concluding points:

1. The polyurethane formation can be followed by monitoring the change in intensity of the NCO stretching band at 2270

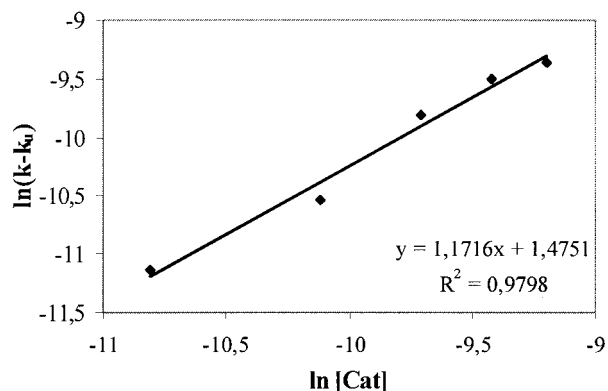


Figure 4 Plot of natural logarithm of $k - k_u$ vs. natural logarithm of DBTDL concentration for the catalyzed polyurethane formation between GAP-diol and Desmodur N-100 with NCO/OH ratio of 1 but different catalyst concentrations at 60°C.

cm^{-1} in the IR spectrum. Thus, quantitative FTIR spectroscopy provides good means to study the polyurethane formation in the bulk state.

2. The polyurethane formation between GAP-diol and Desmodur N-100 obeys a second-order rate law up to 50% conversion, beyond which some deviations are observed. This might be attributed to the gel formation.
3. The enthalpy and entropy of activation for the polyurethane formation between GAP-diol and Desmodur N-100 could be obtained from the evaluation of kinetic data at different temperatures in the range of 50–80°C: $\Delta H^\ddagger = 44.1 \pm 0.5 \text{ kJ/mol}$, and $\Delta S^\ddagger = -196 \pm 2 \text{ J/mol} \cdot \text{K}$. The large negative value of the activation entropy implies an associative pathway, which is consistent with second-order kinetics. The small value of the activation enthalpy, compared to the dissociation energies of the breaking bonds, also supports the associative mechanism.
4. The polyurethane formation between GAP-diol and Desmodur N-100 is rather slow at an acceptable curing temperature and, therefore, needs to be speeded up by using a catalyst. Remarkable rate enhancement can be achieved by adding dibutyltin dilaurate as a catalyst into the mixture up to 50 ppm. Thus, curing of GAP becomes feasible at a usual working temperature of 60°C.

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REFERENCES

1. Agrawal, J. P.; Walley, S. M.; Field, J. E. *J Propuls Power* 1997, 13, 463; Kubota, N. *J Propuls Power* 1995, 11, 677; Frankel, M. B.; Grant, L. R.; Flanagan, J. E. *J Propuls Power* 1992, 8, 560; Kubota, N.; Yano, Y.; Miyata, K. *Propellants Explos Pyrotech* 1991, 16, 287; Chen, J. K.; Brill, T. B. *Combust Flame* 1991, 87, 157; Wagner, R. I.; Wilson, E. R.; Grant, L. R.; Flanagan, J. E. U.S. Pat. 4,937,361 (1990); Kubota, N. *J Propuls* 1990, 6, 68; Kubota, N.; Sonobe, T. *Propellants Explos Pyrotech* 1988, 13, 172.
2. Sutton, G. P. *Rocket Propulsion Elements*; John Wiley & Sons Inc.: New York, 1992, 6th ed.
3. Kuo, K. K.; Summerfield, M. *Fundamentals of Solid-Propellant Combustion*, Progress in Astronautics and Aeronautics; American Institute of Astronautics and Aeronautics: New York, 1984, vol. 90.
4. Desilets, S.; Villeneuve, S.; Laviolette, M.; Auger, M. *J Appl Polym Sci* 1997, 35, 2991.
5. (a) Bui, V. T.; Ahad, E.; Rheume, D.; Raymond, M. P. *J Appl Polym Sci* 1996, 62, 27; (b) Kubota, N.; Snobe, T. *Propellants Explos Pyrotech* 1988, 13, 172; (c) Shen, S. M.; Chiu, Y. S.; Wang, S. W.; Chen, S. *Thermochim Acta* 1993, 221, 275; (d) Shen, S. M.; Leu, A. L.; Chen, S.; Yeh, H. C. *Thermochim Acta* 1991, 180, 251; (e) Shen, S.; Wang, S. W.; Chiu, Y. S.; Chen, S. I.; Chang, F. M.; Huang, C. C. *Thermochem Acta* 1993, 216, 255.
6. Muthiah, R. M.; Krishnamurthy, V. N.; Gupta, B. R. *J Appl Polym Sci* 1992, 44, 2043.
7. (a) Coutinho, F. M. B.; Rocha, M. G. *J Polym Sci A* 1988, 26J, 3167; (b) Coutinho, F. M. B.; Rocha, M. G. *Eur Polym J* 1991, 27, 213; (c) Coutinho, F. M. B.; Rezende, L. C.; Quijada, R.; Petrobras, C. *J Polym Sci A* 1986, 24, 727; (d) Coutinho, F. M. B.; Rezende, L. C.; Quijada, R.; Petrobras, C. *J Polym Sci A* 1986, 24, 3021; (e) Aranguren, M. I.; Williams, R. J. *J. Polymer* 1986, 27, 425.
8. Chang, M. C.; Chen, S. A. *J Polym Sci A* 1987, 25, 2543.
9. Kincal, D.; Özkar, S. *J Appl Polym Sci* 1997, 66, 1979.
10. Greenshield, J. N.; Peters, R. H.; Stepto, R. F. T. *J Chem Soc* 1964, 5101.
11. Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill, Inc.: New York, 1995, 2nd ed.
12. Connors, K. A. *Chemical Kinetics—The Study of Reaction Rates in Solution*; VCH Publishers, Inc.: New York, 1990.
13. Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Oxford University Press: Oxford, 1999, 3rd ed.
14. Saunders, J. H.; Frisch, K. C. *Polyurethanes Chemistry and Technology*; Krieger Publishing Company: New York, 1978.
15. Deschères, I.; Pham, Q. *Macromol Chem* 1987, 188, 1909.
16. (a) Desilets, S.; Villeneuve, S.; Laviolette, M.; Auger, M. *J Polym Sci A* 1997, 35, 2991; (b) Lomölder, R.; Plogmann, F.; Speier, P. *J Coat Technol* 1997, 69, 51.