Curing Kinetics of Liquid Crystalline Epoxy Resins Based on Bisphenol-S Mesogen with DDE by Nonisothermal DSC Data

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The curing kinetics for a system of Sulfonyl bis(4,1-phenylene)bis[4-(2,3-epoxypro pyloxy)benzoate] (p-SBPEPB) with 4,4'-diaminodiphenyl ether (DDE) were investigated by nonisothermal differential scanning calorimetry (DSC). The dependencies of the apparent activation energy Ea and the conversion α during overall curing reaction were revealed by Ozawa's method. The results shown the Ea decreased drastially from 107 to 75 KJ/mol with α in the initial stages (α = 0–20%), the average apparent activation energy Ea of p-SBPEPB/DDE is 82.81 KJ/mol and was relatively constant in the 0.5 to 0.9 conversion interval. Some parameters were evaluated using the two kinetic models of Šesták–Berggren (S-B) equation and JMA model. The liquid crystalline (LC) phase had formed and was fixed in the system during the curing process.

INTRODUCTION

Liquid crystalline epoxy resin (LCER) is an important thermosetting polymer, and has been widely applied in a number of fields such as electronics, advanced composites, and nonlinear optics. [1–4]. Curing reactions of LCER with curing agents can form highly orderly and densely crosslinked LC polymer networks under suitable curing conditions. As a result, the epoxy polymer may develop an LC

structure during the curing process. Curing initiates a phase transition from an isotropic to LC state that is likely to introduce dramatic changes into the overall curing kinetics. Therefore, the curing kinetics of LC systems should be even more complex than that of isotropic epoxy systems. The study of the cure kinetics contributes both to a better knowledge of the process development and to improving the quality of the polymeric materials.

Thus far, many investigators have reported the synthesis of LCER based on hydroquinone or bisphenol and their cure kinetics [4–8]. However, there are no reports about the synthesis and curing kinetics of LCER based on bisphenol-S mesogen until now. We had studied the cure kinetics of nonliquid crystalline bisphenol-S epoxy resin with isothermal DSC method [9]. In this paper, the cure kinetics of the LCER based on bisphenol-S mesogen, namely, sulfonyl bis(4,1-phenylene)bis [4-(2,3-epoxypro pyloxy)benzoate] (p-SBPEPB) with 4,4′-diaminodiphenyl ether (DDE) is examined by nonisothermal DSC at different heating rates. The dependencies of the apparent activation energy Ea and the conversion α are revealed for the overall curing reaction by the Ozawa method [10], and some kinetic parameters are obtained according to Šesták-Berggren (*S-B*) autocatalytic model and JMA model [9,11]. The phase behavior is determined and the curing mechanism of LCER is proposed.

EXPERIMENTAL

Materials

The 4,4′-sulfonyldiphenol (bisphenol-S, BPS) was chemically pure grade and recrystallized in toluene; the melting point is 240°C. Allyl bromide (Jiangsu, Fangqiao Chem. Co. China), 4-hydroxy ethyl benzoate and all other reagents were all analytically pure grades and supplied by the Beijing Chemical Reagent Co. China. The p-SBPEPB was synthesized and characterized according to the literature [2,5]. The molecular structure of p-SBPEPB has the following form:
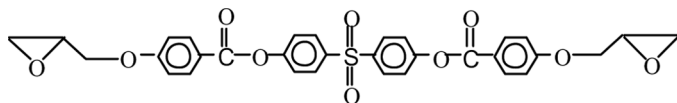
The epoxy value of p-SBPEPB is 0.27 mol/100 g, melting point T_m is 155°C, the clearing point T_i is 302°C, and the LC phase is nematic in nature.

DSC Measurements

Differential scanning calorimeter (DSC, Diamond Perkin Elmer Co., USA) was calibrated with high-purity indium. The 4,4-diaminodiphenyl ether (DDE) was used as curing agent. The p-SBPEPB/DDE sample was prepared with a stoichiometric ratio of one epoxy group to one N-hydrogen. The p-SBPEPB and DDE were mixed homogeneously and ground to fine powder at ice bath temperature. About 4 mg sample, weighed accurately, was placed into an aluminum DSC sample cell and sealed with an aluminum lid. The entire operation was carried out in a dry chamber. Nonisothermal DSC was employed to study the curing behavior [12,13]. The dynamic DSC analysis was performed at five heating rates β: 5, 10, 15, 20, 25 K/min under a nitrogen flow of 20 ml min^{-1} from 303 to 500 K, for all samples.

RESULTS AND DISCUSSION

Kinetic Theory Model of DSC Analysis

The rate of the curing reaction of thermosetting resins can be described by Eq. (1) as follow:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where k is a temperature-dependent reaction rate constant and has an Arrhenius type dependence between k and temperature T. α is the extent of reaction or conversion, $f(\alpha)$ is a function of conversion α and depends on the kinetic model function (see below).

Considering that the rate Eq. (1) is valid for dynamic curing and $\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT}$, where $\beta = dT/dt$ is the heating rate (K/min), the Eq. (1) can be modified as follows:

$$\beta \frac{d\alpha}{dT} = A \cdot e^{(-Ea/RT)} \cdot f(\alpha) \tag{2}$$

where T is the temperature, in K, A is the pre-exponential factor, Ea is the apparent activation energy, and R is the gas constant (8.314 J mol/K).

For the nonisothermal curing process, the equation for isoconversional method can be expressed in several ways including Flynn, Wall, Ozawa and Kissinger methods and so on [14]. Equation (3) is known as Ozawa's method [6,10], which can be applied to different conversions α of the entire curing process. Thus, for a given α, the apparent activation energy Ea can be obtained from linear regression according to Eq. (3)

$$\ln \beta = A' - 1.052 \frac{Ea}{RT} \tag{3}$$

The experimentally evaluated values of Ea were used to find the appropriate kinetic model which best describes the conversion function of the process studied. Once Ea has been determined, the most suitable kinetic model can be evaluated with the functions y(α) and z(α) according to Eq. (4) and Eq. (5) [11,12].

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp(x) \tag{4}$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)T/\beta \tag{5}$$

where x is reduced activation energy (Ea$/RT$), β represents the heating rate (K min^{-1}), T is the absolute temperature (K) and π(x) denotes an approximation of the temperature integral, which was approximated using the fourth rational expression [12,13] as in Eq. (6).

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{6}$$

For practical reasons, the y(α) and z(α) functions are normalized within (0,1) range. The maximum α_M of the y(α) function and α_P^∞ of the z(α) function suggest the choice of the most suitable kinetic model characterizing the curing process.

Nonisothermal DSC Analysis

Figure 1 shows the DSC curves of the p-SBPEPB/DDE cured system at five heating rates. The relationships of conversion α vs. dynamic curing temperature T for p-SBPEPB/DDE systems are shown in Figure 2. As seen from Figure 2, at the same conversion α value, the isoconversion temperature was higher when the heating rate increased. According to α-T and the Ozawa equation (3), from the plots of ln β vs. $1/T$, the apparent activation energy Ea at any conversion α can be calculated, and the results are shown in Figure 3. In Figure 3, the linear coefficients of ln β with $1/T$ all fall between 0.997 and 0.999, and it shows that this curing system well obeys kinetic model [10].

As seen from Figure 3, the Ea changes at various conversions α, and gradually decreases with increasing α in the curing system. For p-SBPEPB/DDE, the Ea values decrease from 107 to 75 kJ mol^{-1} in the started stages of $\alpha = 0$ to 0.2. This result is coincident with the conclusions of Ehers and Vyazovkin [15,16]. The mechanism of curing reaction for epoxy resins with amine is complex, and the primary
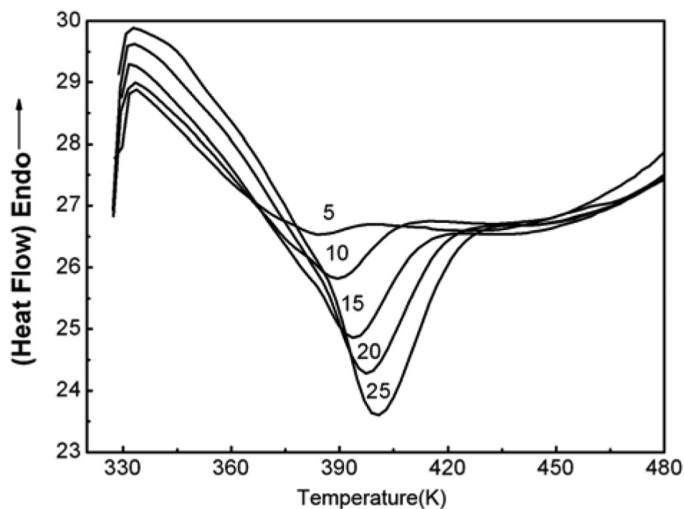
FIGURE 1 DSC curve of p-SBPEPB/DDE cured system at different heating rates.

amine has a higher Ea in a noncatalyzed pathway. After the reaction started, the hydroxyl group is created first. Then the transition state of alcohol-catalyzed reaction occurs, having a lower Ea than non-alcohol-catalyzed reactions [15]. From 0.2–0.5 for α, the Ea increases
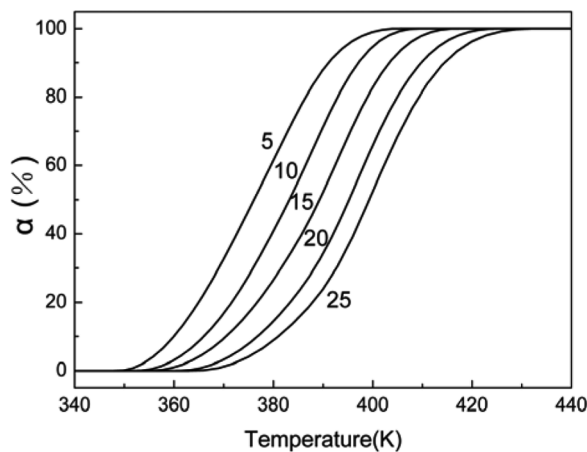

FIGURE 2 α vs. T curves of p-SBPEPB/DDE cured system at different heating rates.

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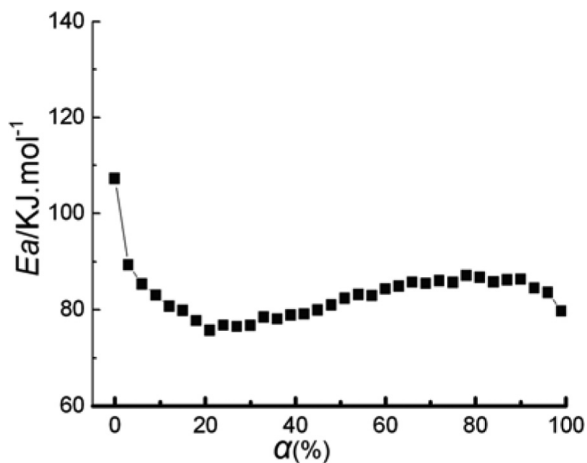
FIGURE 3 The activation energy change E_a calculated by the Ozawa method at various α for p-SBPEPB/DDE curing systems.

a little from 75–82.75 kJ mol^{-1}. This can be associated with the formation of LC phase, which significantly affects the kinetic parameters of the curing reaction (Figure 4), since the rate of the chemical reaction generally depends on the transport properties of the reaction medium. After that, the E_a was relatively constant for the interval of $0.5 < \alpha < 0.9$. In the final stage of $\alpha = 0.9$–1, the E_a again decreases a little from 88 to 80 kJ mol^{-1}, which is associated with gelation and vitrification in the curing reaction process. A diffusion control becomes

FIGURE 4 POM morphology texture of curing p-SBPEPB/DDE.

operative and the primary amines have all changed to secondary amines in the reaction anaphase, where the secondary amines have a lower Ea in the presence of hydroxyl groups [15–17].
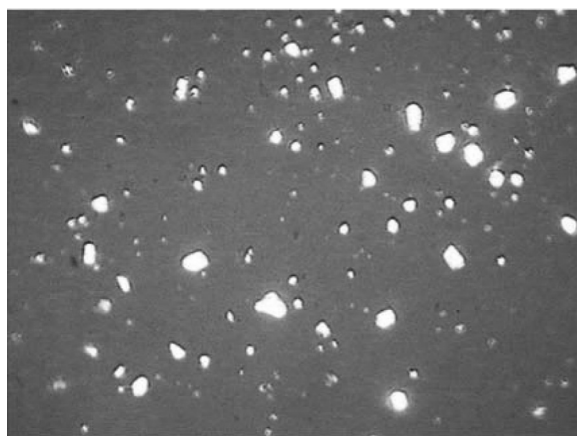
Figure 5 shows the variation of $y(\alpha)$ and $z(\alpha)$ values with conversion α. For practical reasons, the $y(\alpha)$ and $z(\alpha)$ functions are normalized within $(0,1)$ range. Table 1 lists the values of α_M, α_p and α_P^∞. The α_p value taken as the conversion α at the DSC peak.

As can be noted, $\alpha_M \neq 0$ and the α_M values are lower than the α_p values, $\alpha_P^\infty \in (0, \alpha_p)$. So the curing process of this curing system can be described using a two-parameter autocatalytic model of
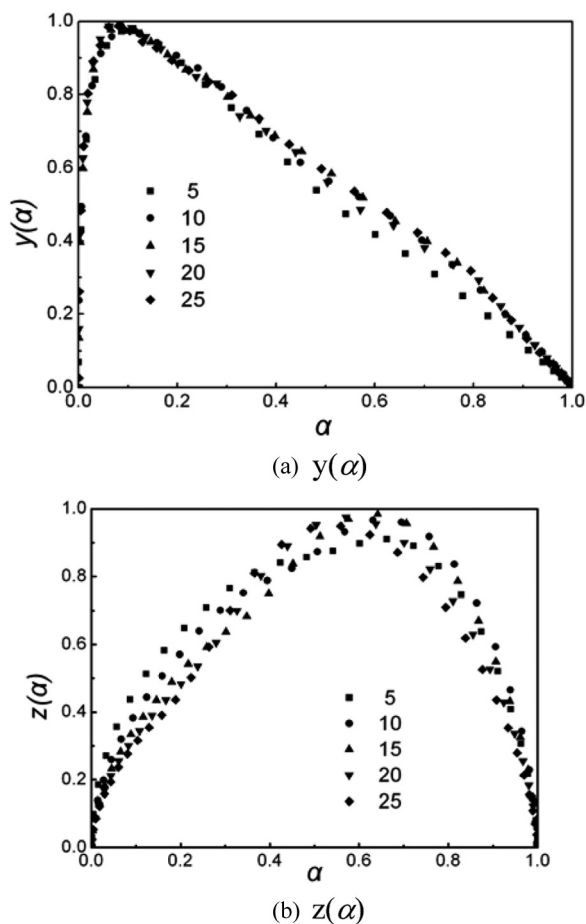

(a) $y(\alpha)$

(b) $z(\alpha)$

FIGURE 5 Variation of normalized y(a) and z(a) function vs. conversion for p-SBPEPB/DDE (a) $y(\alpha)$; (b) $z(\alpha)$.

TABLE 1 Values of α_p, α_M, α_P^∞ Obtained from DSC Data of p-SBPEPB/DDE

Heating Rate (°C/min)	α_p	α_M	α_P^∞
5	0.652	0.0830	0.658
10	0.637	0.0846	0.629
15	0.631	0.0596	0.637
20	0.580	0.0548	0.571
25	0.513	0.0553	0.554

Šesták-Berggren (S-B) of Eqs. (7) and (8) [11,12], and the value of conversion corresponding to the maximum of $z(\alpha)$ function α_P^∞ is constant (0.632) for JMA model of Eq. (9) [9].

$$f(\alpha) = k\alpha^m(1-\alpha)^n \tag{7}$$

$$\ln[(d\alpha/dt) \cdot e^x] = \ln A - n\ln[\alpha_p \cdot (1-\alpha)] \tag{8}$$

where k is the rate constant, A is the pre-exponential factor and m and n are the reaction orders.

$$f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{1-(1/m)} \tag{9}$$

$$A = \frac{\beta Ea \exp(Ea/RT_p)}{RT_p^2} \tag{10}$$

where T_p is the peak temperature at the different heating rates.

## Application of Autocatalytic Model S-B (*m, n*)

Table 2 lists the kinetic parameters (m, n, $\ln A$, and Ea) that were experimentally obtained according to the proposed S-B kinetic model. The kinetic parameter n and $\ln A$ are obtained from the slope and intercept of the linear dependence $\ln[(d\alpha/dt) \cdot e^x]$ vs. $\ln[\alpha^p \cdot (1-\alpha)]$ according to Eq. (8), where $m = p \cdot n$ and $p = \alpha_M/(1-\alpha_M)$. The linear coefficients of kinetic parameters in Table 2 all fall between 0.992–0.999, which further indicates that the curing system well obeys the S-B model. A is related to the activation entropy change, ΔS [18]. Then, ΔS for the studied curing systems was evaluated using Eq. (10) and listed in Table 2. The negative values of ΔS indicate that the activated complexes have a more ordered structure than the reactants [19].

$$A = \frac{kT}{h} \cdot \exp\left(\frac{\Delta S}{R}\right) \tag{10}$$

TABLE 2 Apparent Kinetic Parameters Evaluated for Nonisothermal Curing from S-B Model and JMA Model

Model	Heating rate (°C/min)	E_a (KJ mol⁻¹)	ln A	Mean	m	Mean	n	Mean	ΔS (J K⁻¹ mol⁻¹)	Mean
S-B	5		25.25		0.083		0.92		−37.07	
	10		25.46		0.076		0.82		−35.47	
	15	82.81	25.43	25.32	0.054	0.065	0.85	0.86	−35.80	−36.68
	20		25.27		0.049		0.85		−37.21	
	25		25.20		0.064		0.86		−37.84	
JMA	5		25.19		1.094				−37.59	
	10		25.46		1.097				−35.47	
	15	82.81	25.52	25.41	1.065	1.075			−35.01	−35.96
	20		25.45		1.06				−35.69	
	25		25.42		1.06				−36.05	

where k is the Boltzmann constant, h is the Planck constant and T is the peak temperature of DSC curves. The experimental curves of $d\alpha/dt$ vs. the temperature T (symbols) and theoretical curves (full lines) calculated using the kinetic parameters corresponding to each heating rate (see Table 2) are compared in Figure 6. In Figure 6, a good agreement can be seen between the theoretical curves and those experimentally determined. This means that the two-parameter S-B (m, n) model can give a good description of the curing process for the studied curing system.
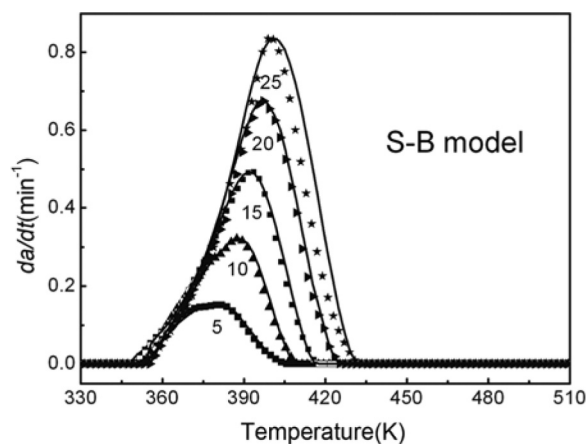
FIGURE 6 Experimental (symbols) and calculated (full lines) DSC curves for S-B model.
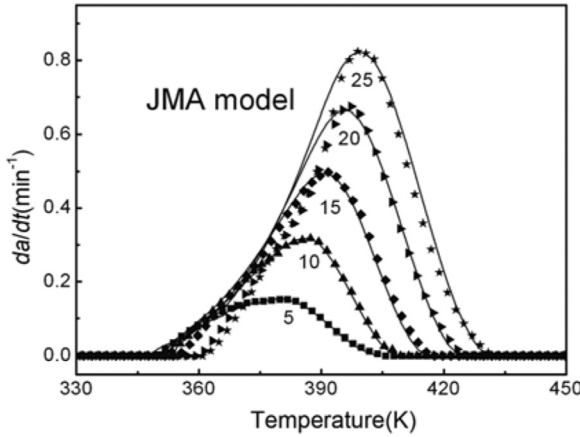
FIGURE 7 Experimental (symbols) and calculated (full lines) DSC curves for JMA model.

Application of Model JMA (*m*)

If the y(α) function has a maximum at $\alpha_M \rightarrow 0$ and $\alpha_M \in (0, \alpha_p)$, i.e., for $m > 1$, the JMA model can be used to describe the curing system [8]. The parameter m is calculated as $m = [1 + \ln(1 - \alpha_M)]^{-1}$. Knowing the value of the activation energy and the kinetic model, the pre-exponential factor A is calculated using the Eq. (10). Using the α_M value in Table 2 gives the parameter m of JMA model as 1.075. The comparison of experimental data and the theoretical temperature dependence of curing rate is shows in Figure 7. As seen from Figure 7, that the theoretical curves do not correspond very well with the experimental data at $\beta > 15$ K/min. But a good agreement can be seen between the theoretical curves and those experimentally determined at $\beta \leq 15$ K/min. Interestingly, values of A calculated from the two models are approximately the same. This shows that the JMA model can give a good description of the curing process for this curing system at lower heating rate β, too.

CONCLUSIONS

1. The curing kinetics of p-SBPEPB with DDE can be examined by nonisothermal DSC technique at different heating rates and can be evaluated by an autocatalytic kinetic Šesták-Berggren model at different heating rates ($\beta < 25$ K/min) and obey a JMA model at a lower heating rate ($\beta \leq 15$ K/min).

2. The apparent activation energy *E*a decreased drastically in the initial stages ($\alpha = 0$–0.2) and was relatively constant between 0.5 and 0.9 conversion interval. The average *E*a is 82.81 KJ/mol.

3. The liquid crystalline phase had formed and was fixed in the system during the curing process.

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