

# Reaction Kinetics of Liquid Crystalline Epoxy Cured with Aromatic Diamine: Its Synthesis and Mechanical and Electrical Characteristics

J. Y. LEE,<sup>1</sup> M. J. SHIM,<sup>2</sup> H. K. LEE,<sup>3</sup> S. W. KIM<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, The University of Seoul, 90 Jeonnong-Dong, Dongdaemun-Gu, Seoul 130-743, Korea

<sup>2</sup> Department of Life Science, The University of Seoul, Seoul 130-743, Korea

<sup>3</sup> Department of Chemical Engineering, Woosuk University, Jeonbuk 565-800, Korea

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**ABSTRACT:** The effect of the molar ratio of diglycidyl ether of 4,4'-biphenyl (DGEBP) to *p*-phenylene diamine (PDA) on the cure reaction rate was studied by the Kissinger and isoconversional equations. The cure mechanism was studied by FTIR analysis and the liquid crystalline phase structure was analyzed by wide angle X-ray diffraction (WAXD). With an increasing molar ratio of DGEBP/PDA, the preexponential factor was increased by the increasing collision probability between epoxide groups and primary or secondary amine groups in noncatalytic or catalytic modes. The activation energy also increased because of the increasing content of rigid rodlike mesogen and the high crosslink density, which hindered the diffusion of functional groups. The activation energies obtained from the Kissinger equation were in good agreement with average values obtained from the isoconversional equation. The WAXD pattern showed a smectic layer structure with a layer thickness of 15.3 Å and an intermolecular distance of 4.3 Å. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2372–2380, 2001

**Key words:** liquid crystalline epoxy; smectic; Kissinger equation; isoconversional equation; crosslink

## INTRODUCTION

Liquid crystalline (LC) compounds having aromatic mesogenic groups and reactive end-functional groups can be used to form LC order in a polymeric network structure. The resulting networks can form a new class of thermosets for advanced mechanical, electrical, and optical ap-

plications because of their unique properties (e.g., anisotropic orientation, low coefficient of thermal expansion, and LC phase development) during curing.<sup>1–3</sup> The concept of liquid crystallinity seems to be inappropriate to describe a cross-linked structure, but it can be achieved during the formation of linear chains and branches before reaching the gel point of the network. It is retained through the curing of the resin, and it is well known that at low fractional conversion the addition reaction of monomers leads to the formation of oligomers with linear or moderately branched structures, regardless of whether or not it is a LC polymer.<sup>4–7</sup>

Correspondence to: S.-W. Kim (swkim@uiscc.uos.ac.kr).

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Epoxides constitute an important class among the LC thermosets, and many aspects were intensively investigated by many researchers for several decades. Their networks are formed by chemical reactions between an epoxy-containing LC compound and curing agents (e.g., amines, acid anhydrides, and Lewis acids), and the resulting cured resins combine the unique properties of a liquid crystal and a polymer network.<sup>8,9</sup> In other words, the relatively poor properties of LC polymers in the transverse direction can be overcome by the introduction of crosslinks between the chains.

The cure mechanism of a conventional epoxy with amines is well known and the same mechanism can be applied to LC epoxy compounds.<sup>10–12</sup> The following are the main elementary reactions in the epoxy–amine compound:



where PA, SA, and TA designate the primary, secondary, and tertiary amines, respectively; E represents the epoxide; and —OH is the hydroxyl group attached to the SA or TA. Equations (1), (3), and (5) are noncatalytic reactions and eqs. (2) and (4) are catalytic reactions. Each elementary reaction has a different rate constant, and these reactions take place competitively and serially in the same reactant mass. However, it is very difficult to derive each rate constant. Thus, the cure kinetics are mostly interpreted by the consuming rate of the epoxide group with the assumption that the heat during the cure reaction is proportional to the conversion of the epoxy monomer through differential scanning calorimetry (DSC).

Many equations were developed to investigate the cure kinetics of the epoxy system, including the  $n$ th-order reaction model, the autocatalytic reaction model, and the diffusion control model.<sup>13–16</sup> All kinetic models start with the following basic equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (6)$$

or in the integrated form,

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = \int k dt \quad (7)$$

where  $d\alpha/dt$  is the instant cure rate,  $\alpha$  is the fractional conversion at a time  $t$ ,  $k$  is the Arrhenius rate constant, and  $f(\alpha)$  is a function form of  $\alpha$  that depends on the reaction mechanism.

Kissinger derived the following equation<sup>13</sup> for when the temperature varies with time at a constant heating rate,  $q = dT/dt$ :

$$-\ln\left(\frac{q}{T_p^2}\right) = \frac{E}{RT_p} - \ln\left(\frac{AR}{E}\right) \quad (8)$$

where  $q$  is the heating rate,  $T_p$  is the temperature at which  $d\alpha/dt$  is maximum,  $E$  is the activation energy,  $R$  is the gas constant, and  $A$  is the preexponential factor. This method gives a relatively accurate activation energy and preexponential factor by calculating the relationship between  $-\ln(q/T_p^2)$  and  $1/T_p$ .

The Kissinger equation gives only one activation energy from the data of  $T_p$ . A more complete determination of the activation energy at any selected conversion can be calculated by the isoconversional equation,<sup>16</sup> which is

$$E = -R \frac{d(\ln q)}{d(T^{-1})} \quad (9)$$

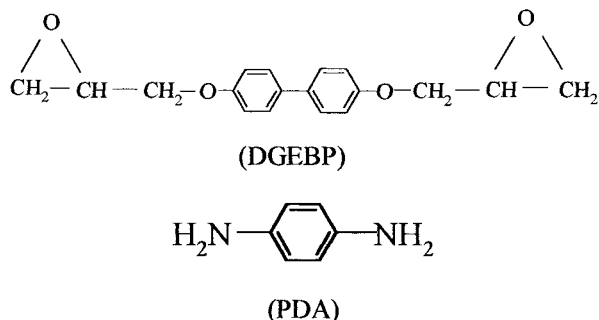
where  $E$ ,  $q$ , and  $R$  are the same terms in the Kissinger equation and  $T$  is the temperature for a selected conversion at each heating rate. Activation energies can be obtained from the slope.

In this article we describe the cure reaction kinetics of a LC epoxy monomer having the biphenol mesogenic group cured with aromatic diamine at various molar ratios. To calculate the kinetic parameters, DSC analysis under dynamic condition was conducted and the DSC data were introduced to the Kissinger and isoconversional equations. The cure reaction mechanism was confirmed by FTIR analysis and a wide angle x-ray diffraction (WAXD) analysis was conducted to analyze the LC phase structure.

## EXPERIMENTAL

### Materials

The chemical structures of diglycidyl ether of 4,4'-biphenyl (DGEBP) and *p*-phenylenediamine (PDA, mp 146°C) are as follows:



The LC epoxy monomer was directly synthesized from commercial 4,4'-dihydroxybiphenyl as reported by Lu et al.<sup>8</sup> DSC traces, transition enthalpies, and temperatures for the synthesized epoxy monomer were recorded with a Solomat DSC-4000 at a heating rate of 10°C/min and then cooling at 5°C/min in an atmosphere of nitrogen gas.

### Sample Mixing

The DGEBP/PDA (molar ratios of 1/1, 3/2, and 2/1) systems were obtained by the following procedure: 1.5 g of DGEBP was put into about 10 mL of tetrahydrofuran and heated for about 30 min until a clear solution was obtained. The solution was cooled to 30°C, and a stoichiometric amount of PDA was added and stirred for about 5 min. Then the solvent was removed and dried in a vacuum oven at room temperature. The mixtures were stored at -13°C in a freezer.

### DSC Analysis

Dynamic DSC analysis was carried out. An aluminum pan containing 3–4 mg of the mixed sample was placed in the DSC cell, and it was heated according to the program of a constant heating rate from room temperature to 300°C. The heating rates were 3, 5, 10, and 20°C/min under a nitrogen purge gas at a flow rate of 20 mL/min.

### FTIR Analysis

FTIR analysis was carried out to study the cure mechanism between DGEBP and PDA. The mixed sample was cured at a constant tempera-

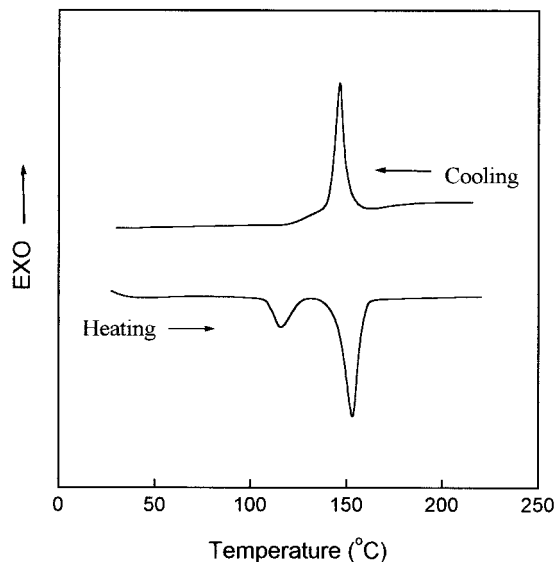
ture for various times and the partially cured sample was analyzed by FTIR spectroscopy (Bomen MB 104) at a resolution of 2 cm<sup>-1</sup> from 4000 to 400 cm<sup>-1</sup>. The characteristic bands for epoxide, amine, and hydroxyl groups were recorded and compared.

### WAXD Analysis

The WAXD pattern was measured using a diffractometer (RINT2000) with copper filtered Cu K $\alpha$  radiation. The X rays were produced by a Philips Electronics XRG3100 generator operated at 40 kV and 40 mA. With a nominal sample to film distance in the camera of 5 cm, exposure times of 1.5 h were typical. The samples for X-ray studies were prepared by isothermal curing of the LC epoxy thermoset on aluminum foil in an oven followed by cooling to room temperature in air.

## RESULTS AND DISCUSSION

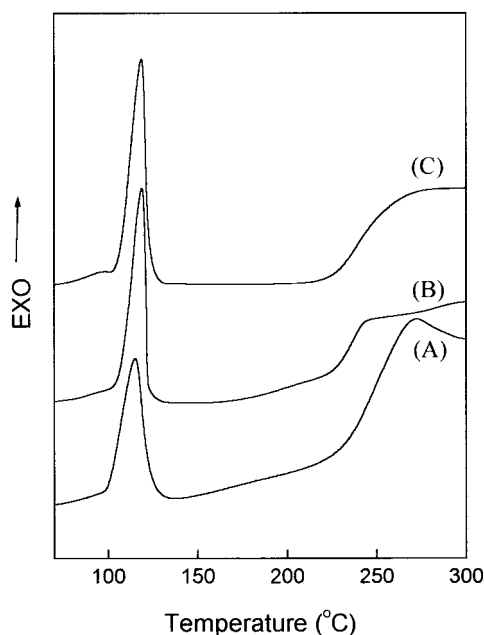
A DSC trace of the synthesized DGEBP, LC epoxy monomer is shown in Figure 1. A dynamic scan was performed at a heating rate of 10°C/min from room temperature to 230°C, and the sample was cooled at a constant rate of 5°C/min from 230°C to room temperature. On heating, two phase transitions appeared: a smectic transition at 115°C and an isotropic transition at 153°C. However, only



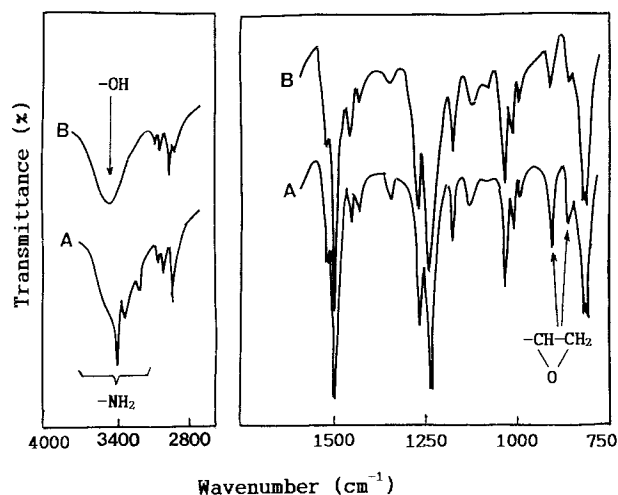
**Figure 1** Dynamic DSC curves for the synthesized DGEBP performed at a heating rate of 10°C/min and a cooling rate of 5°C/min.

one phase transition appeared at 146°C during cooling that was due to supercooling.<sup>17</sup> These results were similar to those in the literature.<sup>17,18</sup> The smectic transition enthalpy was  $\Delta H = -93.6$  J/g and the isotropic transition was  $\Delta H = -237.3$  J/g.

Figure 2 shows dynamic DSC curves for DGEBP cured with PDA at different molar ratios. The exothermic peak at around 120°C was attributed to the generation of heat during the cure reaction between the epoxide group and primary or secondary amine groups, and the cure mechanism was confirmed by FTIR analysis (Fig. 3). The exothermic peak showed a very steep slope, meaning that the cure reaction took place rapidly in a short temperature range. The total exothermic heats were 114.1, 133.8, and 146.9 kJ/mol for the epoxide for the respective 1/1, 3/2, and 2/1 molar ratios of DGEBP/PDA. An endothermic peak for melting was not observed at around 115 or 153°C, which corresponds to the smectic or isotropic transition temperatures of DGEBP, and also did not appear at around 146°C, which represents the melting of PDA. However, a very small endothermic peak appeared at about 106°C for the curve of 2/1 DGEBP/PDA, which had a relatively high DGEBP content compared to the other stoichiometric ratios. These results indicated that the cure reaction of the systems oc-



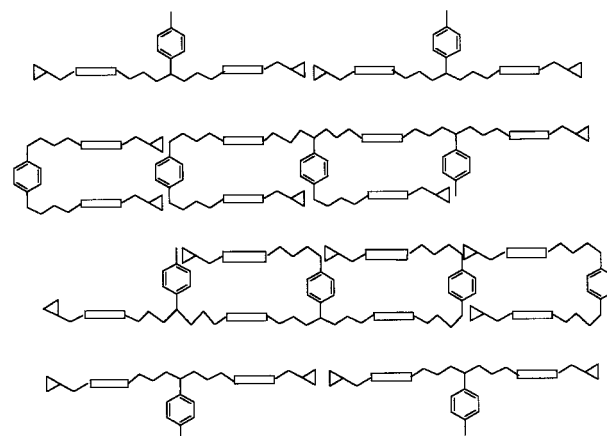
**Figure 2** Dynamic DSC curves for DGEBP/PDA systems at 10°C/min with DGEBP/PDA molar ratios of 1/1 (spectrum A), 3/2 (spectrum B), and 2/1 (spectrum C).



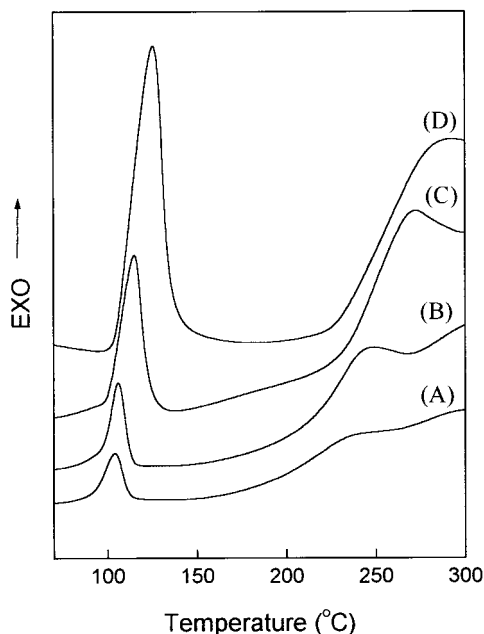
**Figure 3** FTIR spectra of 1/1 DGEBP/PDA cured at 130°C with curing times of 0 (spectrum A) and 30 min (spectrum B).

curred prior to complete melting of the DGEBP. The postcuring peak at around 260°C was overlapped with thermal decomposition, so the cure kinetics in this region could not be studied.

Figure 3 shows the FTIR spectra of 1/1 DGEBP/PDA cured at 130°C for 0 (spectrum A) and 30 min (spectrum B). It is well known that the *p*-phenylene group does not take part in the chemical reaction during the cure of the system, so the out of plane =C—H bending around 825  $\text{cm}^{-1}$  was taken as a standard within the experimental error range in order to compare the intensities of characteristic bands. In spectrum A the characteristic bands of the epoxy ring vibration of DGEBP appeared at 915 and 862  $\text{cm}^{-1}$ , and those



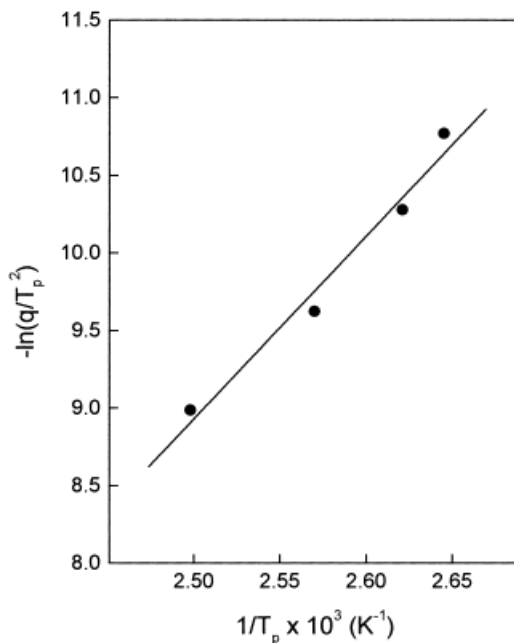
**Figure 4** The smectic structure of the cured DGEBP/PDA system.



**Figure 5** Dynamic DSC curves for 1/1 DGEBP/PDA at four different heating rates: 3 (spectrum A), 5 (spectrum B), 10 (spectrum C), and 20°C/min (spectrum D).

of the primary amine of PDA were at 3374, 3309, and 3200  $\text{cm}^{-1}$ , which were due to symmetric, asymmetric, and overtone vibrations, respectively. As the cure reaction proceeded the bands of the epoxy ring decreased and those of the primary amine were overlapped with a new broad band at around 3432  $\text{cm}^{-1}$ , which was attributed to the hydroxyl group produced by the reaction of the epoxy ring with primary and secondary amines as shown in eqs. (1)–(4). Thus, the epoxy and curing agent monomers were changed to oligomers and they were arranged as shown in Figure 4, resulting in a smectic structure that was confirmed by WAXD analysis.

Figure 5 shows dynamic DSC curves for 1/1 DGEBP/PDA at four different heating rates. All curves showed only one sharp exothermic peak, regardless of the heating rate, and an endother-



**Figure 6** A Kissinger plot for 1/1 DGEBP/PDA.

mic peak for melting was not observed. The temperature at which the instant conversion rate was maximum ( $T_p$ ) and the heating rate ( $q$ ) were obtained from these curves, and they are listed in Table I. The data of the third and fourth columns were introduced to the Kissinger equation, and  $1/T_p$  versus  $-\ln(q/T_p^2)$  is plotted in Figure 6. The linear plot is expressed by the following equation:

$$-\ln\left(\frac{q}{T_p^2}\right) = 11.78 \times 10^3 \cdot \frac{1}{T_p} - 20.53$$

The activation energy was calculated from the slope and the preexponential factor from the  $y$  intercept, and these values were 97.94 kJ/mol and  $9.71 \times 10^{12} \text{ min}^{-1}$ .

The heats generated during the cure reaction of the system at 3, 5, 10, and 20°C/min were 88.9, 103.2, 114.1, and 117.8 kJ/mol, respectively, for

**Table I** Cure Kinetics Parameters for 1/1 DGEBP/PDA

$q$ (°C/min)	$T_p$ (K)	$1/T_p \times 10^3$ ( $\text{K}^{-1}$ )	$-\ln(q/T_p^2)$	$E$ (kJ/mol)	$A$ ( $\text{min}^{-1}$ )
3	378.1	2.64	10.77	97.94	$9.71 \times 10^{12}$
5	379.4	2.62	10.28		
10	389.2	2.57	9.62		
20	400.4	2.50	8.99		

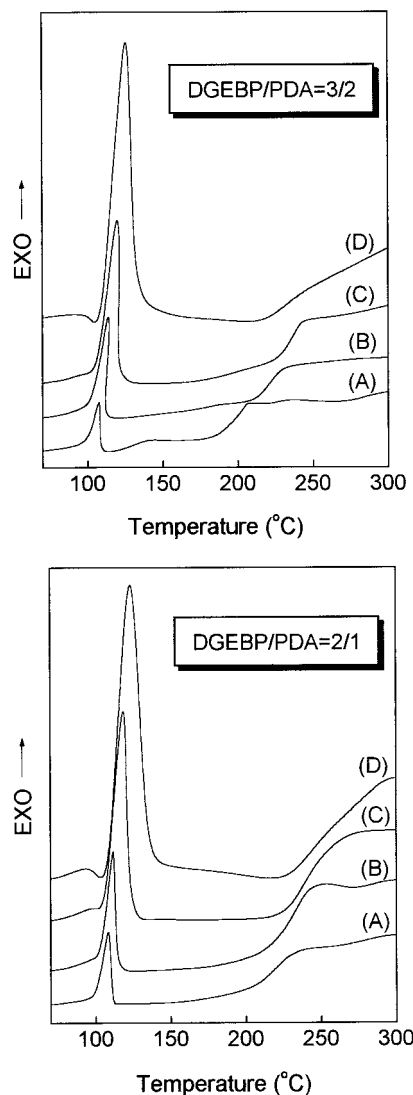
the epoxide. The value increased with the increasing heating rate. This was attributed to the rigid rodlike mesogen and the high crosslink density that hindered the diffusion of end-functional groups. At a low heating rate the epoxy system stayed at a low temperature for a long time, so there was enough time for the mesogen group to be arranged and stacked regularly; the arranged mesogen resulted in the high crosslinked network. Therefore, the mobility of the functional groups was hindered more and the cure reaction was difficult. On the contrary, at a high heating rate there was little time for the mesogen to arrange because the system was exposed to high temperature in a short time. Thus, easy diffusion of the functional groups gave much exothermic heat. As a natural consequence, the exothermic heat increased with the increasing heating rate.

Figure 7 shows dynamic DSC curves for the 3/2 and 2/1 DGEBP/PDA systems at various heating rates. All curves showed one sharp exothermic peak, regardless of the heating rate, and the endothermic heat for melting was observed only at 20°C/min. The endothermic peak at around 106°C was sharp because of the increasing molar ratio of DGEBP, whose LC phase melts at around that temperature. The  $T_p$  and  $q$  values were obtained from these curves and they were introduced to the Kissinger equation to plot Figure 8. The linear plots were expressed by the following equations:

$$-\ln\left(\frac{q}{T_p^2}\right) = 15.44 \times 10^3 \cdot \frac{1}{T_p} - 29.61 \quad (\text{DGEBP/PDA} = 3/2)$$

$$-\ln\left(\frac{q}{T_p^2}\right) = 17.87 \times 10^3 \cdot \frac{1}{T_p} - 35.99 \quad (\text{DGEBP/PDA} = 2/1)$$

The activation energies were calculated from the slopes and the preexponential factors from the y intercepts, and these values are listed in Table II. As the DGEBP content increased the activation energy and preexponential factor increased. The preexponential factor was increased because of the increasing probability of collision between epoxide and amine groups. The activation energy also increased, and it was attributable to the increasing content of rigid rodlike mesogen and the high crosslink density that hindered the diffusion of functional groups. Table II also shows that the rate constant obtained from the Arrhenius equa-

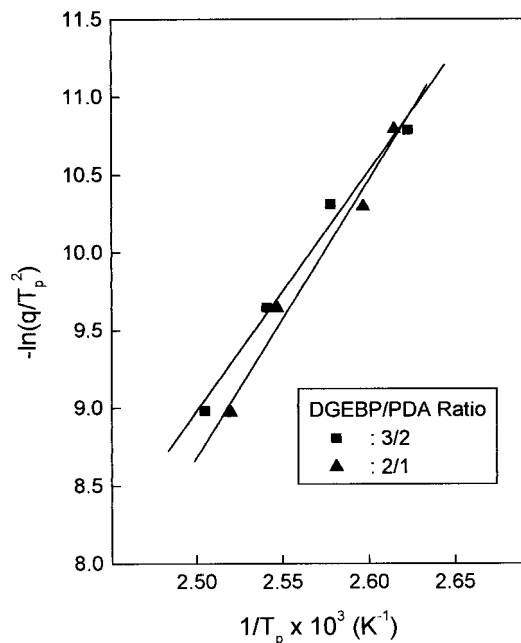


**Figure 7** Dynamic DSC curves for 3/2 and 2/1 DGEBP/PDA at heating rates of 3 (spectrum A), 5 (spectrum B), 10 (spectrum C), and 20°C/min (spectrum D).

tion at 373 K increased as the molar ratio of DGEBP/PDA increased.

Table III shows the increasing heat generation with the increasing molar ratio of DGEBP/PDA and the heating rate. At a higher molar ratio of DGEBP/PDA, the probability of the exothermic reaction between the epoxide and amine groups [eqs. (1)–(4)] increased; at a higher heating rate, the less arranged mesogen and the lower crosslink network made the mobility of the functional groups easy and, as a natural consequence, the exothermic heat decreased.

Figure 9 shows the conversion curves at four heating rates for 1/1 DGEBP/PDA system, which



**Figure 8** Kissinger plots for 3/2 and 2/1 DGEBP/PDAs.

was obtained by integrating the DSC curves in Figure 5. The isoconversional temperatures were obtained from the conversion curves at any selected conversion, and  $1/T \times 10^3$  according to  $\ln(q)$  are listed in Table IV. To get the activation energy at each conversion, the relationships of the variables at the conversion of 0.1–0.5 were discerned (Fig. 10) and the linear expression for each straight line was obtained. All slopes corresponded to  $-E/R$  at these particular conversions, and the activation energies are listed in Table V. The values were in the range of 89–116 kJ/mol at different degrees of conversion. The values increased with increasing conversion and the increment of the activation energy was due to the rigid mesogen and crosslink, which restricted the diffusion of functional groups.

Table V also contains the activation energies at these particular conversions for DGEBP/PDA sys-

**Table II** Cure Kinetics Parameters for DGEBP/PDA Systems with Different Molar Ratios

DGEBP/PDA	$E$ (kJ/mol)	$A$ ( $\text{min}^{-1}$ )	$k$ ( $\text{min}^{-1}$ )
1/1	97.94	$9.71 \times 10^{12}$	0.19
3/2	122.37	$1.12 \times 10^{17}$	0.81
2/1	140.57	$7.63 \times 10^{19}$	1.57

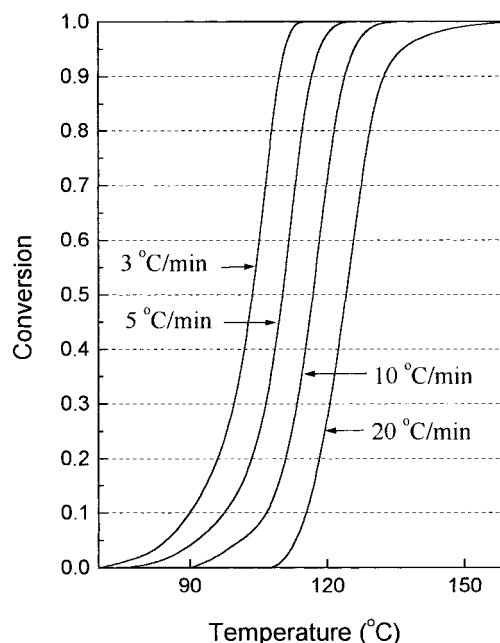
$k$ , Arrhenius rate constant at 373 K.

**Table III** Exothermic Heat for DGEBP/PDA Systems with Different Molar Ratios

DGEBP/PDA	Heating Rate ( $^{\circ}\text{C}/\text{min}$ )	Exothermic Heat (kJ/mol of Epoxide)
1/1	3	88.9
	5	103.2
	10	114.1
	20	117.8
3/2	3	90.6
	5	116.8
	10	133.8
	20	149.3
2/1	3	118.4
	5	126.1
	10	146.9
	20	153.2

tems with different molar ratios, and these values also increased with increasing conversion. The average values for the systems with molar ratios of 1/1, 3/2, and 2/1 were 106.9, 122.2, and 140.3 kJ/mol, respectively, which was in good agreement with those obtained from the Kissinger equation.

Figure 11 shows the WAXD pattern for the 1/1 DGEBP/PDA system cured at  $130^{\circ}\text{C}$  for 30 min. The two peaks at  $2\theta = 20.4^{\circ}$  and  $5.8^{\circ}$  are charac-



**Figure 9** Conversion curves at different heating rates for the 1/1 DGEBP/PDA system.

**Table IV** Data of  $\ln(q)$  and  $T^{-1}$  for 1/1 DGEBP/PDA System

$\ln(q)$	$T^{-1} \times 10^3 \text{ (K}^{-1}\text{)}$				
	Conversion				
	0.1	0.2	0.3	0.4	0.5
1.10	2.75	2.71	2.68	2.67	2.65
1.61	2.70	2.65	2.63	2.62	2.61
2.30	2.63	2.60	2.59	2.57	2.56
3.00	2.57	2.55	2.54	2.53	2.52

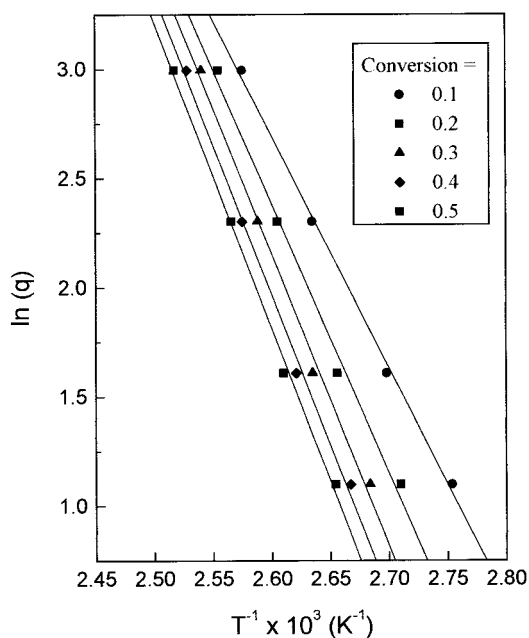
teristic diffraction peaks for a smectic structure.<sup>19</sup> The former corresponds to an intermolecular correlation and the latter corresponds to the layer spacing. To obtain the intermolecular distance and the layer thickness, the peak values were introduced to Bragg's equation, which gave a layer thickness of 15.3 Å and an intermolecular distance (lateral packing of LC molecules) of 4.3 Å. The smectic layer structure is shown in Figure 4.

## CONCLUSION

The effect of the molar ratio of DGEBP/PDA on the cure rate was studied by the Kissinger and

isoconversional equations. The cure reaction mechanism was confirmed by FTIR analysis, and the WAXD analysis was conducted to analyze the LC phase structure.

All dynamic DSC curves showed only one sharp exothermic peak, regardless of the heating rate; this meant that the cure reactions between the epoxide groups and primary or secondary amine groups took place in the same stage. As DGEBP content increased, the preexponential factor was increased due to the increasing probability of collision between the epoxide and amine groups. The activation energy also increased because of the increasing content of rigid rodlike mesogen and the high crosslink density, which hindered the diffusion of functional groups. The rate constant also increased with the increasing DGEBP/PDA ratio. The activation energies for each system ob-

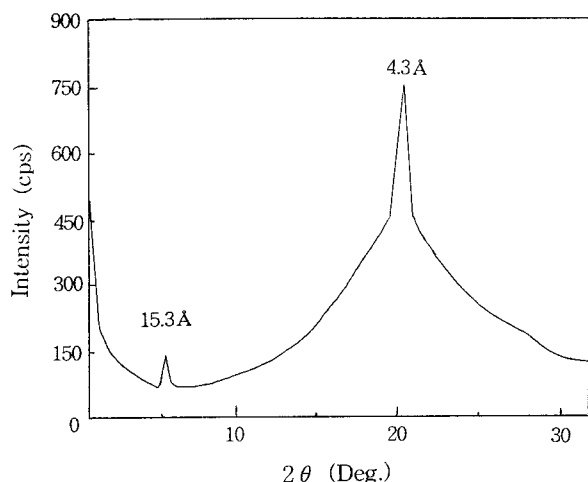


**Figure 10** Isoconversional plots at various conversions for the 1/1 DGEBP/PDA system.

**Table V** Activation Energy for DGEBP/PDA Systems with Different Molar Ratios by Isoconversional Equation

DGEBP/PDA	Conversion	$E$ (kJ/mol)
1/1	0.1	88.9
	0.2	103.1
	0.3	111.4
	0.4	114.7
	0.5	116.4
3/2	0.1	110.6
	0.2	117.2
	0.3	121.4
	0.4	127.2
	0.5	134.7
2/1	0.1	108.1
	0.2	136.3
	0.3	151.3
	0.4	151.3
	0.5	154.6





**Figure 11** The WAXD pattern for the 1/1 DGEBP/PDA system cured at 130°C for 30 min.

tained from the Kissinger equation agreed with average values obtained from the isoconversional equation. The WAXD pattern showed a smectic layer structure whose layer thickness was 15.3 Å and whose intermolecular distance was 4.3 Å.

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