JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 2029–2039 (1977)

Kinetics and Energetics of a Fast Polyurethane Cure

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Synopsis

Methods for obtaining kinetic data on bulk polymerizing systems are reviewed, and adiabatic temperature rise is found to be the most useful for fast systems. An adiabatic method is described and used to study the polymerization of poly(ϵ-caprolactone triol) with chain-extended 1,6-hexane diisocyanate catalyzed with dibutyltin dilaurate.

INTRODUCTION

Thermoset processing typically involves the flow of reactive materials into a mold, where a polymerization reaction with crosslinking occurs. Once the part is sufficiently rigid, it is removed from the mold and the cycle repeated. The introduction of reaction injection molding[1] (RIM) during the past few years has widened the scope of thermoset processing, particularly for polyurethane polymers. RIM equipment allows large molds to be filled in 2 to 3 sec, while improvement in chemical formulation has decreased gel times to the order of 7 sec. Both thermoset and thermoplastic elastomers can be formed with the process.

The RIM process is complex and does not lend itself to simple analysis. It involves both flow and simultaneous exothermic reaction to form an infinite molecular network. During processing, material properties change from liquid to elastomeric, with temperature changes influencing both reaction rate and physical properties.

Kamal[1] has pointed out that, in order to do mathematical modeling of thermoset processing, one needs (a) reaction kinetics: $r_A = f(c)$; (b) reaction energetics: ΔH, $C_p(T,c)$; (c) an expression to relate viscosity to the state of the reactants: $\eta = \eta(T,c,\dot{\gamma})$.

A method is presented here for obtaining the reaction kinetics and energetics for a fast, highly exothermic polymerization. The method has been applied to obtain data for the cure of a thermosetting liquid polyurethane system. Viscosity variation during the cure of this system is discussed elsewhere.[2]

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METHODS OF MEASURING REACTION KINETICS

Conventional Methods

A large number of methods have been used to monitor the kinetics of network polymerization reactions. Kamal[1] and Mussatti[3] have given extensive reviews. These methods fall into two groups: (1) methods which directly monitor the concentration of unreacted endgroups, for example, titration of endgroups, IR, and UV spectroscopy; (2) measurement of a physical property which can be functionally related to the extent of reaction; these properties include shear and flexural modulus, viscosity, swelling, dc conductivity, and heat evolution (DTA and DSC methods).

Some of these methods can be used both before and after the gel point, for example, the spectroscopic and thermal methods. Others, such as viscosity or modulus measurement, can be used only before or after the gel point. The methods are generally applicable to slow and moderately fast cures (say, longer than 10 min). During fast cures with gel times less than 10 min, two factors inherent in most thermoset cures become overwhelming. They are (a) the highly exothermic nature of most of these systems; (b) the low thermal conductivities which prevent the heat from being removed or the temperature being effectively controlled.

Even when the samples actually monitored are small, substantial reaction and heating may occur during the mixing of the reactants, degassing, transfer to the equipment, and thermal stabilization in the equipment.

One way of circumventing the problem is to reduce chemical reactivity, by reducing either the catalyst concentration or reaction temperature. This however, requires an extrapolation back to the conditions of interest. Reaction rate is by no means always linear with catalyst concentration.[4,5] Temperature reduction can result in reactant solidification or high viscosities which prevent mixing of the reactants. It is, therefore, desirable to measure the chemical kinetics directly on a highly reactive system.

Adiabatic Reaction Method

In this study, chemical kinetics of a fast polymerization were obtained by analyzing the temperature rise measured during an adiabatic reaction. This method has been used for thermosets by Stonecypher et al.[6] and Allen.[7] They measured polymerization rates of solid propellant binders with reaction times of 200 min or more. Such a slow reaction demands a specialized temperature control apparatus. When the reaction lasts only a few minutes, no expensive equipment is required as there is little time for heat to be lost. The thermoset's low thermal conductivity further reduces heat loss from the center. The highly exothermic nature of most fast polymerization reactions provides a temperature rise which is easy to monitor. A fast thermoset cure is thus particularly well suited to provide adiabatic temperature rise data.

Douglas and Eagleton[8] have tabulated analytic solutions to adiabatic reactor problems with complex kinetics, using average heat capacities. When C_p varies significantly with temperature, the following equations become applicable: Heat of reaction:

$$(-\Delta H) = \frac{\rho}{c_0} \int_{T_0}^{T_{\max}} C_p(T)dT \tag{1}$$

Fraction of reactive groups reacted (for balanced stoichiometry):

$$1 - \frac{c}{c_0} = \left\{ \int_{T_0}^{T} C_p(T)dT \Big/ \int_{T_0}^{T_{\max}} C_p(T)dT \right\} \tag{2}$$

Energy balance:

$$\rho C_p(T) \frac{dT}{dt} = r_A(-\Delta H) \tag{3}$$

If we assume the reaction kinetics can be described as an nth order reaction,

$$r_A = A\mathrm{e}^{-E_R/RT}c^n \tag{4}$$

then eq. (3) becomes

$$\ln \left(\frac{\rho C_p(T)}{(-\Delta H)} \frac{dT}{dt}\right) = \ln A - \frac{E_R}{RT} + n \ln c \tag{5}$$

If $C_p(T)$ is known, $(-\Delta H)$, c, and dT/dt can be measured or calculated from the adiabatic temperature rise. By making measurements at a series of temperatures, values of A, E_R, and n can be obtained by least-squares approximation. This method was used by Stonecypher et al.[6]

Values can be obtained graphically by using the following form of eq. (3):

$$\ln \left[\frac{\rho C_p(T)}{(-\Delta H)c_0(c/c_0)^n} \frac{dT}{dt}\right] = \ln A{c_0}^{n-1} - \frac{E_R}{RT} \tag{6}$$

Plotting the left-hand side versus $1/T$ for various values of T will yield a straight line with the correct value of n if eq. (4) holds throughout the reaction.

URETHANE POLYMERIZATION KINETICS

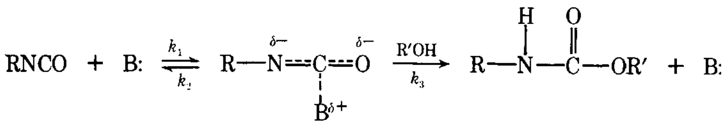
The chemistry of urethane systems has been extensively studied.[9,10] The simple urethane linkage is the major reaction product of the isocyanate–hydroxyl reaction. Of the main secondary reactions, allophanate formation requires temperatures of 393° to 413°K to be significant; water is necessary for urea formation, and temperatures above 373°K are required for subsequent biuret formation. There is a wide variety of polyisocyanates and polyols which can be used to manufacture polyurethanes. Consequently, the main research effort, even today, is in the synthesis of polyurethanes with desirable or improved properties.

In contrast, studies of urethane kinetics have not been extensive. They have focused mainly on the relative reactivities of different monomeric groups and catalysts.[11] Kinetic measurements on solution polymerizations are of little use in predicting bulk polymerization rates, since a solvent may affect both the rate and mechanism of a catalyzed reaction.[5,12]

Further complications may arise during bulk polymerization of thermosets. Reactants become highly viscous and then elastomeric. Kinetics may change during reaction, especially after gelling. Mussatti[3,16] found that reactions rates increased beyond the gel point for a crosslinked polyurethane. Vilesova et al.[17]

found no change. Valles and Macosko[18] found a decrease in rate beyond the gel point for a hydrosilation system. French et al.[19] have even found that reaction stops completely short beyond the gel point in polyurethane and epoxy systems. This is in contrast to a number of studies in which complete reaction was measured, even for highly crosslinked polyurethane systems.[20–22] In the present study, the reaction of a moderately catalyzed sample was found to go to completion by IR.

The base-catalyzed reaction is thought to proceed by the mechanism suggested by Baker and Holdsworth:[13]



$$\mathrm{RNCO} + \mathrm{B{:}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{R{-}\overset{\delta-}{N}{=}\underset{B^{\delta+}}{C}{=}\overset{\delta-}{O}} \xrightarrow[k_3]{\mathrm{R'OH}} \mathrm{R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OR'} + \mathrm{B{:}}$$

The basic catalyst can be the reactive polyol, the urethane product, added catalyst, or even a polar solvent. The solvent polarity will also affect the rate of complex formation.

With metal catalysts, a multistep mechanism has been proposed. It suggests that the metal complexes with oxygen atoms of both the isocyanate and hydroxyl groups (ref. 9, p. 172). The resulting close proximity of the reactive groups accounts for the superior catalytic action of the metals.

It is clear that the reaction cannot be expected to follow simple-order kinetics. Complete determination of the rate constants is a very difficult task. Stanford[14] and Greenshields et al.[12] have tried to apply simplified forms of equations derived from the Baker mechanism, with only moderate success. Anzuino et al.[15] emphasize that, despite extensive study, there is still no satisfactory method of determining rate constants for the urethane reaction from the rate of disappearance of —NCO.

In view of the complexities of the reaction kinetics and the limited scope of the present work, it was decided to use an *n*th order type of expression

$$r_A = Ae^{-E_R/RT}c^n \tag{4}$$

where A, E_R, and n can be fitted to describe the rate of isocyanate group disappearance. If necessary, a different set of parameters could be used to describe the kinetics at low and high extents of reaction.

EXPERIMENTAL

Materials

Experiments were performed using a bulk, two-component urethane polymerization: a triol, A_3, reacting with a diisocyanate, B_2. The materials are similar to those used in reaction injection molding.[23]

B_2 was a bifunctional, NCO-terminated prepolymer formed by reacting 1,6-hexamethylene diisocyanate (HDI) with a deficient quantity of tripropylene glycol (TPG). The HDI (Mobay) was purified by distillation under vacuum (approximately 100 microns Hg, 358°K) and reacted with as-received TPG (Union Carbide Corp.) under nitrogen for 48 hr at 318°K. The prepolymer had 18.55 ± 0.2% NCO by weight, and a viscosity of 1.75 N·s/m^2 (17.5 poises) at 299°K.

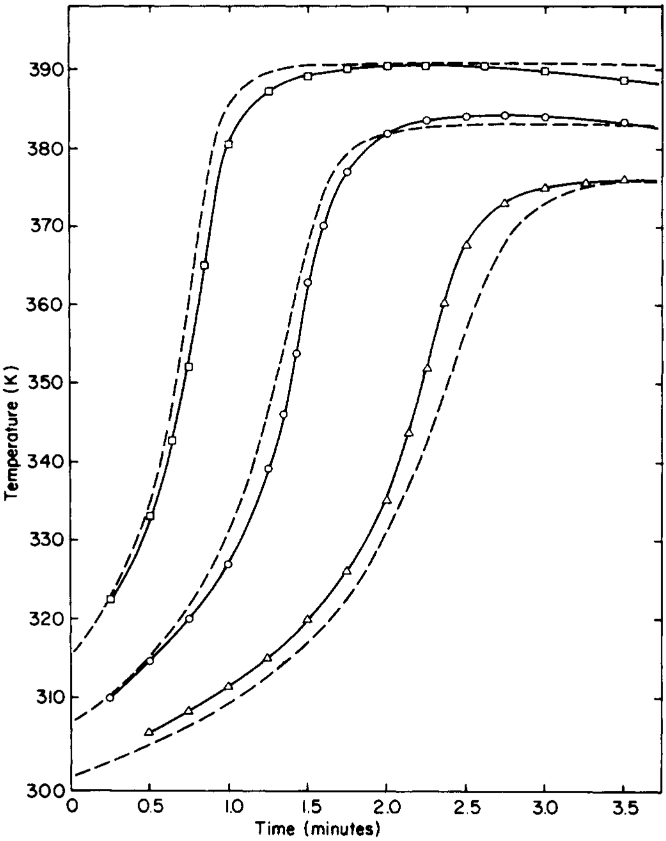


Fig. 1. Adiabatic reaction temperature rises: (—) experimental; (- - -) theory.

The triol (PCP-0300, Union Carbide Corp.) was used as received. Union Carbide reports an OH equivalent of 313 mg KOH/g, acidity of 0.11% by weight, and water content of 0.02% by weight. These values were checked by Mussatti (ref. 3, p. 31) and found to be within the reported limits or within ±10% of the reported values. Viscosity at 299°K was 1.2 N·s/m^2.

Catalyst, dibutyltin dilaurate (DBTDL), was used as received (D-22, Union Carbide Corp., density 1.021 g/cc at 394°K, formula weight 565). The catalyst was added to the triol to a concentration of 0.21% by volume, to give 1.68 mole DBTDL/m^3 in the final mixture of 1 volume triol to 1.25 volume NCO prepolymer. Maximum variation in catalyst concentration was ±0.04 mole/m^3.

At room temperature, both reactants are liquids with similar viscosities. All functional groups are expected to be of equal reactivity. The triol OH groups are 99% primary. Functional groups are separated by at least six carbon atoms, so substitution effects are unlikely. (This allows standard polycondensation theory to be applied for calculation of $\overline{M}_n$ and $\overline{M}_w$ during polymerization.[2])

Experimental Procedure

Reactions were conducted in a cylindrical glass container 58 mm high, 38 mm in diameter. The container, with approximately 12 g of preweighed diisocyanate, was preheated in a water bath. A stoichiometric quantity of similarly preheated

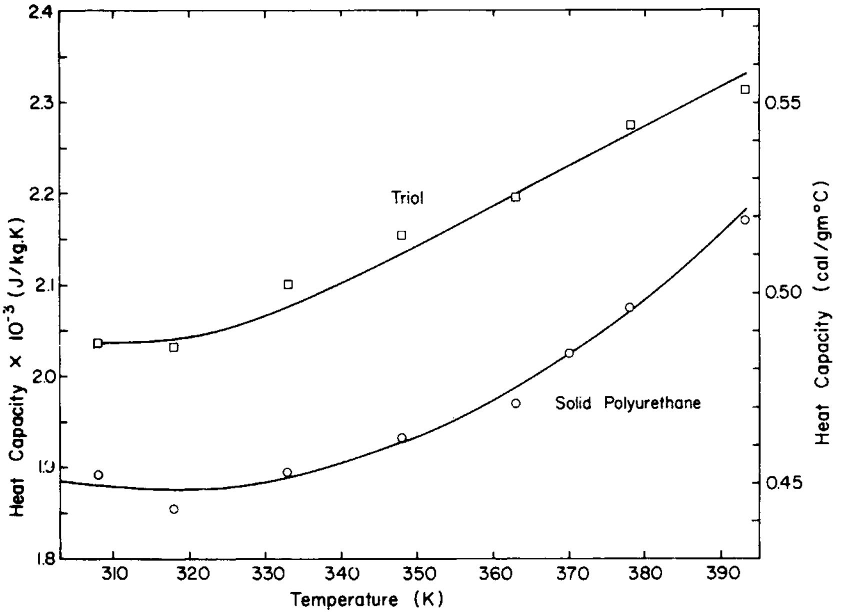


Fig. 2. Heat capacity of triol and polymer by DSC measurements.

triol was added by syringe. The container was fitted into a block of polymeric insulating foam and mixed intensively for 15 sec with a motor-driven paddle mixer. A stopper with a copper–constantan thermocouple protruding from its center was placed on the container. The thermocouple output was monitored continuously on a strip chart recorder.

RESULTS

Experimental Results

The solid lines in Figure 1 show the experimentally observed temperature rises from three different initial temperatures. The reactions are fast, being essentially complete within 1 to 3 min.

An approximate gel point can be observed by pulling gently on the thermocouple during reaction. Once the mixture gels, the thermocouple resists movement. It was noted that temperature continued to rise beyond this point, indicating that reaction does indeed continue in the elastomeric state.

Fine air bubbles were entrained during the mechanical mixing of the liquid reactants. These bubbles serve to reduce the already low thermal conductivity of 0.19 W/m·°K, even further (copper has a thermal conductivity of 400 W/m·°K, aluminium, of 200 W/m·°K).

Other factors also aid in ensuring that adiabatic conditions are maintained. The reactions are very fast. The majority of the total temperature rise of 76.3 ± 0.8°K is completed within 1 min for all reactions. This provides little time for heat loss by conduction. During the 2 min immediately following the maximum temperature, temperature at the center decreased at an average rate of 1.6 ± 0.2°K/min. Broyer and Macosko[24] have shown that at this point, the rate

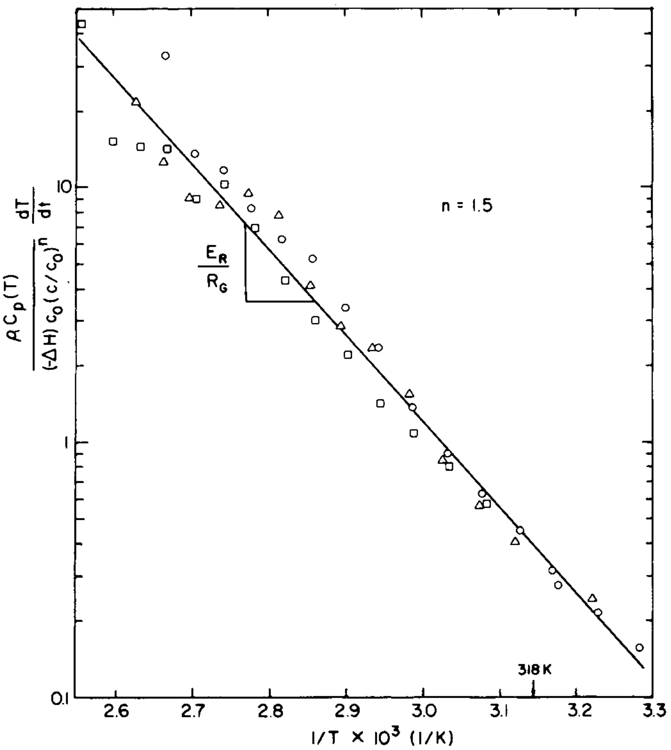


Fig. 3. Kinetic plot for adiabatic reaction data. Initial temperatures: (○) 300°K; (△) 307°K, (□) 315°K.

of heat loss is at its maximum. Therefore, at most, 2–6% of the total heat of reaction could be lost during reaction.

A combination of short total reaction times, fast rate of temperature rise during the major part of the reaction, and slow heat loss resulting from low thermal conductivity ensures that reaction conditions are close to adiabatic.

Heat Capacity

In order to apply eq. (6) to obtain A, E_R, and n, information on heat capacity $C_p(T)$ is required. The C_p of the triol and of the reacted polymer were measured on a Perkin-Elmer DSC-2 differential scanning calorimeter, using 10-mg samples in sealed aluminium pans. The C_p of aluminium was used as a reference, and the coolant was liquid nitrogen. The temperature was scanned from 298° to 393°K at 10°K/min using 8.374 mJ/s for full-scale deflection.

The results are shown in Figure 2. The polymer C_p is in general agreement with the value of $(1.76\text{–}1.84) \times 10^3$ J/kg·°K given by *Modern Plastics Encyclopedia*[25] for cast polyurethanes, as well as that of $(1.92 \pm 0.8) \times 10^3$ J/kg·°K at 398°K given by Brandrup and Immergut[26] for four crosslinked, unfilled rubbers.

The triol heat capacity was 10% higher than that of the polymer. Brandrup and Immergut[26] reported an average of 3% reduction in C_p during the crosslinking of four unfilled elastomeric gums. Kamal[1] found the monomer C_p to be higher than that of the polymer for epoxy and polyester systems. He also tried to monitor the change in C_p during the reaction. The variations in C_p he obtained seem to be unusually large (e.g., (1.26–8.37) × 10^3 J/kg·°K for an epoxy cure) and leave his method open to reexamination.

In this study, polymer C_p was used throughout. The polymer C_p variation between 298° and 393°K could be described by

$$C_p(T) = 1875 + 0.209|T - T_{\mathrm{ref}}| + 0.0502(T - T_{\mathrm{ref}})^2 \qquad C_p \text{ in J/kg}\cdot{}^\circ\mathrm{K} \qquad T_{\mathrm{ref}} \equiv 318^\circ\mathrm{K} \tag{7}$$

Heat of Reaction

Once $C_p(T)$ is known, the heat of reaction ΔH can be calculated from eq. (1). For eq. (1) to hold, the reaction must go to completion. To test this, the reaction of a moderately catalyzed (0.32 mole DBTDL/m^3) sample was monitored on a Perkin–Elmer infrared spectrophotometer Model 521 at 307°K. The sample was mounted between NaCl mull plates and the 2270 cm^{-1} NCO peak was monitored continuously. It was found that the reaction proceeded to 99% completion within 4 hr.

To compensate for heat losses during triol transfer and mixing, small adjustments were made to the initial temperatures of two of the experiments. The third experiment was started at room temperature, so the uncertainty was reduced. Viscosity is higher at the low temperatures, so more chance of heat generation during mixing exists. Mixing time was, however, only 15–30 sec. The two initial temperatures were adjusted to slightly below the water bath temperatures to bring the calculated heats of reaction into agreement with that of the experiment started at room temperature. The experiment with the 308°K water bath was estimated to have started at 307°K and the experiment with a 318°K bath, at 315°K.

A value of $\Delta H = -60.33 \pm 0.62$ kJ/equiv NCO reacted (-14.41 ± 0.15 kcal/equiv NCO) was obtained. There are surprisingly few published results to which this can be compared. Saunders and Frisch[9] quote a value of −108.8 kJ/equiv NCO obtained by Bayer in 1947 for HDI reacting with 1,4-butanediol. Lovering and Laidler[27] obtained values between −77.5 and −104.7 kJ/equiv NCO reacted for aromatic isocyanates and diisocyanates. Heat of reaction depended mainly on the type of isocyanate, but variations were also observed for different types of alcohols.

An attempt was made to verify the value of ΔH obtained by monitoring the polymerization reaction on the Perkin–Elmer DSC-2. The intermediate catalyst concentration of 0.32 mole DBTDL/m^3 was used. Isothermal runs were made at 338° and 348°K. Two scans were made between 298° and 393°K, with a scan rate of 2.5°K/min. The following results were obtained. Isothermal runs: $\Delta H = -51.5, -48.9$ kJ/equiv NCO; scans: $\Delta H = -64.4, -57.8$ kJ/equiv NCO. In both cases, heat of reaction generated during material transfer and equipment stabilization is lost. It was estimated that this may have been as high as 20% of the total. The higher values obtained for scans may reflect the higher temperatures forcing reaction to completion at a rate discernable to the equipment.[22] These results do indicate that the value obtained from the adiabatic reaction method is reasonable.

Kinetic Expression

Values of dT/dt were obtained graphically from Figure 1, and eq. (6) was plotted for values of $n = 0.5$ to 2.0 in increments of 0.25. Values of c were calculated from eq. (2). A value of $n = 1.5$ was judged to give the best fit to a straight line. The plot is shown in Figure 3.

The kinetic expression obtained was

$$r_A = 8.319 \times 10^8 e^{-64{,}640/RT} c^{1.5} \text{ equiv NCO/m}^3 \cdot \text{min} \tag{8}$$

and

$$c_0 = 2.638 \times 10^3 \text{ equiv NCO/m}^3.$$

DISCUSSION

The overall accuracy of the data obtained can be evaluated by simulating the adiabatic temperature rises. Equations (3) and (8) were integrated numerically with a fourth-order Runga–Kutta procedure, using the above thermal and kinetic data. The results are shown by the dashed lines in Figure 1. Note that only the slopes of the temperature rise curves are used to obtain reaction kinetics, not the absolute time. The time at which reaction commences remains uncertain, since mixing continued for 15–30 sec. In plotting Figure 1, 15 sec after the start of mixing was taken as time zero.

The theoretical–experimental agreement seen in Figure 1 is fairly good, displaying deviations of ±8%. In absolute terms, this is an average error of +7.5 sec in the slowest reaction, −3 sec in the fastest. Note that eqs. (1)–(4), assuming C_p constant, can be combined to give

$$t = \frac{1}{A}\frac{\rho C_p}{(-\Delta H)c_0{}^n}\int_{T_0}^{T}\frac{dT}{e^{-E_R/RT}\left(1 - \dfrac{\rho C_p \cdot (T - T_0)}{(-\Delta H)c_0}\right)^n} \tag{9}$$

or

$$t = \frac{1}{A} f(E_R, n, T) \tag{10}$$

A constant percentage error in simulating the temperature rise may thus be interpreted as indicating a correct activation energy but an error in the preexponential factor. The deviations in Figure 1 cannot be explained solely in terms of an error in A, since two curves are faster and one is slower than the data. Uncertainty in time zero is probably also of significance.

CONCLUSIONS

Adiabatic reaction monitoring is a convenient method for obtaining chemical kinetics of fast, exothermic thermoset cures. The kinetic expression obtained is both reasonable and unobtainable by other means. A first-order kinetic expression previously obtained for the same system using intermediate catalyst concentrations[16] yielded reaction rates 100% too slow on extrapolation to the high catalyst concentration used in this study. This nonlinear dependence on

DBTDL catalyst concentration has been previously observed by Lipatova et al.[4] and Borkent and Van Aardsten.[5]

For the most accurate work, $C_p(T,c)$ should be known. Dependence on T should certainly be included, as was done here, in view of the large temperature increases. Polymer C_p increases 15% over the temperature range encountered in this study.

The ΔH obtained was lower than the few values given in the literature. DSC measurements confirmed that the value of −60 kJ/equiv NCO is not unreasonable. The possibility of reaction stopping short of completion was ruled out by IR measurements. Heat losses during reaction, which would cause the value of ΔH measured to be low, were estimated at 2% to 6% at most. The reaction conditions can therefore be considered adiabatic and the value of ΔH obtained to be ±10% accurate.

Certain drawbacks are, however, inherent in the method. While reactions conditions are best kept adiabatic by a very fast cure, other errors become magnified. More reaction can occur during mixing, and it becomes difficult to accurately measure the steep slopes of the temperature rise curves. Thermocouple response time may become important.

The high temperatures produced can result in undesirable side reactions and polymer degradation. This study used a relatively low NCO-content diisocyanate (18.55% by weight), so 393°K was not exceeded and the probability of side reactions was small. Commerical systems have higher NCO contents, e.g., toluene diisocyanate has 48.2%, 4,4′-diphenylmethane diisocyanate (MDI) has 33.6%, and the MDI-based liquid diisocyanates (Upjohn Co. Isonate 180, and Mobay Co. Mondur PF) have ~23% by weight.

This and other methods employing temperature scans (such as DSC and DTA) have the inherent disadvantage of measuring low-temperature kinetics at low conversions and high-temperature kinetics at high conversions. For a simple reaction mechanism with constant parameters this does not matter. When a complex reaction mechanism occurs, different steps may limit the reaction rate at different temperatures and extents of reaction. Kinetic parameters obtained from a scan could give erroneous isothermal results. A number of workers have, however, applied a single kinetic expression obtained from DSC scans to describe complete thermoset cures.[1,28]

This work was supported by grants from the National Science Foundation, Division of Materials Research, Grant No. DMR75-04508, the Union Carbide Corporation, and the University of Minnesota Computer Center.

Notation

A	preexponential factor in kinetic expression
c	reactive group concentration (g-equiv/m^3)
C_p	heat capacity (J/kg·°K)
E_R	activation energy of reaction (J/g-mole)
$\overline{M}_n$	number-average molecular weight
$\overline{M}_w$	weight-average molecular weight
n	order of kinetic expression
R	gas constant (8.3192 J/g-mole·°K)
r_A	reaction rate (g-equiv/m^3·min)

t	time (min)
T	temperature (°K)
ΔH	heat of reaction (J/g-equiv)
ρ	density (g/cc)
η	viscosity ($N \cdot s/m^2$)
$\dot{\gamma}$	shear rate (s^{-1})

References

1. M. R. Kamal, *Polym. Eng. Sci.*, **14**, 231 (1974).

2. S. D. Lipshitz and C. W. Macosko, *Polym. Eng. Sci.*, **16**, 803 (1976); S. D. Lipshitz, Ph.D. Thesis, Dept. of Chem. Eng. and Mat. Sci., University of Minnesota, 1976.

3. F. G. Mussatti, Ph.D. Thesis, Dept. of Chem. Eng. and Mat. Sci., University of Minnesota, 1975.

4. T. E. Lipatova, L. A. Bakalo, S. S. Ishchenko, and R. F. Gongalo, *Soviet Progress in Polyurethane Series,* Vol. I, Technomic Pub., Conn., 1973, pp. 49–56.

5. G. Borkent and J. J. Van Aardsten, in *Polymerization Kinetics and Technology,* N. A. J. Platzer, Ed., Advances in Chemistry Series, ACS, Washington, D.C., 1973.

6. T. E. Stonecypher, *CEP Symp. Ser.*, **61**, 7 (1966).

7. E. L. Allen, *Ind. Eng. Chem., Fundam.*, **8**, 828 (1969).

8. J. M. Douglas and L. C. Eagleton, *Ind. Eng. Chem., Fundam.*, **1**, 116 (1962).

9. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry, and Technology,* Part I, Interscience, New York, 1962; *ibid.*, Part II, 1964, p. 622.

10. P. Wright and A. P. C. Cummings, *Solid Polyurethae Elastomers,* Maclaren, London, 1969.

11. H. A. Smith, *J. Polym. Sci.*, **6**, 1299 (1968).

12. J. N. Greenshields, R. H. Peter, and R. F. T. Stepto, *J. Chem. Soc.*, **86**, 5101 (1964).

13. J. W. Baker and J. B. Holdsworth, *J. Chem. Soc., London,* 713 (1947).

14. J. L. Stanford, Ph.D. Thesis, Chem. Dept., University of Manchester, December 1972.

15. E. Anzuino, A. Pirro, G. Rossi, and L. Polo Friz, *J. Polym. Sci.*, **13**, 1657 (1975); *ibid.*, **13**, 1667 (1975).

16. S. D. Lipshitz, F. G. Mussatti, and C. W. Macosko, *SPE Tech. Papers,* **21**, 239 (1975).

17. M. S. Vilesova, N. P. Spasskova, L. V. Lesnevskaya, G. N. Guseva, L. G. Izrailev, and V. M. Zolotarev, *Polym. Sci. USSR,* **14**, 1883 (1972). Translated from Vysokomol. *Soedin.*, **A14**, 1685 (1972).

18. E. M. Valles and C. W. Macosko, *ACS Coat. Plast. Prepr.*, **35**(2), 44 (1975).

19. D. M. French, R. A. H. Strecker, and A. S. Tompa, *J. Appl. Polym. Sci.*, **14**, 599 (1970).

20. A. F. Maslyuk, S. A. Zubko, and V. V. Magdinets, *Soviet Progress in Polyurethanes Series,* Vol. II, Technomic Pub., Conn., 1975, pp. 120–3.

21. C. J. Page, Ph.D. Thesis, Chem. Dept., University of Manchester, Inst. of Sci. and Tech., 1974.

22. W. C. Darr, P. G. Gemeinhardt, and J. H. Saunders, *J. Cell. Plast.*, **2**, 266 (1966).

23. A. S. Wood, *Mod. Plast.*, **51**(6), 54 (1974); *ibid.*, **53**(6), 38 (1976).

24. E. Broyer and C. W. Macosko, *A.I.Ch.E. J.*, **22**, 268 (1976).

25. J. Agranoff, Ed., *Modern Plastics Encyclopedia,* Vol. 52, 10A, McGraw-Hill, New York, 1975–1976, p. 488.

26. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook,* Wiley, New York, 1975, p. V-7.

27. E. G. Lovering and K. J. Laidler, *Can. J. Chem.*, **40**, 26 (1962).

28. R. B. Prime, *Polym. Eng. Sci.*, **13**, 365 (1973).

Received February 25, 1976