Kinetics of Curing Reaction of Urethane Function on Base-Catalyzed Epoxy Reaction

J. L. HAN,[1] **Y. C. CHERN,**[2] **K. H. HSIEH,**[2] **W. Y. CHIU,**[2] **C. C. M. MA**[3]

[1] Department of Chemical Engineering, National I-Lan Institute of Agriculture and Technology, I-Lan, Taiwan

[2] Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

[3] Department of Chemical Engineering, National Tsing-Hua University, Hsin-Chu, Taiwan

ABSTRACT: The kinetic study on the effect of aromatic-connected carbamate (Ar-carbamate) on the curing reaction of phenyl glycidyl ether (PGE) catalyzed by tertiary amine was carried out through thermal analysis of the reaction by differential scanning calorimetry (DSC). By isothermal DSC analysis, the consumption rate of the epoxide group of PGE was found to be a first-order reaction in the presence of aromatic-connected carbamate in the reaction. It was found that the reaction system has a low activation energy ($E_a = 4.63$ kcal/mol) as compared to the system without Ar-carbamate ($E_a = 6.89$ kcal/mol). A reaction mechanism was proposed for this reaction system. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 121–127, 1998

Key words: aryl-connected carbamate (Ar-carbamate); epoxide group; tertiary amine; kinetic

INTRODUCTION

It is important to study the relationship between reaction kinetics and the properties of a cured resin in order to improve properties through the proper choice of processing. The polyurethane (PU)−crosslinked diglycidyl ether of bisphenol A (DGEBA) has been found to possess better toughness.[1–2] Therefore, the reaction kinetics of the PU−crosslinked epoxy reaction catalyzed by tertiary amine are worth investigating. In this work, we propose a model reaction in which the carbamate compound is added to the reaction system of tertiary amine-catalyzed epoxide. The model reaction is used to describe the reaction kinetics of the PU−crosslinked epoxy reaction catalyzed by tertiary amine.

According to his study on the curing reaction of epoxy with tertiary amine, Fricke proposed the following kinetic equation:

$$d\alpha/dt = k\alpha^m(1 - \alpha)^n$$

to describe an autocatalytic reaction,[3] where k and α are the reaction constant and conversion, respectively, and m and n are reaction orders. Recently, we also proposed a reaction mechanism for the epoxide catalyzed by tertiary amine.[4] Furthermore, from our previous studies,[5] it was found that, in the presence of aromatic-connected carbamate compound, the reaction rate of epoxide catalyzed by tertiary amine was clearly accelerated. The role that aromatic-connected carbamate compound plays in the reaction mechanism for the reaction system of epoxide catalyzed by tertiary amine is presented in this article.

Table I   Materials

Designation	Description	Source
PGE	Phenylglycidylether	Tokyo Chem. Ind.
BDMA	Benzyldimethylamine	Dow Chem. Co.
n-Butanol	*n*-Butanol	Hayashi Pure Chem.
MDI	4,4′-Diphenyl methane diisocyanate	Bayer Chem. Co.

EXPERIMENTAL

Material

The materials used and their designations are listed in Table I.

Preparation of Aromatic-Connected Carbamate Compound

One equivalent of aromatic isocyanate [that is, 4,4′-diphenyl methane diisocyanate (MDI)] was charged into a reaction kettle and heated until melted. Then, one equivalent of *n*-butanol was added and mixed with the molten MDI. The temperature was maintained at approximately 68°C during the reaction, which was carried out under dry nitrogen. A sample of the reacting mixture was withdrawn every hour for the infrared (IR) analysis, and the absorption peak of the —NCO group at 2270 cm^{-1} gradually decreased during the reaction (Fig. 1).[6] This indicated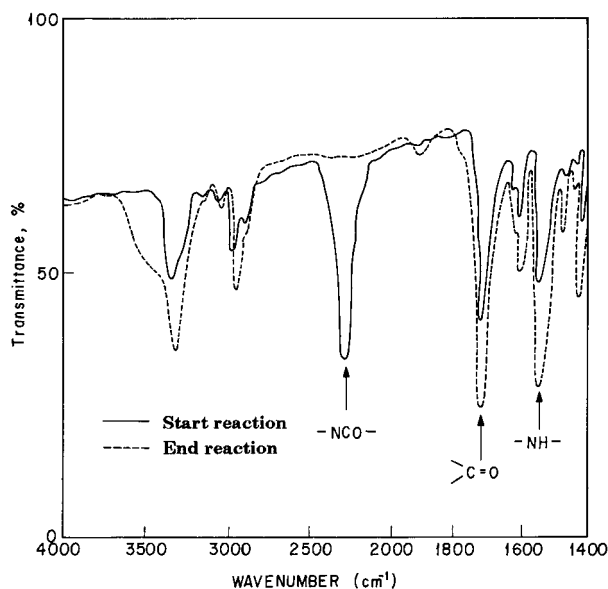 that the hydroxyl group of the *n*-butanol had reacted with the —NCO group of the MDI, and the absorption peaks of carbamate at 1720–1740 cm^{-1} for —NH— bending appeared in Figure 1.[7–9]

Infrared Measurement

IR analysis was performed with a Hitachi 270-30 IR spectrophotometer. The sample was placed directly on a KBr pellet.

Conversion Measurement from Differential Scanning Calorimetry

The conversion measurement from differential scanning calorimetry (DSC) is documented in the
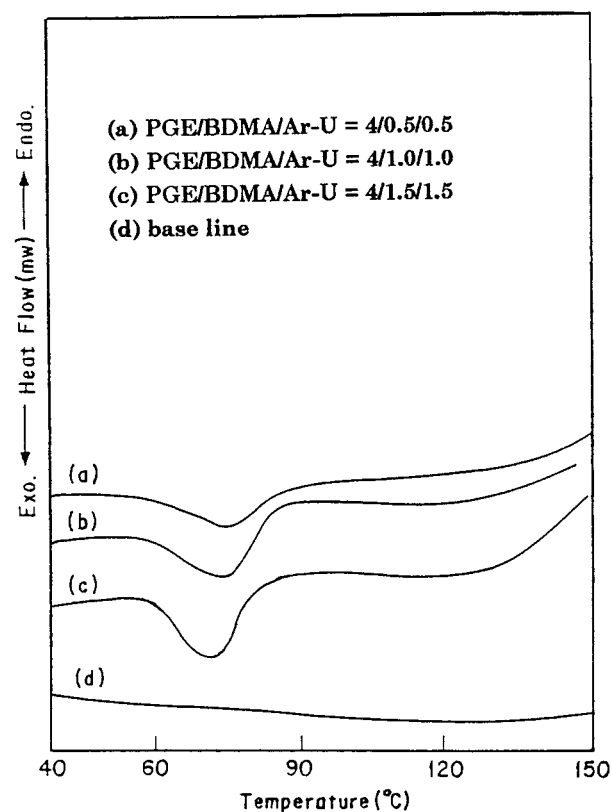

Figure 1   Infrared spectra of Ar-carbamate formation during the reaction.

Figure 2   Dynamic scanning DSC curves of PGE–BDMA–Ar-carbamate reaction system at various compositions (scanning rate: 5°C/min).
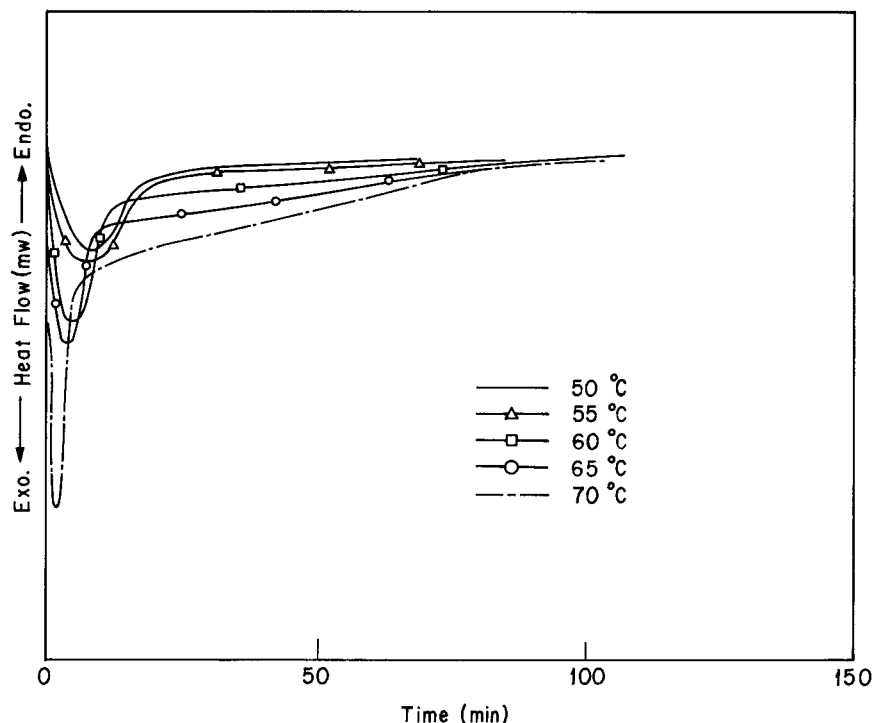
Figure 3 Isothermal DSC curves of PGE–BDMA–Ar-carbamate reaction system with an equivalent ratio of 4/0.5/0.5.

literature.[10–15] The epoxy compound was kept in a vacuum at 60°C for about 12 h in order to remove gas or moisture in the epoxy. Then, the mixture of a known weight (about 10 mg) of the epoxy with various contents of BDMA and aromatic-connected carbamate compound (Ar-carbamate) were put into the DSC aluminum pan (Perkin–Elmer DSC-7 unit) for conversion measurement. The DSC was calibrated with indium metal before the test. The DSC was performed with a heating rate of 5°C/min and a temperature range from 30 to 250°C. The isothermal mode was also performed. The total heat of isothermal reaction (ΔH_T) at temperature T was determined from the isothermal DSC curve. The area under the curve up to any time t represented the heat of reaction at time t, ΔH_t. After the isothermal test, the sample pan was quenched, and then the residual heat of the reaction (ΔHr) was measured from the following dynamic DSC curve. Then the total heat of reaction (ΔH) was obtained as the sum of ΔH_T and ΔHr. (that is, $\Delta H = \Delta H_T + \Delta Hr$). The conversion ($\alpha$) at time t and temperature T was calculated by $\alpha(t, T) = \Delta H_t/\Delta H$.

KINETIC EQUATION

In the PGE–BDMA–Ar-carbamate reaction system, the aromatic-connected carbamate compound (Ar-

carbamate) was found to combine with the catalyst BDMA to form a 1 : 1 complex, which catalyzed the epoxide groups in the ring-opening reaction.[5] Therefore, the rate equation for the consumption of epoxide group in the presence of Ar-carbamate is proposed as follows:

$$-d[\text{Ep}]/dt = k[\text{complex}]^m[\text{Ep}]^n \qquad (1)$$

where $k = A \times \exp(-E_a/RT)$, and $[\text{Ep}]$ and $[\text{complex}]$ are the concentrations of the epoxide group and complexes, respectively. k, E_a, and A are rate constant, activation energy, and frequency factor, respectively, and m and n are the reaction orders. Equation (1) can be substituted by the conversion, $\alpha = ([\text{Ep}]_0 - [\text{Ep}])/[\text{Ep}]_0$, and becomes

$$d\alpha/dt = k'(1 - \alpha)^n \qquad (2)$$

$$k' = k[\text{complex}]^m[\text{Ep}]_0^{n-1} \qquad (3)$$

where $[\text{Ep}]_0$ is the initial concentration of epoxide group.

Taking logarithms on both sides of eq. (2),

$$\ln(d\alpha/dt) = n \cdot \ln(1 - \alpha) + \ln k'$$

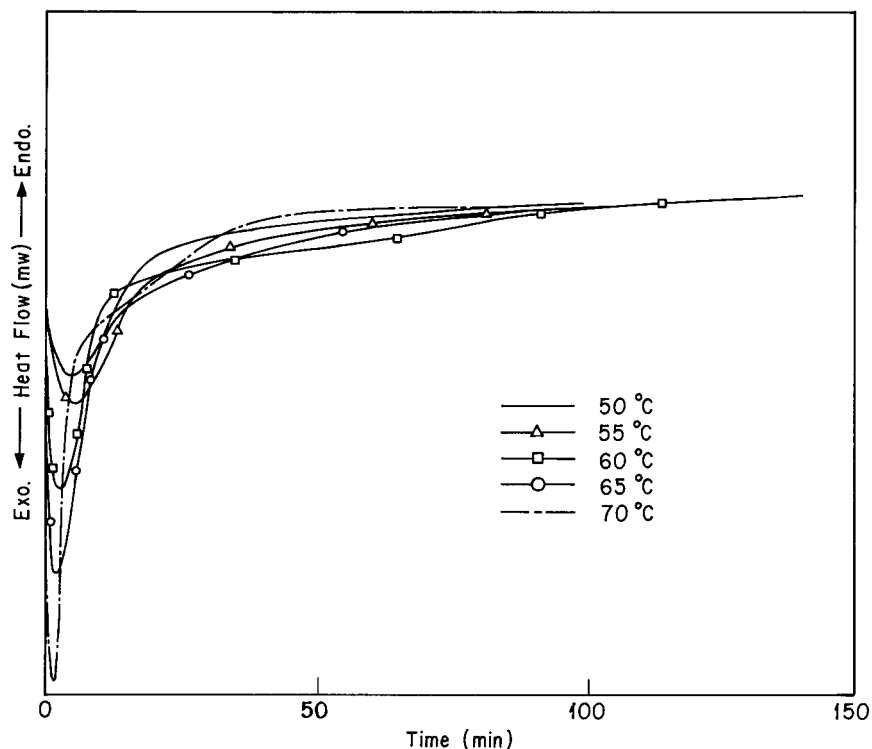Thus, n and k' can be determined from the

Figure 4 Isothermal DSC curves of PGE–BDMA–Ar-carbamate reaction system with an equivalent ratio of 4/1/1.

slope and the intercept, respectively, of the plot of in $(d\alpha/dt)$ versus $\ln(1 - \alpha)$, where α and $d\alpha/dt$ values are computed from the DSC data of the reaction. Similarly, taking logarithms on both sides of eq. (3),

$$\ln k' = m \cdot \ln[\text{complex}] + \ln k \, [\text{Ep}]_0^{n-1} \quad (5)$$

The n, k, and m can be determined from eq. (5) using more than three different concentrations of the complex related to their k' values. Furthermore, the constants A and E_a can be obtained from the plot of $\ln k$ versus $(1/T)$ by eq. (6), as follows:

$$\ln k = \ln A - (E_a/R) \cdot (1/T) \quad (6)$$

RESULTS AND DISCUSSION

Dynamic DSC Analysis

The dynamic scanning DSC data of PGE–BDMA–Ar-carbamate systems at various component compositions are shown in Figure 2. The varied equivalent ratios of BDMA and aromatic carbamate to PGE did not shift the peak temperature of the reaction. This implies that the same reac-

tion mechanism could be employed in PGE–BDMA–Ar-carbamate system within our experimental conditions in this work. The kinetic rate equation is proposed as eq. (1).

Reaction Kinetics

The kinetic study was performed by isothermal DSC. The heat of reaction (ΔH_t or ΔH) was determined from the peak area of the DSC, as mentioned in the experimental section. The conversion(α) is defined as the fraction of reaction heat to the total heat of the reaction, as follows:

$$\text{conversion}(\alpha) = \Delta H_t / \Delta H \quad (7)$$

The isothermal DSC curves of PGE–BDMA–Ar-carbamate reaction system are shown in Figures 3–5 at various temperatures and compositions. The conversions, calculated according to eq. (7) at various times for the PGE–BDMA–Ar-carbamate reaction system, are plotted in Figures 6–8. Following the procedures mentioned in the previous part, to find the reaction orders in eq. (1), the rate equation was found to obey the following[5]:
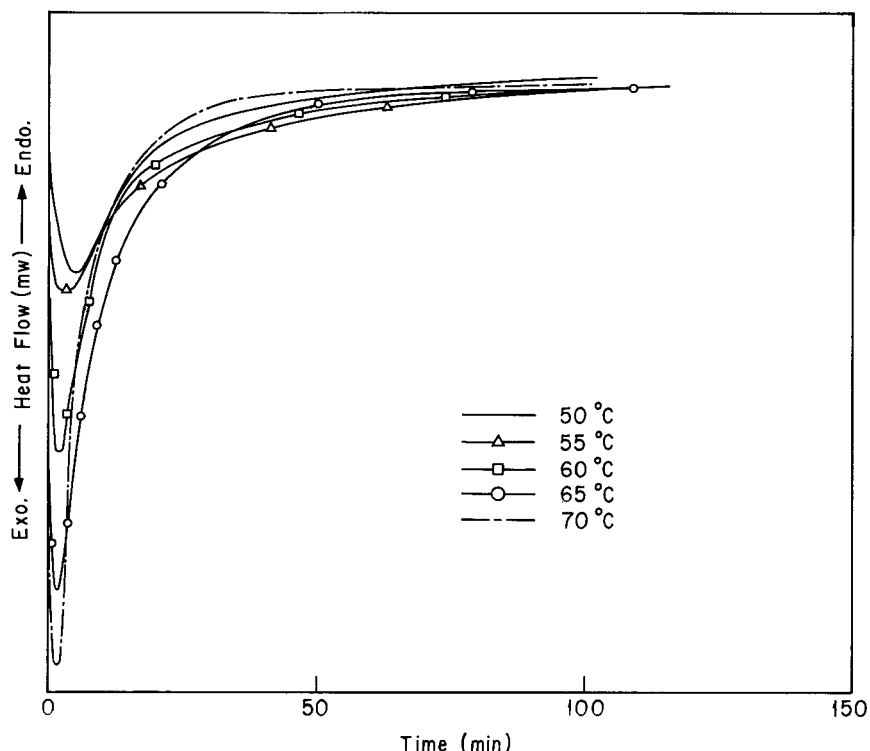
Figure 5 Isothermal DSC curves of PGE–BDMA–Ar-carbamate reaction system with an equivalent ratio of 4/1.5/1.5.

$$-d[\text{PGE}]/dt \cong k[\text{BDMA}]_0^2[\text{PGE}] \qquad (8)$$

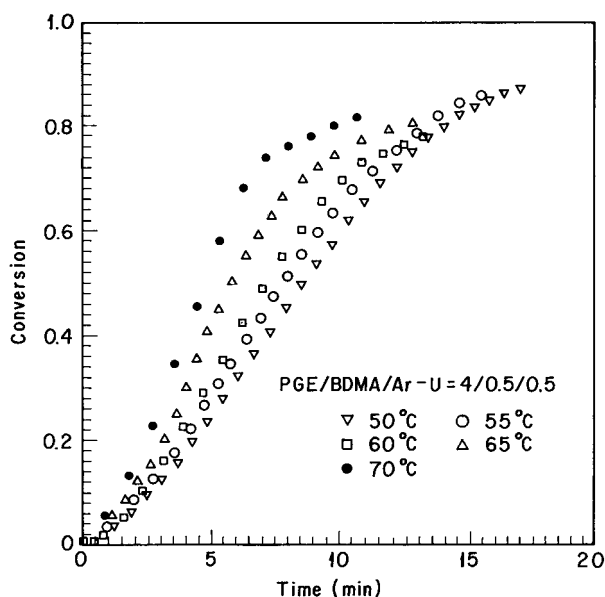being second order in the catalyst (BDMA) and

Figure 6 Conversion–time relation for the PGE–BDMA–Ar-carbamate (4/0.5/0.5) system at various reaction temperatures.

first order in the epoxide (PGE). Furthermore, in order to obtain the activation energy (E_a) and frequency factor (A) according to eq. (6), the values of reaction constants (k) should be measured at five different temperatures, that is, 50, 55, 60, 65, and 70°C, respectively. Then A and Ea can be determined from the intercept and the slope, respectively, from the plot of ln k versus $1/T$, as shown in Figure 9. It was found that E_a = 4.63 kcal/mol and $A = 3.01 \times 10^{10}$. Comparing with the activation energy of 6.89 kcal/mol,[4] for the epoxide group catalyzed by tertiary amine in the absence of Ar-carbamates, it has rather low activation energy, so the aromatic-connected carbamate obviously accelerated the reaction of epoxide catalyzed by tertiary amine.

Reaction Mechanism

From the observation of the above experimental data [eq. (8)], it was found that the consumption rate of the epoxide group was proportional to the first order of epoxide group in the reaction. From our previous study,[5] tertiary amine and aromatic carbamate would form a 1 : 1 complex catalyst first and then catalyze the epoxide group in the

Figure 7 Conversion–time relation for the PGE–BDMA–Ar-carbamate (4/1/1) system at various reaction temperatures.

ring-opening reaction. Therefore, a reaction mechanism can be proposed as appears in Scheme 1.

According to the mechanism in Scheme 1, the consumption rate of epoxide group is written as

$$-d[\text{Ep}]/dt$$

$$= k_2[\text{Ep}] + k_3[\text{Ep}]([(\text{complex})(\text{Ep})_i] \quad (9a)$$

Figure 8 Conversion–time relation for the PGE–BDMA–Ar-carbamate (4/1.5/1.5) system at various reaction temperatures.

Figure 9 Plot in Arrehenius form of the reaction rate constant and temperature.

Step (3) is the propagation reaction of the anionic polymerization, $k_3 \gg k_2$, with $(\text{complex})(\text{Ep})_i$ as the propagation center. The concentration of $[(\text{complex})(\text{Ep})_i]$ is a function of the $(\text{complex})_{\text{cat.}}$; thus, it is assumed that

Scheme 1

$\Sigma \ [(\mathrm{complex})(\mathrm{Ep})_i] \ = \ f \ ([\mathrm{complex}]_{\mathrm{cat.}}) \ = \ k \times [\mathrm{complex}]_{\mathrm{cat.}}$ Then equation (9a) becomes

$$-d[\mathrm{Ep}]/dt \cong k_3 k[\mathrm{complex}]_{\mathrm{cat.}}[\mathrm{Ep}] \quad (9\mathrm{b})$$

where $[\mathrm{complex}]_{\mathrm{cat.}}$ is the concentration of the $(\mathrm{complex})_{\mathrm{cat.}}$. Assuming that step (1) reaches equilibrium, then

$$[\mathrm{complex}]_{\mathrm{cat.}} = (k_1/k_1')[\mathrm{NR}_3][\mathrm{Ar\text{-}U}]$$
$$= k_{\mathrm{eq}}[\mathrm{NR}_3][\mathrm{Ar\text{-}U}] \quad (9\mathrm{c})$$

where the $k_{\mathrm{eq}} = (k_1/k_1') = $ the equilibrium constant. Let $[\mathrm{NR}_3]_0 = [\mathrm{Ar\text{-}U}]_0 = C_0 = $ the initial concentration of the tertiary amine or the aromatic carbamate, and $[\mathrm{complex}]_{\mathrm{cat.}} = C = $ concentration of the $(\mathrm{complex})_{\mathrm{cat.}}$, then $[\mathrm{NR}_3] = [\mathrm{Ar\text{-}U}] = (C_0 - C)$.

From eq. (9c), we obtain $C = k_{\mathrm{eq}}(C_0 - C)^2$ or $k_{\mathrm{eq}} = C/(C_0 - C)^2$. Assuming k_{eq} is small (that is, $C_0 \gg C$), then $C \cong k_{\mathrm{eq}}C_0^2$ or $[\mathrm{complex}]_{\mathrm{cat.}} \cong k_{\mathrm{eq}}[\mathrm{NR}_3]_0^2$, substituting in eq. (9b),

$$-d[\mathrm{Ep}]/dt \cong k_3 k k_{\mathrm{eq}}[\mathrm{NR}_3]_0^2[\mathrm{Ep}]$$
$$= K[\mathrm{NR}_3]_0^2[\mathrm{Ep}] \quad (9\mathrm{d})$$

where $K = k_3 k k_{\mathrm{eq}}$. Equation (9d) conforms well with eq. (8).

CONCLUSION

A reaction mechanism for PGE−BDMA−Ar-carbamate system is proposed, where the tertiary amine and the aromatic carbamate forms a 1 : 1 complex catalyst first and then catalyzes the epoxide group in the ring-opening reaction. The consumption rate of the epoxide group is proportional to the first order of the epoxide group and the second order of the tertiary amine concentration.

It has a rather low activation energy, so in the presence of aromatic-connected carbamate, the reaction of epoxide catalyzed by the tertiary amine is obviously accelerated through complex formation with catalyst and the epoxide ring-opening mechanism.

REFERENCES

1. J. L. Han, S. M. Tseng, J. H. Mai, and K. H. Hsieh, *Angew. Makromol. Chem.,* **182,** 193 (1990).
2. J. L. Han, S. M. Tseng, J. H. Mai, and K. H. Hsieh, *Angew. Makromol. Chem.,* **184,** 89 (1991).
3. S. Y. Pusstcioglu, A. L. Fricke, and J. C. Hassler, *J. Appl. Polym. Sci.,* **24,** 937 (1979).
4. J. L. Han, K. H. Hsieh, and W. Y. Chiu, *J. Appl. Polym. Sci.,* **50,** 1099 (1993).
5. J. L. Han, K. H. Hsieh, W. Y. Chiu, and L. W. Chen, *J. Polym. Res.,* **2,** 2, 15 (1996).
6. L. Hepburn, *Polyurethane Elastomer,* Applied Science, New York, 1982, p. 307.
7. L. J. Bellamy, *The Infrared Spectra of Complex Molecular,* John Wiley, New York, 1954, p. 191.
8. D. Dolphin and A. Wick, *Tabulation of Infrared Spectral Data,* John Wiley, New York, 1977, p. 396.
9. G. Socrates, *Infrared Characteristic Group Frequencies,* John Wiley, New York, 1980, p. 79.
10. H. E. Kissinger, *Anal. Chem.,* **29,** 11, 1702 (1957).
11. R. B. Prime, *Thermal Characterization of Polymeric Material,* A. Tuei, Ed., Academic Press, New York, 1985, p. 435.
12. M. R. Kamal and S. Sonronr, *Polym. Eng. Sci.,* **13,** 59 (1973).
13. K. Horie, I. Mita, and H. Kambe, *J. Polym., Sci.,* **A1,** 2839 (1982).
14. P. E. Willard, *Polym. Eng. Sci.,* **12,** 120 (1972).
15. C. C. Riccardi, H. E. Adebbo, and R. J. J. Williams, *J. Appl. Polym. Sci.,* **29,** 2481 (1984).