Cure Properties of Epoxies with Varying Chain Length as Studied by DSC

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ABSTRACT: The cure of diglycidyl ether of bisphenol A (DGEBA) and a homologous series of poly(ethylene oxide) diglycidyl ether (PEODE) epoxy resins with 4,4'-diaminodiphenyl sulfone (DDS) was studied by scanning and isothermal differential scanning calorimetry (DSC). The heat of polymerization was relatively independent of monomer structure and chain length when determined by isothermal DSC. Variations in the heats of polymerization determined by the scanning method were attributed to degradative reactions at higher temperatures during the scan. The activation energies determined by scanning DSC experiments were relatively constant at 61 ± 3 kJ/mol. However, using an isothermal cure method, the activation energies were found to vary with monomer structure and extent of cure. The isothermal kinetics were analyzed in terms of the autocatalytic model on the basis of competing reaction paths involving catalysis by either initial impurities or hydroxyl groups produced *in situ*. The activation energies of both reaction paths were found to vary with monomer structure and degree of conversion. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1479–1488, 1999

Key words: epoxy resin; DSC; cure kinetics; activation energy

INTRODUCTION

Epoxy resins are widely used in coating and structural applications,¹ because the cured thermosetting polymer can be tailored to suit specific performance characteristics. As a result of their high-crosslink density and aromatic backbone, most epoxy resins are rigid materials and fail by brittle fracture.² The earliest epoxy resins marketed³ were those based on the condensation reaction of epichlorohydrin and bisphenol A, using an alkaline catalyst such as sodium hydroxide.⁴ This method is still the major route for the manufacture of most resins marketed today. The resins formed may be regarded as glycidyl ethers of bisphenol A, with the oligomeric nature of the resin controlling the length and molecular weight

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of the epoxy chain. The shortest chain-length monomer available is the commonly used diglycidyl ether of bisphenol A (DGEBA) resin, shown schematically in Figure 1. Similarly, aliphatic diols of various chain lengths can be substituted for bisphenol A, resulting in a range of more flexible poly(ethylene oxide) diglycidyl ether (PEODE-n) epoxy derivatives also shown in Figure 1.

The glycidyl group is a highly strained, threemembered ring ether⁵ and readily reacts with hardening agents by nucleophilic attack on the α -carbon of the epoxy ring. A range of chemical agents with active hydrogen atoms can be used to cure epoxy resins,⁶ although the most important curing reactions occur with amines. Here, the overall curing process involves an attack of the amine group on the terminal carbon atom of the glycidyl unit, subsequently converting the epoxide to a hydroxyl group (Scheme 1).

According to Tanaka,⁷ the curing mechanism involves a complex intermediate, stabilized by the

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4,4'-diaminodiphenyl sulfone (DDS)

Figure 1 Amine and epoxy resin starting materials.

formation of a hydrogen-bonded species (Scheme 2). This hydrogen bonding causes the electron deficient epoxy complex (4) to become more susceptible to nucleophilic attack by the incoming amino group.

Because the curing process actually produces hydroxyl groups that can act as the hydrogen bonding species, the epoxy-diamine reaction becomes autocatalytic as it proceeds. Hence, the overall mechanism of epoxy reaction relies on the presence of free-proton donors and the formation of a stabilized complex intermediate.

It is important to understand how the epoxy network develops kinetically, as this is related to the final network structure and determines physical and engineering properties.⁸ During the early phase of polymerization, the viscosity of the sys-



Scheme 1



tem is relatively low and molecular motion is not restricted. As the reaction proceeds, a highly branched macromolecule begins to form and a steep increase in viscosity is indicative of the onset of gelation. Beyond gelation and dependent on the proximity of the ultimate glass transition (T_g) of the material to the cure temperature (T_{cure}), the system may pass from the rubbery state to the glassy state, causing a dramatic decrease in the segmental motion of the polymer chains and a rapid rise in the modulus. Subsequently, the reaction rate slows as it becomes increasingly diffusion controlled and virtually stops when the T_g is in the vicinity of T_{cure} .⁹

To measure epoxy cure kinetics, the reaction process must be monitored as the material passes from the liquid to the rubber state and/or to the vitrified state. Differential scanning calorimetry (DSC) is the most widely used method for monitoring cure as the rate of heat evolved is directly proportional to the rate of reaction.^{10–12} In addition, DSC may be operated in the dynamic mode with a constant scanning rate (heating or cooling) or in the isothermal mode for a given cure temperature.

In the dynamic mode, a temperature scan of the catalyzed epoxy monomer sample produces an exothermic curing peak in the DSC trace. Kissinger¹³ showed that analysis of scanning exotherms obtained by varying the scan rate can give an average activation energy E_a as

$$-\ln(\Phi/T_p^2) = E_a/RT_p - \ln(AR/E_a)$$
(1)

where Φ is the heating rate, T_p is the temperature of peak exothermic cure, A is a pre-exponential constant, and R is the gas constant. Unfortunately, this method can only analyze the overall process and a complex reaction exotherm may actually conceal several competing reactions, including primary and secondary amine attack on epoxy groups, homopolymerization, etherification, and degradation.¹⁴ This makes the analysis of E_a and polymerization kinetics from temperature scanning DSC experiments fraught with difficulty. In contrast, isothermal measurements of epoxy cure and their interpretation may be somewhat more informative.¹⁵ Analysis of DSC data usually assumes that the total area under the exothermic peak ΔH_{total} is equal to the overall heat of polymerization after complete reaction. The fractional conversion α is therefore determined by dividing the heat evolved during isothermal cure up to a particular time ΔH_t by the total exothermal energy

$$\alpha = \Delta H_t / \Delta H_{\text{total}} \tag{2}$$

At a given time or temperature, the overall reaction rate can be described as a function of conversion and temperature 12,13

$$d\alpha/dt = f(\alpha)k(T) \tag{3}$$

where $f(\alpha)$ is a function of the fractional conversion and k(T) is the apparent rate constant. If the rate constant has an Arrhenius form as in

$$k(T) = A \exp(-E_a/RT) \tag{4}$$

then eqs. (3) and (4) can be used to analyze isothermal experiments at several curing temperatures and thus yield the activation energy at a particular conversion.

Horie et al.¹⁶ summarized the overall kinetic cure scheme of an epoxy/diamine system (Scheme 3) as follows:

$$A_1 + E + (HX)_A \xrightarrow{k_1} A_2 + (HX)_A \tag{5}$$

$$A_1 + E + (HX)_0 \xrightarrow{k_{1c}} A_2 + (HX)_0 \tag{6}$$

$$A_2 + E + (HX)_A \longrightarrow A_3 + (HX)_A \tag{7}$$

$$A_2 + E + (HX)_0 \xrightarrow{k_{2c}} A_3 + (HX)_0 \tag{8}$$

where E, A_1 , A_2 , and A_3 represent epoxide, primary, secondary, and tertiary amine groups, respectively. $(HX)_0$ signifies a catalyst impurity initially present in the system, whereas $(HX)_A$ is the hydroxyl catalyst formed during the amine–epoxy reaction. If e, a_1 , a_2 , and x are the concentrations of E, A_1 , A_2 , and $(HX)_A$ at time t, respectively, and if e_0 , a_0 , and C_0 are the initial concentration of E, A_1 , and $(HX)_0$, then the rate of reaction of epoxide at time t can be given by the equation¹⁶:

$$-de/dt = [(e_0 - x)(a_1 + a_2/2)](k_1x + k_{1c}C_0) \quad (9)$$

Equation (9) assumes that the reaction of epoxy groups with aminohydrogens on primary and secondary amines are of equal probability. If the epoxy-amine mixture is stoichiometric $(e_0 = 2a_0)$, then the rate of epoxy conversion (-1/e)(de/dt) can be simplified to

$$d\alpha/dt = e_0^2 (1 - \alpha)^2 (k_1 \alpha + k_{1c} C_0 / e_0) / 2 \quad (10)$$

Subsequent manipulation results in the following equation for epoxy curing with impurity catalysis and autocatalysis:

$$d\alpha/dt = K_1(1 - \alpha)^2(\alpha + K_{1c}/K_1)$$
(11)

where K_1 is $e_0^2 k_1 / 2$ and K_{1c} is $e_0 C_0 k_{1c} / 2$.

In this study, we investigate the cure kinetics of a series of epoxy resins with varying crosslink density as part of a more thorough investigation of their structure–property relationships.

EXPERIMENTAL

The epoxy resins used in this study were DGEBA (Shell Epikote 8283, Geelong, Vic., Australia) and a series of increasingly flexible PEODE-n derivatives (Polysciences Inc., Warrington, PA), where the ethylene oxide sequence length (n) varied as 1, 4.5, 9, and 14. The amine curing agent was 4,4'-diaminodiphenyl sulfone (DDS, Ciba–Geigy HD976, Thomastown, Vic., Australia). The chemical structures are shown in Figure 1. The materials were used as supplied, without further purification.

The mass of resin per epoxy group, or epoxy equivalent weight (EEW), was determined by acid titration.¹⁷ The epoxy was reacted with a known excess of hydrochloric acid (HCl) in dimethylformamide (DMF) and back titrated with sodium hydroxide to determine the amount of unreacted HCl. The molecular weight of the epoxy resin was calculated from the EEW by assuming the resin was bifunctional.

Monomer	$egin{array}{llllllllllllllllllllllllllllllllllll$	Experimental M_w by GPC, $M_{ m GPC}$ (g/mol)	$egin{array}{llllllllllllllllllllllllllllllllllll$
DGEBA	340	381	460
PEODE-1	174	298	265
PEODE-4.5	328	438	433
PEODE-9	526	836	633
PEODE-14	746	944	833

Table I Molecular Weight Characterization of Monomeric Starting Materials

Gel permeation chromatography (GPC) was performed on the epoxy resins to estimate the average molecular weight and molecular weight distribution. The resins were dissolved in tetrahydrofuran before analysis and the sample solution injected (100 μ L) onto the 100 Å Ultrastyragel column (Waters, Milford, MA) with a flow rate of 1.0 mL/min at 30°C. The molecular weights of the epoxy resins were calculated from a calibration curve constructed using polystyrene standards with narrow polydispersity.

All network polymers synthesized in this study were prepared from stoichiometric mixtures of the epoxy resin and DDS. The DDS was assumed to be 100% reactive and sufficient diamine was added to provide one amine proton for each epoxy functional group. Samples were prepared by mixing the appropriate epoxy and amine components in a beaker and by heating to 130°C while stirring. When the solution became transparent, the catalyzed resin was cooled and stored in a freezer until required so as to minimize the onset of any curing reactions.¹⁸

Calorimetric measurements were made using a Perkin-Elmer DSC-7 under a constant purge of nitrogen gas (20 mL/min). Calibration was performed with known masses of pure indium and zinc. Accurately weighed amounts of catalyzed epoxy-diamine resin (10-20 mg) were placed in sealable aluminum sample pans specifically designed for DSC use and studied by isothermal- or temperature-scanning DSC. Catalyzed epoxy samples were cured isothermally in the DSC at 20°C intervals between 120 and 220°C. Each sample was ramped to the desired isothermal curing temperature by using a nominal heating rate of 200°C/min. It was assumed that negligible curing occurred during this ramping period. Scanning experiments were also performed on catalyzed samples and involved ramping the cure temperature to a predetermined value by using temperature scan rates varying between 1 and 30°C/min. Following cure, the samples were rescanned at 10°C/min to determine the T_g of the cured materials.

RESULTS AND DISCUSSION

Epoxy Resin Characterization

GPC¹⁸ was used as a relative measure of polydispersity and molecular weight of the epoxy resins, whereas epoxy group titration was used as a quantitative measure of molecular weight. The GPC molecular weight and molar mass calculated by titration were in reasonable agreement with theoretical values; the results are shown in Table I. As expected, the measured molecular weight increased as the number of ethylene oxide units increased. The theoretical molecular weight was consistently higher than the GPC and titration values, possibly due to oligomers and unreacted impurities initially present in the systems. The shorter chain length PEODE derivatives had multimodal GPC curves, whereas the longer chain length PEODE systems showed lower polydispersity with single, broad peaks. The actual concentration of epoxy groups, determined by titration, was used in the calculation of all stoichiometric quantities for sample preparation.

Scanning Cure Kinetics

Temperature scanning DSC can give useful preliminary information on the curing kinetics of epoxy systems.¹² DSC temperature scans were performed on the catalyzed resins with scan rates of 1–30°C/min and the overall heats of polymerization, ΔH_{total} , were determined in joules per gram. The heat of polymerization per mol of ep-



Figure 2 Scanning DSC traces for selected systems at 5°C/min.

oxide, $\Delta H'_{\rm total}$ was calculated in kilojoules per mol according to 19

$$\Delta H'_{\text{total}} = \Delta H_{\text{total}} (M_{\text{epoxy}} + 0.5M_{\text{amine}})/2 \quad (12)$$

where $M_{\rm epoxy}$ and $M_{\rm amine}$ are the molecular weights of the epoxy and amine, respectively. Figure 2 shows the cure of selected epoxy systems at a scan rate of 5°C/min. The overall heat of polymerization was averaged from scanning DSC runs at five different scan rates and is listed in Table II. This initial work provided useful information for understanding molecular mobility and curing processes in the epoxy systems. Variations in the total heat of polymerization and peak curing temperature confirmed that monomer structural differences affected the curing process. An increase in the number of ethylene oxide units in the epoxy backbone resulted in less exothermic heat released during cure, due to the reduction in epoxy groups present per gram. Unexpectedly. the heat of reaction per mol of epoxide also varied slightly with chain length. Nae²⁰ and Greenfield²¹ noted that the heat of cure per mol of epoxy in

epoxy-amine systems should theoretically remain constant. In the present study, differences in the PEODE resin structure may have affected the amount of energy released by epoxy ring opening, as observed by DSC, with the shortest chain length PEODE-1 releasing the most energy. In addition, the decrease in the amount of heat released per mol of epoxide is concomitant with a higher peak curing temperature required to cure the longer chain-length systems (see Fig. 2), so that the reduction in $\Delta H'_{total}$ may be partly due to degradative reactions that occur as the scan reached higher temperatures.

The exothermic peak temperature in scanning DSC (T_p) gives an indication of the maximum rate of cure for a given heating rate. The peak curing temperature of the PEODE resins increased as the chain length increased, reflecting that higher molecular weight epoxies polymerize slower at a given temperature. This may be caused by the lower concentration of reactive groups or the lower reactivity of the longer chainlength derivatives (Table II). The extent of cure at T_p was approximately constant for each resin at about 40–50% cure independent of heating rate.

As expressed in eq. (1), the temperature at the peak exotherm (T_p) depends on the heating rate.¹³ Figure 3 shows examples of plots of the Kissinger equation that were used to determine the average E_a for the overall reaction. The activation energy results in Table II indicate that an energy barrier of similar magnitude was involved in the cure of each resin system, irrespective of monomer structure.

Isothermal Cure Kinetics

Isothermal cure was investigated to establish an accurate kinetic model for the cure of the epoxy systems. The isothermal experiments were conducted at various cure temperatures ranging from 120-240 °C. The total heat of polymerization

Table IIAverage Heat of Polymerization, Peak Curing Temperature, and Activation EnergyObtained from Scanning DSC

Monomer	Average Heat of Polymerization, $\Delta H_{\rm total}~({ m J/g})$	Average Heat of Polymerization, $\Delta H'$ (kJ/mol)	$\begin{array}{c} {\rm Peak} \\ {\rm Temperature,} \\ {T_p} \ (^{\rm o}{\rm C}) \end{array}$	Kissinger Activation Energy, E _a (kJ/mol)
DGEBA	281.6 ± 10	82.2 ± 3.5	213	61.8 ± 1.9
PEODE-1	496.8 ± 20	96.6 ± 4.0	194	58.0 ± 1.7
PEODE-4.5	266.4 ± 7	74.2 ± 2.0	203	64.6 ± 1.9
PEODE-9 PEODE-14	$\begin{array}{c} 176.7\pm10\\ 136.8\pm10\end{array}$	$\begin{array}{c} 66.9 \pm 4.0 \\ 65.5 \pm 5.0 \end{array}$	$\begin{array}{c} 229 \\ 254 \end{array}$	$\begin{array}{c} 59.7 \pm 1.8 \\ 60.2 \pm 1.8 \end{array}$



Figure 3 Kissinger plot [eq. (1)] of activation energies for DGEBA/DDS and selected PEODE/DDS epoxy systems.

was obtained from the average of at least four isothermal temperatures above the maximum attainable T_g . Many authors have previously noted^{22–24} that the heat of reaction obtained by scanning DSC is consistently lower than that for isothermal DSC experiments. Table III shows that this was generally also the case with the aliphatic epoxy systems in this study. The difference is thought to have resulted from degradation of the polymer and baseline uncertainties at the higher temperatures for thermally scanned samples. The isothermal heat of polymerization per mol of epoxy, $\Delta H'_{total}$ in Table III, remained more constant for all chain lengths than in scanning DSC, confirming this degradation hypothesis.

It is also widely accepted that isothermal experiments generate more reliable kinetic parameters.²⁴ Isothermal activation energies were determined at conversions corresponding to the maximum reaction rate²⁵ and compared with the corresponding values obtained from scanning



Figure 4 Conversion (α) versus time curves for PEODE-1/DDS system at different cure temperatures determined by isothermal DSC.

DSC (Table III). In contrast to the E_a obtained by scanning experiments (Kissinger¹³ method), isothermal activation energies decreased slightly as the chain length increased. This may be due partly to the difficulty in accurately calculating the isothermal E_a for PEODE-9 and PEODE-14 due to degradation that cannot be separated by DSC analysis, coupled with poor peak definition in the rate versus conversion curves for these systems (see Fig. 7). Another reason for a chainlength effect on E_a is related to the impurity catalysis and autocatalysis reaction steps and is discussed below.

The change in conversion with time for the isothermal cure of the PEODE-1/DDS system is shown in Figure 4. The rate of conversion increased with increasing cure temperature, as did the ultimate level of conversion. As shown in Figure 5, the cure process was mainly dependent on the structure of the epoxy resin. Longer chain length systems such as PEODE-14 cured slower than the shorter systems at any given tempera-

 Table III Comparison of Heats of Polymerization and Activation Energies from Scanning and Isothermal DSC

	Heat of Polymerization, $\Delta H'_{\mathrm{total}}$		Activation Energy, E_a	
Monomer	Average from Scanning DSC (kJ/mol)	Average from Isothermal DSC (kJ/mol)	Scanning DSC Analysis (kJ/mol)	Isothermal Rate Maximum (kJ/mol)
DGEBA PEODE-1 PEODE-4.5	82.2 ± 3.5 96.6 ± 4.0 74.2 ± 2.0	82.5 ± 3.5 90.2 ± 2.0 82.9 ± 2.0	$61.8 \pm 1.9 \\ 58.0 \pm 1.7 \\ 64.6 \pm 1.9$	$61.9 \pm 1.5 \ 63.4 \pm 1.6 \ 61.4 \pm 1.5$
PEODE-9 PEODE-14	$\begin{array}{c} 66.9 \pm 4.0 \\ 65.5 \pm 5.0 \end{array}$	$\begin{array}{c} 83.8 \pm 4.0 \\ 76.6 \pm 4.5 \end{array}$	$\begin{array}{c} 59.7 \pm 1.8 \\ 60.2 \pm 1.8 \end{array}$	$\begin{array}{c} 60.5 \pm 2.4 \\ 53.8 \pm 2.4 \end{array}$



Figure 5 Conversion (α) versus time curves for PEODE/DDS systems with varying chain length at 200°C cure temperature determined by isothermal DSC.

ture, confirming the scanning DSC results from Table II, in which longer chain-length epoxies exhibited higher peak curing temperatures.

Typically, the dependence of isothermal reaction rate $(d\alpha/dt)$ on time showed a maximum. Figure 6 shows isothermal DSC rate versus conversion data at different temperatures for the PEODE-1/DDS epoxy system, whereas Figure 7 shows curing rates at 200°C for the entire PEODE chain-length range. The decrease in reaction rate with increasing chain length is consistent with the scanning DSC results (Fig. 2, Table II) and may be attributed to the decreasing concentration of reactive groups or a reduction in epoxy group reactivity in these resin mixtures. After the DSC equilibrated at the isothermal cure temperature, the DSC results showed a nonzero initial rate, indicating that initial impurity catal-



Figure 6 Rate $(d\alpha/dt)$ versus conversion (α) for PE-ODE-1/DDS system at different cure temperatures determined by isothermal DSC.



Figure 7 Rate $(d\alpha/dt)$ versus conversion (α) for PEODE/DDS system with varying chain length at 200°C cure temperature determined by isothermal DSC.

ysis of the epoxy-diamine system occurred at the very earliest stages of the reaction. In addition, a maximum in the reaction rate was generally observed at conversions of about 20–30%, which is consistent with autocatalysis resulting from the formation of additional hydroxyl groups.^{16,26} All reaction rates approached zero as each system reached full cure, although the conversion did not necessarily reach 100% before the reaction ceased.

To analyze the curing kinetics, it is necessary to apply the equation expressing the rate of conversion as a function of conversion and temperature [eq. (3)]. The rate constant k is often assumed to follow an Arrhenius form [eq. (4)]. Given this assumption, eqs. (3) and (4) can be combined to give¹⁸

$$\ln(d\alpha/dt) = Bg(\alpha) - E_{\alpha}/RT$$
(13)

where B is a constant and g is a function of α . Thus, a graph of $\ln(d\alpha/dt)$ versus 1/T at constant conversion should be a straight line with the activation energy for polymerization calculated from the slope. Figure 8 illustrates this plot at conversions of 0–90% and shows how E_a varies with conversion. The change in activation energy as a function of cure (Fig. 9) may be an indicator of changes in curing mechanism. Barton¹⁹ found that the E_a appeared to increase after about 50% conversion, which he attributed to the increase in viscosity of the curing system and increasing diffusion control as vitrification was approached. This explanation for the change in E_a as a result of vitrification is not consistent with the manner



Figure 8 $\ln(d\alpha/dt)$ versus 1/T for PEODE-4.5/DDS system at various conversions determined by isothermal DSC.

in which E_a is determined from the dependence of the logarithm of rate versus the reciprocal temperature, as these plots assume \boldsymbol{E}_a is constant and independent of temperature at each level of conversion. If vitrification causes the rate of cure to decrease, a marked downward deviation from linearity should be observed at constant conversion in the plot of $\ln(d\alpha/dt)$ versus 1/T for temperatures approaching T_g . Thus, plots of $\ln(d\alpha/d\alpha)$ dt) versus 1/T (Fig. 8) may depart from linearity at higher levels of conversion and lower curing temperatures, accentuating the increase in E_a shown in Figure 9. However, the PEODE aliphatic epoxy systems do not vitrify at these curing temperatures, so vitrification effects cannot be involved here. It is possible that the increasing difficulty in forming the hydrogen-bonded intermediate species as the network structure devel-



Figure 9 Activation energy (E_a) of epoxy systems as a function of conversion by assuming a single reaction process (eq. 13) determined by isothermal DSC.



Figure 10 Rate $(d\alpha/dt)$ versus conversion (α) curves from eq. (11) (dashed line) compared with experimental results (solid line) for PEODE-1/DDS determined by isothermal DSC.

oped (Scheme 2) contributed to the variation in E_a .

It is also possible that the variation in E_a with conversion may be a consequence of the presence of two rate processes [eqs. (5) and (7) compared with eqs. (6) and (8)] with differing activation energies. To analyze this possibility, the cure kinetics of each system was fitted to the autoaccelerated rate model¹⁶ in eq. (11). The rate process was thus separated into an initial impurity catalysis component [eqs. (6) and (8)] and an autocatalysis component [eqs. (5) and (7)], each with its own activation energy rather than a single value for the overall process.

Curves of experimental rate versus conversion compared well with the theoretical curves predicted from eq. (11), as shown in Figure 10 for the POEDE-1/DDS system at 140 and 200°C. Given that eq. (11) is a suitable approximation to the epoxy cure, the constants K_{1c} (initial impurity catalysis) and K_1 (autocatalysis due to hydroxyl groups produced *in situ*) can be calculated as a function of temperature at various conversions. The rate at zero conversion yields the impurity catalysis rate constant K_{1c} . Substitution of K_{1c} into eq. (11) yields the rate constant K_1 at selected conversions. For example, at 20% conversion ($\alpha = 0.2$)

$$d\alpha/dt = 0.128K_1 + 0.64K_{1c} \tag{14}$$

The two rate constants were plotted logarithmically versus 1/T at particular degrees of conversion and the activation energies were compared with the E_a calculated assuming a single



Figure 11 Dependence of E_{α} on conversion for PEODE-1/DDS, calculated by assuming a single reaction process [eq. (13), open square and solid line] or calculated by the autocatalytic model with K_{1c} ($\alpha = 0$, dashed line) and K_1 ($\alpha = 0.1-0.8$) from eq. (11) (filled diamond and dashed line).

reaction process (Fig. 11). The fitted value for the rate at zero conversion corresponded to the E_a for K_{1c} due to the effect of initial impurities in each system, and this was assumed to be constant through the entire reaction. Figure 11 shows that for PEODE-1/DDS, the change in activation energy for K_1 (the autocatalysis reaction rate) increased with conversion, as did the activation energy determined with the assumption of a single reaction process. It is possible that this reflects the increasing difficulty in the formation of the hydrogen-bonded transition state (see Scheme 2) as the reaction proceeds. Alternatively, the apparent variation of the activation energy for K_1 may be an artifact of the analytical method used, since the accuracy of E_a depends on the closeness of the fit to the overall rate equation.

Table IV presents a summary of the activation energies for each epoxy using eq. (11) at selected conversions. For the PEODE systems, the activation energy for K_{1c} was approximately independent of epoxy structure, suggesting that the mechanism of impurity catalysis is similar for the different chain-length systems and different from the DGEBA system. The change in overall activation energy, calculated on the basis of a single mechanism (see Figs. 9 and 11), may occur partly because of a change in the activation energy for autocatalysis. The activation energy for K_1 at high cure levels was greater than at lower conversions; however, this variation was not as great as that for E_a , assuming a single reaction process. Because the activation energy of K_1 does not systematically change with chain length, the reason for the dependence on

Table IVActivation Energy Determined by Isothermal DSC Obtained by Fitting Eq. (11)to the Experimental Results at Selected Conversions

$ \begin{array}{ccc} E_a \ [K_{1c} \ (\alpha = 0)] \\ \text{Monomer} \end{array} \begin{array}{c} E_a \ [K_{1c} \ (\alpha = 0)] \\ (kJ/\text{mol}) \end{array} \begin{array}{c} E_a \ [K_1 \ (\alpha = 0.2)] \\ (kJ/\text{mol}) \end{array} \begin{array}{c} E_a \ [K_1 \ (\alpha = 0.4)] \\ (kJ/\text{mol}) \end{array}$	$\begin{array}{c} E_a \ [K_1 \ (\alpha = 0.7)] \\ (\text{kJ/mol}) \end{array}$
DCERA 70.6 ± 1.5 56.1 ± 1.0 52.2 ± 1.0	58.0 ± 1.0
DCEDA 70.0 ± 1.5 50.1 ± 1.0 53.2 ± 1.0	58.9 ± 1.0
PEODE-1 59.8 ± 1.1 68.9 ± 1.3 69.1 ± 1.4	74.3 ± 1.5
PEODE-4.5 60.2 ± 1.0 62.7 ± 1.0 60.8 ± 1.0	64.4 ± 1.1
PEODE-9 63.5 ± 1.0 66.1 ± 1.0 63.2 ± 1.0	75.7 ± 2.0
PEODE-14 65.9 ± 1.1 61.3 ± 1.0 60.5 ± 1.1	69.6 ± 1.5

structure is unclear. It is of interest to note that although the activation energy for impurity catalysis (K_{1c}) for DGEBA is higher than for the POEDE monomers, the reverse is true for the activation energy associated with the autocatalytic reaction. Thus, it appears that greater flexibility of the monomer backbone in the PEODE resins does not necessarily lead to an energetically lower reaction barrier for the autocatalytic reaction.

CONCLUSIONS

The curing behavior of epoxy resins with varying chain length was investigated by DSC. As shown by scanning and isothermal DSC, the cure rate depends on the structure of the epoxy system and decreases with increasing chain length. The heat of polymerization per mol obtained by isothermal DSC appears to be relatively independent of epoxy resin structure. In contrast, the heat of polymerization obtained by scanning DSC was consistently lower and this was attributed to degradation during later stages of the DSC scan, particularly for samples with long backbones that require higher cure temperatures. The activation energies calculated from the DSC scanning method were almost independent of structure. By contrast, the activation energies determined by isothermal DSC assuming a single, overall reaction process showed a variation in E_a with structure and conversion. The dependence of polymerization rate on degree of reaction was found to follow a kinetic expression based on impurity catalysis and autocatalysis. This allowed the respective activation energies to be determined for each process as a function of conversion. The differences in activation energies between PEODE samples with different chain lengths and flexibility were not great, nor did they change systematically. Greater difference was seen between the flexible PEODE monomers and the rigid DGEBA system.

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