

Synthesis of Liquid Crystalline Epoxy and Its Mechanical and Electrical Characteristics—Curing Reaction of LCE with Diamines by DSC Analysis

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ABSTRACT: An aromatic liquid crystalline epoxy monomer based on biphenyl mesogen was synthesized and cured with three different aromatic diamines. The curing reaction characteristics were analyzed by DSC, and the data were introduced to the Kissinger equation to attain the kinetic parameters. Diglycidyl ether of 4,4'-biphenyl (DGEBP)/4,4'-diaminobiphenyl (DABP), and DGEBP/4,4'-methylenediamine (MDA) systems showed an exotherm curing reaction after comelting of the monomers; the DGEBP/*p*-phenylenediamine (PDA) system's curing reaction took place in the solid state without melting of monomers. The activation energy and preexponential factor for the DGEBP/DABP system were 55.6 kJ/mol and $4.0 \times 10^6 \text{ min}^{-1}$, respectively. Those values for DGEBP/MDA and DGEBP/PDA systems were 55.1 kJ/mol and $1.0 \times 10^6 \text{ min}^{-1}$ and 148.8 kJ/mol and $7.7 \times 10^{19} \text{ min}^{-1}$, respectively. The rate constant at 100°C for DGEBP/PDA is 2 times higher than those for DGEBP/DABP and DGEBP/MDA, which have almost the same values. Strictly speaking, the rate constant of DGEBP/DABP is a little higher than that of DGEBP/MDA, and these results are in good agreement with the DSC curves. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2419–2425, 2002

Key words: liquid crystalline epoxy; biphenyl mesogen; DSC analysis; Kissinger equation; curing kinetics

INTRODUCTION

Liquid crystalline polymers (LCPs) are relatively new materials in the marketplace. They represent one of the most exciting developments in engineering plastics, because they have many advantages, especially that they can be melt processed into thick extrudates and molded parts with superior properties compared to fiber rein-

forced thermoplastics. Recently, ordered networks have become the topic of intensive research in the field of LCP materials. This can be partly attributed to the fact that, although main-chain LCPs have excellent mechanical, thermal, and optical properties, dimensional stability, and so forth, these properties in the transverse direction are rather poorer than those in the orientational direction. These problems can be overcome by the introduction of a crosslinking reaction between the main chains, which improves the dimensional stability of these ordered systems. Also, from the scientific point of view, ordered networks provide many new challenges, like the theoretical description of the mechanical deformation of such materials.^{1–5}

It is clear that the curing process of conventional epoxies with diamines is strongly affected

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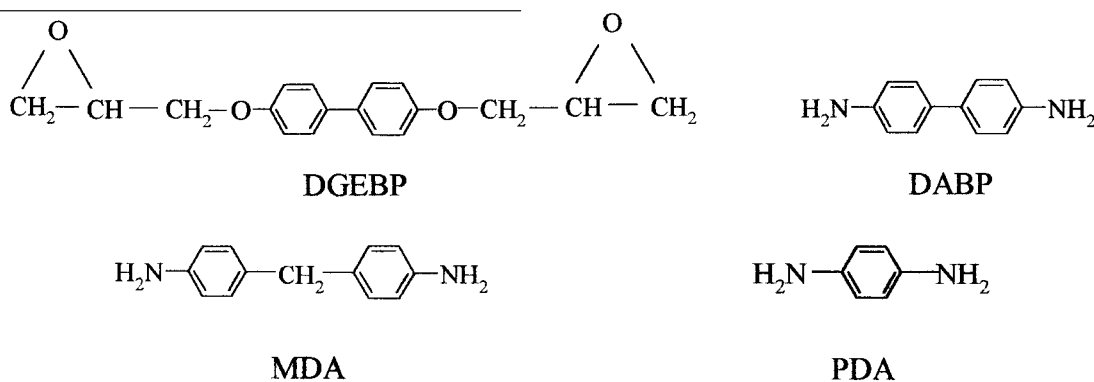
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by crosslinking, while in LC epoxy (LCE)/diamine systems the overall curing reaction is strongly affected by not only the crosslinking but also the LC phases in the LC thermosets.^{6,7}

This study examines the curing reaction characteristics of biphenyl mesogenic diepoxide monomer with aromatic diamines. The cure kinetics are investigated by the following Kissinger equation⁸⁻¹⁰:

$$-\ln\left(\frac{q}{T_p^2}\right) = \frac{E}{RT_p} - \ln\left(\frac{AR}{E}\right) \quad (1)$$

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 preex-



The mixtures of DGEBP and the curing agents (DABP, MDA, or PDA) at the molar ratio of 2:1 were obtained by the following procedures: 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 curing agents were added and stirred for about 5 min. Then the solvent was removed by means of an aspirator with stirring, and the solid mixture was dried in a vacuum oven (74 mmHg) at room temperature for 24 h. The mixtures were stored at -13°C in the freezer.

Dynamic DSC analysis was carried out as follows. The aluminum pan containing about 10 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 nitrogen purge gas at a flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Figure 1 shows the results of dynamic DSC for the DGEBP/DABP system (curve C), LCE

ponential factor. This method gives a relatively accurate activation energy and preexponential factor by calculating the relationship between $1/T_p$ and $-\ln(q/T_p^2)$.

EXPERIMENTAL

Diglycidyl ether of 4,4'-biphenyl (DGEBP, biphenyl mesogenic diepoxide monomer) was synthesized directly from 4,4'-dihydroxy biphenyl reported in the literature by Lu et al.^{11,12} The curing agents were 4,4'-diaminobiphenyl (DABP), 4,4'-methylenediamine (MDA), and *p*-phenylenediamine (PDA). The chemical structures are as follows:

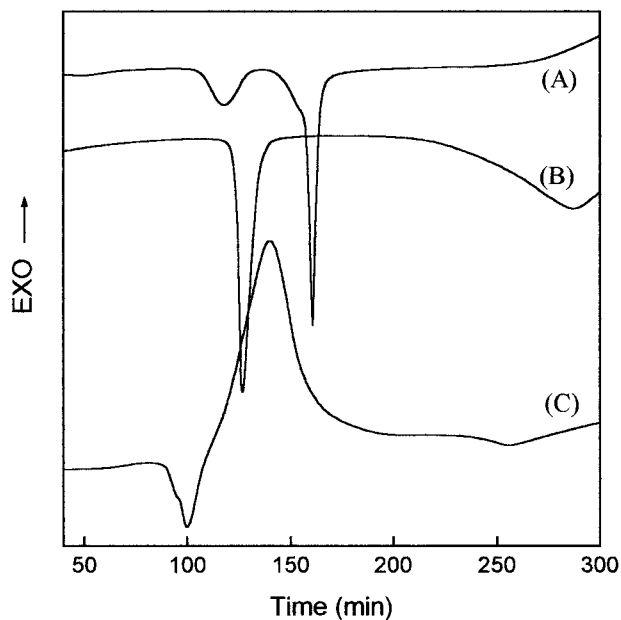
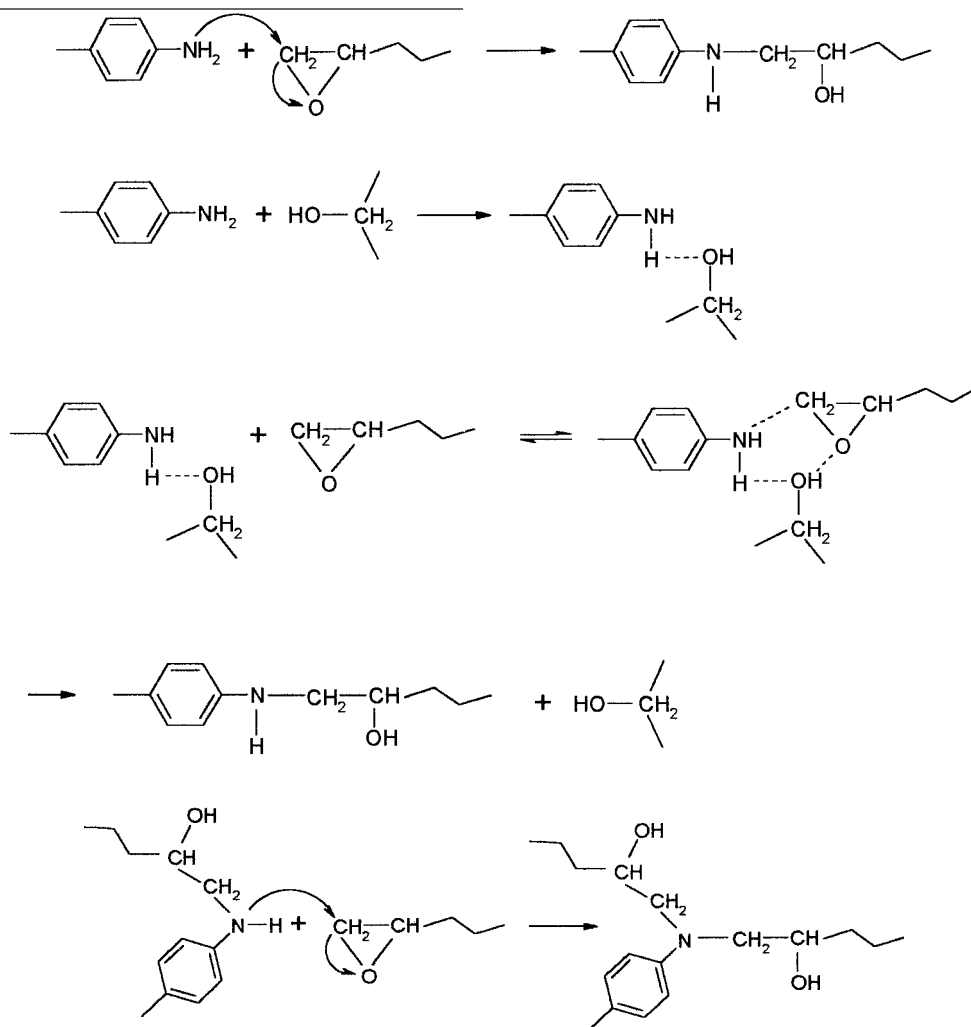


Figure 1 DSC curves for DGEBP (curve A), DABP (curve B), and DGEBP/DABP (curve C) at 10°C/min.

monomer, DGEBP (curve A), and the curing agent DABP (curve B) at 10°C/min. The DGEBP curve shows two phase transitions: a smectic transition at about 115°C and an isotropic transition at about 153°C.^{12,13} Smectic birefringent patterns were observed at 140°C under a polarized optical microscope. The DABP curve shows the melting endotherm at about 126°C. The DGEBP/DABP curve contains an endothermic peak and an exothermic peak. It also shows a little part of another exothermic peak at 256–332°C that is centered at 290°C, which is associated with the overlap of homopolymerization of the unreacted epoxy monomer and the thermal decomposition of the cured epoxy. The endothermic peak at around 100°C is attributed to the comelting of DGEBP and DABP; however, it is far smaller than that of the exothermic peak of the curing reaction centered at 140.2°C, which implies that some of the comelting endotherm is countervailed by the reaction of the

epoxide groups with the amine groups. This means that the restricted mobility of the functional groups in the solid state of the monomers permits only a curing reaction between adjacent groups. Thus, a weak exothermic curve in the early stage is natural and it can hide the endotherm of comelting. However, the functional groups are almost freely movable after melting and it results in a rapid curing reaction. The exotherm in the early stage is mainly caused by the reaction between a primary amine and an epoxide ring, which forms a hydroxyl group and a secondary amine as shown in reaction (2). As the curing reaction proceeds, the hydroxyl group acts as a catalyst in other primary amine–epoxide reactions and secondary amine–epoxide reactions as shown in reaction (3) and some of the secondary amine reacts with the epoxide ring without the hydroxyl group as shown in reaction (4).^{14,15} These reactions are the cause of the strong exotherm.



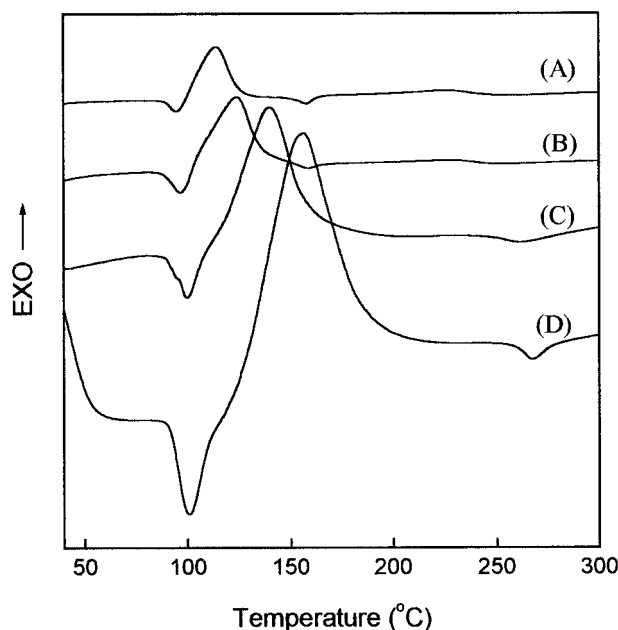


Figure 2 DSC curves for the DGEBP/DABP system at heating rates of 3 (curve A), 5 (curve B), 10 (curve C), and 20°C/min (curve D).

Figure 2 shows the dynamic DSC curves for the DGEBP/DABP system at four different heating rates. All curves show an endothermic peak and an exothermic peak, regardless of the heating rate, and the curves shift to the right-hand side with increasing heating rates. To procure the activation energy and preexponential factor by the Kissinger equation, the temperature where the instant conversion rate is maximum at each heating rate (T_p) and q are obtained from each curve and they are listed in Table I, and $1/T_p$ versus $-\ln(q/T_p^2)$ can be expressed as shown in Figure 3. The linear plot is expressed by the following equation:

$$-\ln\left(\frac{q}{T_p^2}\right) = 6.7 \times 10^3 \frac{1}{T_p} - 6.4 \quad (5)$$

The activation energy could be calculated from the slope and the preexponential factor from the y

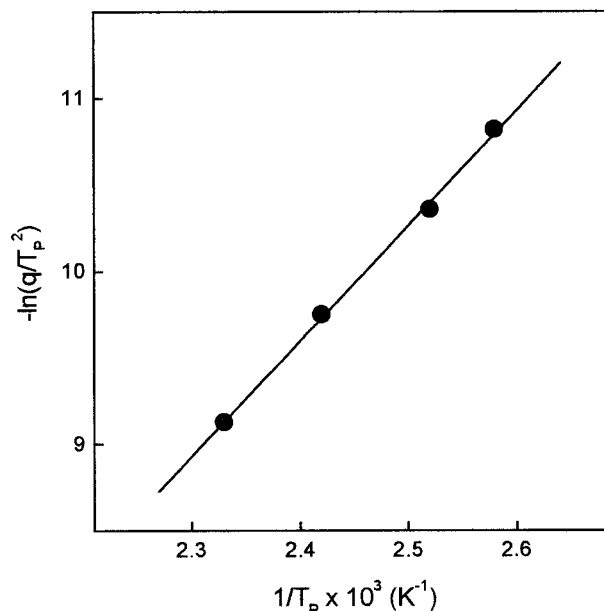


Figure 3 A Kissinger plot for the DGEBP/DABP system.

intersect, and these values are 55.6 kJ/mol and $4.0 \times 10^6 \text{ min}^{-1}$, respectively.

Dynamic DSC curves for DGEBP (curve A), MDA (curve B), and DGEBP/MDA (curve C) are shown in Figure 4. Two phase transitions for DGEBP were already explained in Figure 1, and the MDA curve shows the melting endotherm at 92°C with thermal decomposition at 220.7°C. The DGEBP/MDA curve shows two characteristic peaks. One is an endothermic peak at about 85°C, which is attributed to the melting of MDA; the other is an exothermic peak at around 110–190°C, which is assigned to the curing reaction of epoxide groups of DGEBP with amine groups of MDA. The exothermic curve increases slowly after the monomer melting and shows a rapid increase after some retention temperature. This means that the freely diffused functional groups need higher energy in order to take part in the chemical curing reaction.

Dynamic DSC curves for the DGEBP/MDA system at four different heating rates are shown in

Table I Cure Kinetics Parameters for DGEBP/DABP

q (°C/min)	T_p (K)	$1/T_p \times 10^3$ (K ⁻¹)	$-\ln(q/T_p^2)$	E (kJ/mol)	A (min ⁻¹)
3	387.7	2.58	10.82		
5	396.9	2.52	10.36		
10	413.3	2.42	9.75	55.6	4.0×10^6
20	429.3	2.33	9.13		

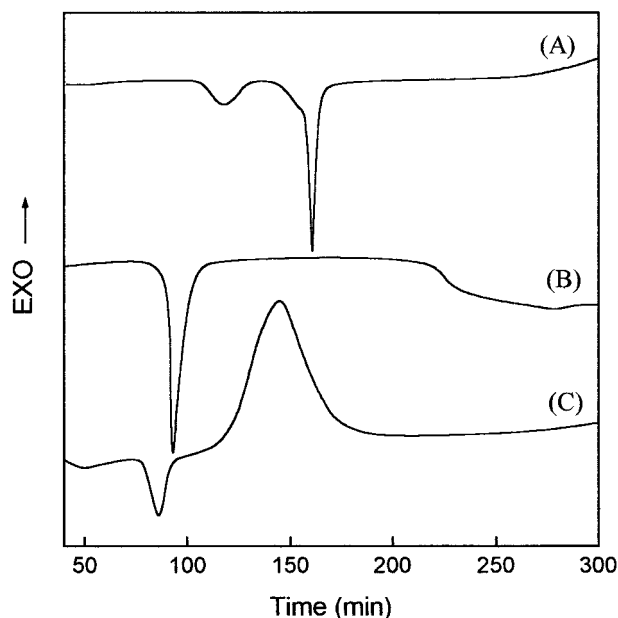


Figure 4 DSC curves for DGEBP (curve A), MDA (curve B), and DGEBP/MDA (curve C) at 10°C/min.

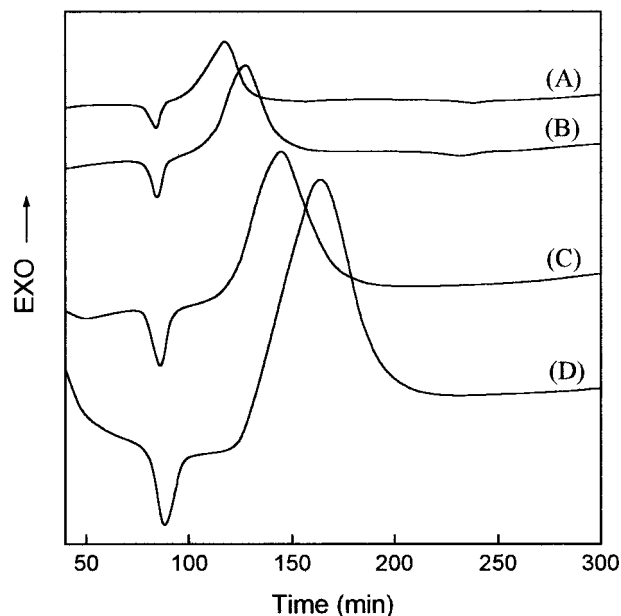


Figure 5 DSC curves for the DGEBP/MDA system at heating rates of 3 (curve A), 5 (curve B), 10 (curve C), and 20°C/min (curve D).

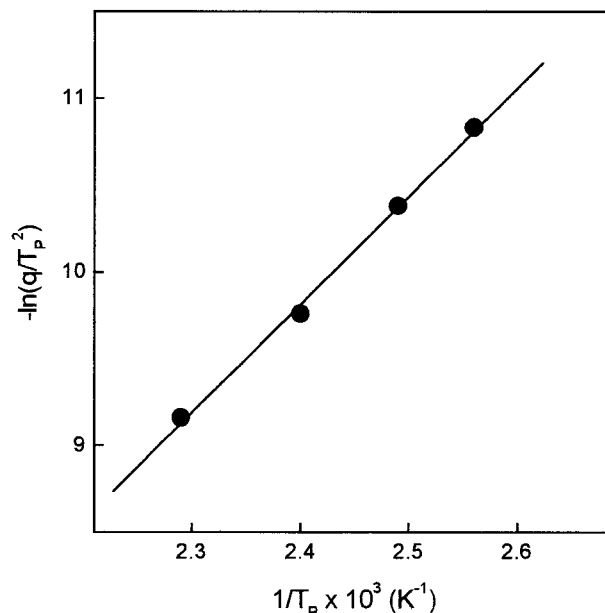


Figure 6 A Kissinger plot for the DGEBP/MDA system.

Figure 5. All curves show a similar shape for the endothermic and exothermic peaks, and they shift to the right-hand side with the increasing heating rate. Each weak endotherm of curves A and B at around 220°C is related to the thermal decomposition of MDA. To get an activation energy and preexponential factor, the T_p and q are obtained from each curve and they are listed in Table II. The data of the third and fourth columns are introduced to 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:

$$-\ln\left(\frac{q}{T_p^2}\right) = 6.2 \times 10^3 \frac{1}{T_p} - 5.1 \quad (6)$$

The activation energy is 51.5 kJ/mol and the preexponential factor from the y intercept is $1.0 \times 10^6 \text{ min}^{-1}$.

Table II Cure Kinetics Parameters for DGEBP/MDA

q (°C/min)	T_p (K)	$1/T_p \times 10^3$ (K ⁻¹)	$-\ln(q/T_p^2)$	E (kJ/mol)	A (min ⁻¹)
3	390.2	2.56	10.83	51.5	1.0×10^6
5	400.8	2.49	10.38		
10	417.2	2.40	9.76		
20	437.2	2.29	9.16		

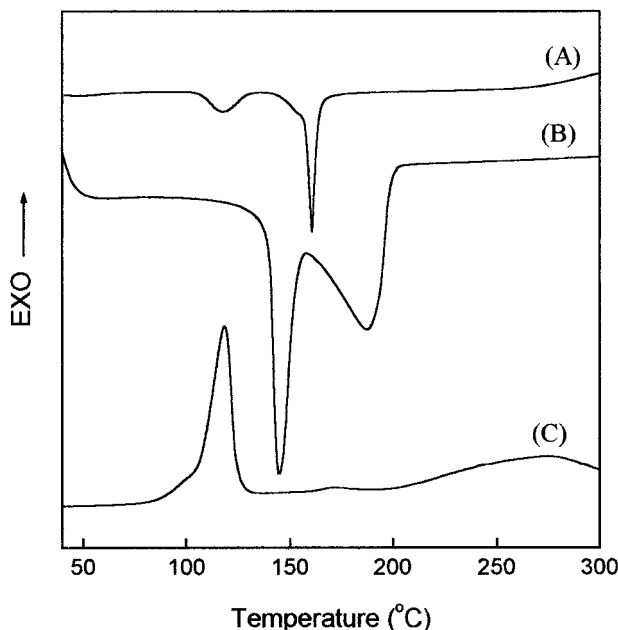


Figure 7 DSC curves for DGEBP (curve A), PDA (curve B), and DGEBP/PDA (curve C) at 10°C/min.

Figure 7 shows dynamic DSC curves for DGEBP (curve A), PDA (curve B), and DGEBP/PDA (curve C) at 10°C/min. The DGEBP curve shows two endotherms at about 115 and 153°C, and the PDA curve shows a melting endotherm at about 145°C followed by thermal decomposition at around 186°C. However, the DGEBP/PDA curve shows a very sharp exothermic peak centered at around 118°C without any endothermic peak. This means that the curing reaction takes place rapidly in the short temperature range in the solid state without melting. The DGEBP/PDA curve also contains a weak exotherm at around 173°C that is associated with the cure reaction between the adjacent unreacted amine and epoxy group, and it shows a medium exotherm at around 277°C that is related to the overlap of homopolymerization of the unreacted epoxy monomer and the thermal decomposition of the cured epoxy. The T_p values at 3, 5, 10, and 20°C/min are 108.1, 111.7, 118.0, and 123.6°C, respectively. These values are introduced to the Kissinger equation, and activation energy and preexponential factor can be obtained from the following equation.

$$-\ln\left(\frac{q}{T_p^2}\right) = 17.9 \times 10^3 \frac{1}{T_p} - 36.0 \quad (7)$$

The activation energy is 148.8 kJ/mol and the preexponential factor is $7.7 \times 10^{19} \text{ min}^{-1}$.

Table III Comparison of Cure Rate for Three Systems

System	E (kJ/mol)	A (min^{-1})	Arrhenius Rate Constant at 100°C (min^{-1})
DGEBP/DABP	55.6	4.0×10^6	6.6×10^{-2}
DGEBP/MDA	51.5	1.0×10^6	6.2×10^{-2}
DGEBP/PDA	148.8	7.7×10^{19}	11.4×10^{-2}

To compare the cure rate for the three systems, preexponential factor and activation energy values are introduced to the following Arrhenius equation to get rate constants at a selected temperature and the data are shown in Table III.

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (8)$$

where k is the rate constant and T is a selected temperature (100°C). The rate constant for DGEBP/PDA is 2 times higher than those for DGEBP/DABP and DGEBP/MDA, which are almost the same values. Strictly speaking, the rate constant of DGEBP/DABP is a little higher than that of DGEBP/MDA. These results are in good agreement with the DSC curves in Figure 8. That

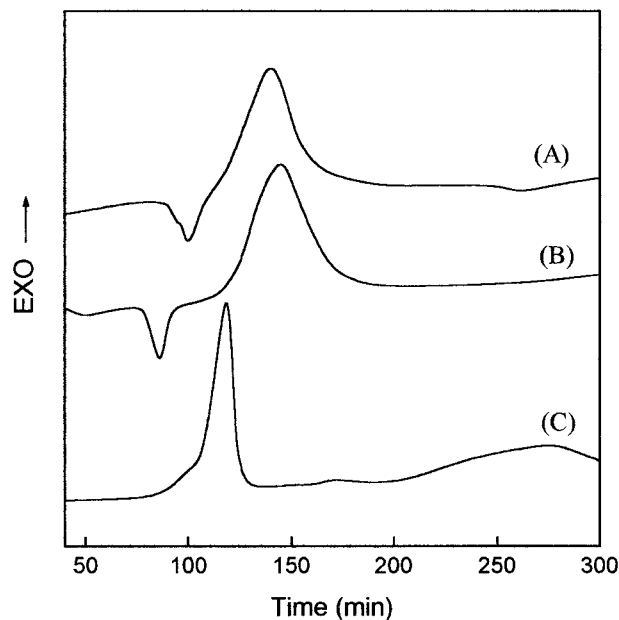


Figure 8 A comparison of DSC curves for DGEBP/DABP (curve A), DGEBP/MDA (curve B), and DGEBP/PDA (curve C) at 10°C/min.

is, the curing reaction of the DGEBP/PDA system starts at the lowest temperature and the exothermic curve of DGEBP/DABP is a little lower than that of DGEBP/MDA. The shape of DGEBP/PDA is very sharp, while those of the other systems are relatively broad. This is due to the fact that the curing reaction of the DGEBP/PDA system takes place only between adjacent groups of the solid state in the short temperature range, while the other systems' reactions happen after comelting of the monomers and the functional groups freely moved to a long distance in the broad temperature range.

CONCLUSIONS

The curing reaction characteristics of LCE monomers with three different aromatic diamines were studied by the Kissinger equation and DSC analysis. The DGEBP/DABP and DGEBP/MDA systems showed an exothermic curing reaction after comelting of the monomers, while the DGEBP/PDA system's curing reaction took place in the solid state without melting of the monomers. The activation energy and preexponential factor for the DGEBP/DABP system were 55.6 kJ/mol and $4.0 \times 10^6 \text{ min}^{-1}$, respectively. Those values for the DGEBP/MDA and DGEBP/PDA systems were 55.1 kJ/mol and $1.0 \times 10^6 \text{ min}^{-1}$ and 148.8 kJ/mol and $7.7 \times 10^{19} \text{ min}^{-1}$, respectively. The rate constant at 100°C for DGEBP/PDA is 2 times higher than those for DGEBP/DABP and DGEBP/MDA, which are almost the same values. Strictly speaking, the rate constant of DGEBP/DABP is a little

higher than that of DGEBP/MDA, and these results well agreed with the DSC curves.

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