

Nonisothermal Cure Kinetics and Diffusion Effect of Liquid-Crystalline Epoxy Sulfonyl bis(1,4-phenylene)bis[4-(2,3-epoxypropyloxy)benzoate] Resin with Aromatic Diamine

Jungang Gao,¹ Li Huo,^{1,2} Yonggang Du¹

¹College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

²Department of Chemistry, Baoding University, Baoding 071000, China

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ABSTRACT: The curing kinetics of the liquid-crystalline epoxy resin sulfonyl bis(1,4-phenylene)bis[4-(2,3-epoxypropyloxy)benzoate] with 4,4'-diaminodiphenylsulfone was investigated by nonisothermal differential scanning calorimetry. The relationship between the apparent activation energy (E_a) and the conversion was determined, and the effects of the molecular structure and the order of liquid crystallinity on E_a are discussed in detail. Some parameters were evaluated with the autocatalytic kinetic model of the Šesták–Berggren (S–B) equation. The results show that there were some deviations of these simulation curves from the experimental curves at high heating rates and in the late stage of the curing reaction. The diffusion effect in the nonisothermal curing reaction is discussed, and a dif-

fusion factor was proposed and introduced into the S–B equation. Then, a modified S–B equation was created, as follows: $\frac{d\alpha}{dt} = K\alpha^m(1-\alpha)^n \times \frac{1}{1+\exp[\frac{1}{C}(\alpha-\alpha_c)]}$, where α is the conversion, t is the time, m and n are reaction orders, K is rate constant, C is the diffusion coefficient, and α_c is the critical conversion. The theoretical simulation curves agreed very well with the experimental data as determined with the modified S–B equation, which may be more useful for describing and predicting the nonisothermal curing reaction kinetics of epoxy resin. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: activation energy; curing of polymers; kinetics (polym.); liquid-crystalline polymers (LCP); thermosets

INTRODUCTION

Liquid-crystalline epoxy resins (LCERs) are important thermosetting polymeric materials. Under suitable curing conditions, the curing reaction of LCERs with a curing agent can form highly ordered and densely crosslinked liquid-crystalline polymer networks, which show interesting properties because of the combination of thermoset and liquid-crystalline formation capabilities.^{1–4} The cure kinetics and reaction mechanism of epoxy resins and LCERs are widely studied by isothermal or dynamic experiments with differential scanning calorimetry (DSC). The experimental data are analyzed by a homogeneous reaction model, normally with an n th-order or autocatalytic equation.^{5–8} In an isothermal curing process, Kamal's model is usually applied to analyze DSC data.⁹ In general, a good fit of experimental data with theoretical simulation is obtained in the early stages of the curing reaction, but deviations are observed at the late stage, particularly near the

vitrification, where the reaction is primarily controlled by diffusion. To take into account the diffusion effect, Kamal's model is extended by the introduction of a diffusion factor [$f(\alpha)$], and diffusion control has been discussed in detail.^{10,11} In nonisothermal curing kinetics, the autocatalytic kinetic model of the Šesták–Berggren (S–B) equation is usually used to describe the curing process,^{12,13} but deviations at the late stage of curing reaction are also observed, as in isothermal DSC analysis with Kamal's model. However, these deviations from simulation in nonisothermal DSC experiments have not been discussed so far.

Sbirrazzuoli and coworkers^{8,14} reported that the curing of LCERs usually leads to the formation of ordered networks (nematic or smectic structure), and the order affects the cure kinetics and apparent activation energy (E_a), so the cure kinetics of LCERs should be more complex than that of isotropic epoxy resins. We synthesized an LCER, sulfonyl bis(1,4-phenylene)bis[4-(2,3-epoxypropyloxy)benzoate] (*p*-SBPEPB), and reported its curing reaction with aromatic diamines and the catalyzing effect of hydroxyl groups.^{15,16} In this study, the curing kinetics of *p*-SBPEPB with 4,4'-diaminodiphenylsulfone (DDS) were investigated by a nonisothermal

Correspondence to: J. Gao (gaojg@mail.hbu.edu.cn).

DSC method. The relationship of E_a with conversion (α) was calculated by Ozawa's method,^{17,18} and the effects of liquid-crystalline structures on E_a are discussed. An $f'(\alpha)$ was introduced into the S-B equation, and some kinetic parameters were evaluated with this modified S-B model. The results show that a good fit of experimental curves with theoretical simulation was obtained for the entire reaction process.

EXPERIMENTAL

Materials

LCER based on the bisphenol S mesogen, *p*-SBPEPB, was synthesized according to a procedure described elsewhere.¹⁵ The molecular structure of *p*-SBPEPB is shown in Scheme 1. *p*-SBPEPB has a nematic mesophase between its melting temperature of 428 K and its clearing temperature of 575 K. The epoxy value of *p*-SBPEPB is 0.30 mol/100 g. DDS and other reagents were all analytically pure grade and were supplied by Beijing Chemical Reagent Co. (Beijing, China).

Characterization of the curing system

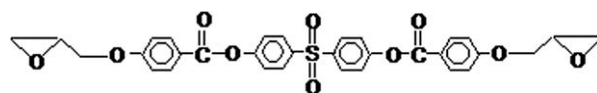
The curing reactions were carried out in a differential scanning calorimeter (Diamond, PerkinElmer Co., USA) calibrated with high-purity indium. DDS was used as the curing agent. The samples of the curing reaction were prepared with a stoichiometric ratio of one epoxy group to one amino-hydrogen in DDS. The mixture of *p*-SBPEPB and DDS was dissolved in ethanol and dried *in vacuo*, and then, it was ground into a fine powder (granularity \approx 0.085 mm) under 0°C. Samples of about 6 mg were placed into aluminum DSC sample pans sealed with aluminum lids and then heated from 298 to 523 K under a nitrogen flow of 20 mL/min. The dynamic DSC analysis was performed at four different heating rates (β 's) of 5, 10, 15, and 20 K/min, respectively.

Kinetic theory model of DSC analysis

The curing rate of the kinetic process ($d\alpha/dt$) can be described by eq. (1), as follows:

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

where k is a temperature-dependent reaction rate constant with an Arrhenius-type dependence between k and temperature T (K) and $f(\alpha)$ is a temperature-dependent kinetic model function. Because the rate equation [eq. (1)] is valid for dynamic curing and $\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT}$, where $\beta = dT/dt$, eq. (1) can be modified as follows:



Scheme 1 Molecular structure of *p*-SBPEPB.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (2)$$

where A is the pre-exponential factor.

For a nonisothermal curing process, the equation for the isoconversional method can be expressed in several ways. Equation (3) is known as *Ozawa's method* and can be applied to different α 's of the curing process.^{13,19,20} Thus, for a given α , E_a can be obtained from linear regression according to eq. (3):

$$\text{Ln}\beta = A' - 1.052 \frac{E_a}{RT} \quad (3)$$

where A' is intergration constant.

The experimentally evaluated values of E_a were used to find the appropriate kinetic model that best described the α function of the process studied. Once E_a was determined, the most suitable kinetic model could be evaluated with the functions $y(\alpha)$ and $z(\alpha)$, according to eqs. (4) and (5):^{12,13}

$$y(\alpha) = \frac{d\alpha}{dt} \exp x \quad (4)$$

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

where x is the reduced activation energy (E_a/RT), T is the absolute temperature (K), and $\pi(x)$ denotes an approximation of the temperature integral, which is approximated with the fourth rational expression:

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

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

RESULTS AND DISCUSSION

E_a

Figure 1 shows the cured DSC curves of *p*-SBPEPB/DDS at four heating rates, respectively. The peak temperatures of the curing system increased when the heating rate was increased.

The relationships of α versus dynamic curing temperature are shown in Figure 2. As shown in Figure 2,

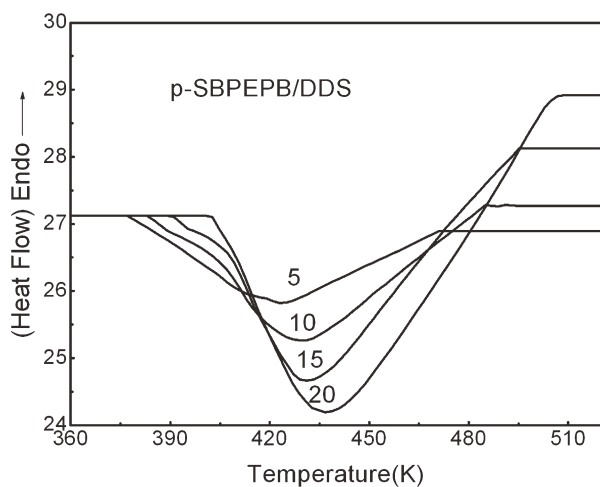


Figure 1 DSC curves of the *p*-SBPEPB/DDS cured systems at different heating rates.

at the same α value, the isoconversion temperature was higher when the heating rate increased. According to $\alpha - T$ and eq. (3), from the plot of $\ln \beta$ versus $1/T$, E_a at any α could be calculated. The linear coefficients of $\ln \beta$ with $1/T$ were all included between 0.9900 and 0.9999, and this showed that the curing system obeyed Ozawa's kinetics model well; the results are shown in Figure 3.

As shown in Figure 3, with the reaction processing, E_a had a small increase at $\alpha = 0-0.3$ and was almost constant at $0.3 \leq \alpha \leq 1.0$, and the E_a for this system approached 85 ± 2 kJ/mol when $\alpha > 0.3$. It was different from the diglycidyl ether of bisphenol S (*p*-BEPSPB)/DDM(4,4'-diaminodiphenylmethane) system reported in our previous work,¹⁵ in which, at the initial stage, E_a for the *p*-BEPSPB/DDM system was higher than that at the last stage. This was attributed to the *p*-BEPSPB having a smectic mesophase (a higher order) and shorter mesogenic length,

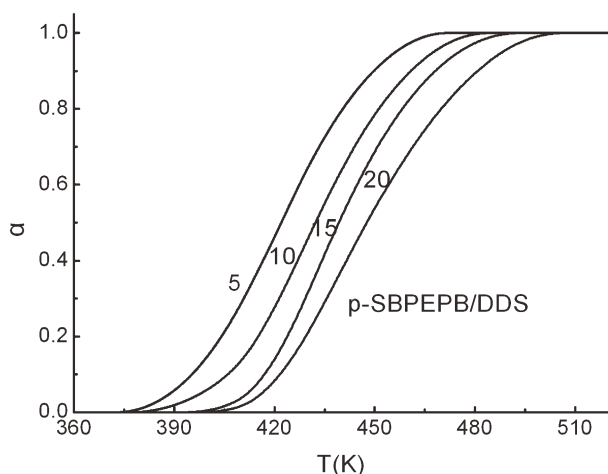


Figure 2 α versus dynamic curing temperature (T) curves of the *p*-SBPEPB/DDS cured systems at different heating rates.

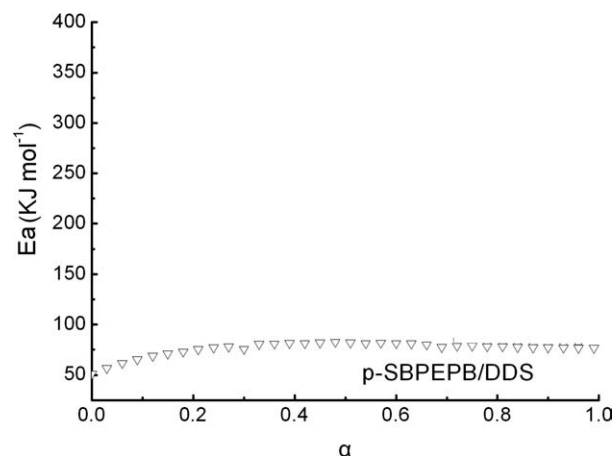


Figure 3 Relationship of E_a versus α calculated by the Ozawa method.

and it had a higher steric effect because the nucleophilic attack of the primary amine needed a higher E_a in the initial stage.²¹ However, the smectic structure of *p*-BEPSPB gradually transferred into a nematic structure when the reaction was going on; therefore, the E_a of the *p*-BEPSPB/DDM system was a gradually decreasing process. However, *p*-SBPEPB was a nematic mesophase, which had a smaller order than that of smectic mesophase and smaller steric effects for the nucleophilic attack of the primary amine, so it had a lower E_a than the *p*-BEPSPB/DDS system at the initial stage of the curing reaction. This result is coincide with the conclusion of Lee and Jang,²² in which they proved that E_a decreased and the reaction rate increased when the mesogenic length increased; there was also a nematic liquid-crystalline phase, which was thought to be due to the liquid character and high chemical reactivity of long mesogenic LCER.

Cure kinetic analysis

Figures 4 shows the variation of the $y(\alpha)$ and $z(\alpha)$ values with α for this curing system. Table I lists the values of α_M and α_P^∞ , together with those of α_P , which was taken as the α maximum at the DSC peak.

As can be noted, the α_M values were lower than the α_P values and $\alpha_M \neq 0$. So the curing process of *p*-SBPEPB/DDS could be described by the two-parameter autocatalytic model of S-B,¹² as follows:

$$f(\alpha) = k\alpha^m(1-\alpha)^n \quad (7)$$

$$\ln[(d\alpha/dt)e^x] = \ln A - n \ln[\alpha_P(1-\alpha)] \quad (8)$$

where k is the rate constant, m and n are all the reaction orders, and x is reduced activation energy (E_a/RT).

Table II lists the kinetic parameters (m , n , $\ln A$, and E_a), which were experimentally obtained

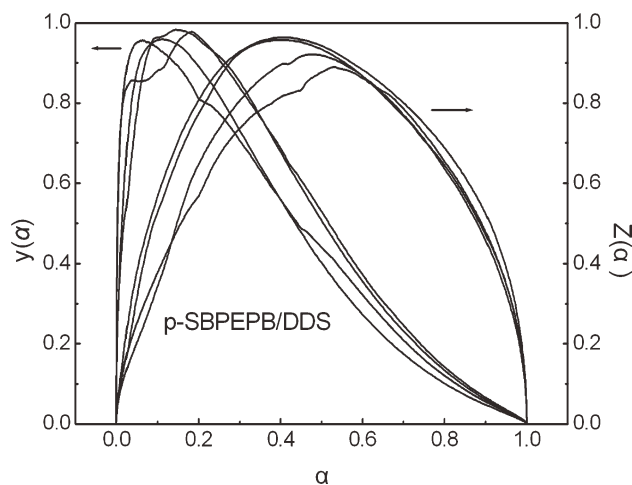


Figure 4 Variation of normalized $y(\alpha)$ and $z(\alpha)$ functions versus α for the p -SBPEPB/DDS cured systems.

according to the proposed S–B kinetic model. The kinetic parameters n and $\ln A$ were obtained by the slope and intercept of the linear dependence $\ln[(d\alpha/dt)e^x]$ versus $\ln[\alpha_p(1 - \alpha)]$ according to eq. (8), where $m = pn$ and $p = \alpha_M/(1 - \alpha_M)$. The linear coefficients of the kinetic parameters in Table II were all between 0.9920 and 0.9990, which further indicated that this curing system obeyed the S–B model well. A is related to the activation entropy (ΔS).²³ Then, ΔS for the studied curing system was evaluated with eq. (9) and is listed in Table II. The negative values of ΔS indicated that the activated complexes had a more ordered structure than the reactants:

$$A = kT/h \exp(\Delta S/R) \quad (9)$$

where k is the Boltzmann constant, h is Planck's constant, T is the peak temperature of the DSC curve, and R is the gas constant.

The experimental curves (symbols) of $d\alpha/dt$ versus T and the simulation curves (full lines) calculated with the kinetic parameters to each heating rate (see Table II) are compared in Figure 5. A good fit was seen between the simulation curves and those experimentally determined for this system in the early stage, but some deviation appeared in the last stage, which was more evident at faster heating rates. This phenomenon has also been discovered in other systems (liquid-crystalline systems or non-liquid-cryst-

TABLE I
The Values of α_p , α_M , and α_p^∞ Obtained from the DSC Data for p -SBPEPB/DDS

Heating rate (K/min)	α_p	α_M	α_p^∞
5	0.528	0.055	0.531
10	0.464	0.180	0.477
15	0.358	0.141	0.408
20	0.366	0.113	0.405

talline systems).^{24–26} However, it was different from isothermal DSC, in which the experimental curves are usually lower than the simulation curves in the last stage; in a nonisothermal process, the experimental curves are usually higher than the simulation curves. In an isothermal process, the deviation is due to the onset of gelation and vitrification, where the mobility of reactive groups are hindered, and the rate of α is controlled by diffusion rather than by kinetic factors.^{10,11,26} However, in a nonisothermal process, the temperature of samples increase gradually with time, and the free volume of materials and molecular activity increase with temperature simultaneously; then, the diffusion rate and kinetic energy of the reactive groups increase, and this leads to an increase in the reaction rate. So, the experimental curves may be higher than the simulation curves in the last stage.

In the isothermal process, Chern and Poehlein,²⁷ on the basis of the theory of free volume consideration and the diffusion effect, introduced an $f(\alpha)$ to the autocatalytic Kamal equation and obtained a semiempirical relationship, and an improved Kamal equation can be used well in the isothermal curing process of a thermosetting resin. For a nonisothermal process, to consider the free volume and diffusion effect, in this study, $f'(\alpha)$ was also considered to introduce the S–B kinetic model. In this relationship, $f'(\alpha)$ is defined as the ratio k_c/k_e , where k_c is the rate constant for chemical kinetics and k_e is the overall effective rate constant:

$$f'(\alpha) = k_c/k_e = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (10)$$

where C is the diffusion coefficient and α_c is the critical conversion depending on the curing temperatures. The plot of $f'(\alpha)$ versus α is shown in Figure 6.

TABLE II
Apparent Kinetic Parameters Evaluated for the Nonisothermal Process of the p -SBPEPB/DDS Cured System

Heating rate (K/min)	E_a (kJ/mol)	$\ln A$	m	Mean	n	Mean	ΔS (J K ⁻¹ mol ⁻¹)	Mean
5	76.034	20.30	0.18	0.33	1.35	2.40	-79.06	-74.53
10		19.6	0.20		1.60		-84.59	
15		21.7	0.46		2.86		-67.58	
20		21.8	0.47		3.81		-66.89	

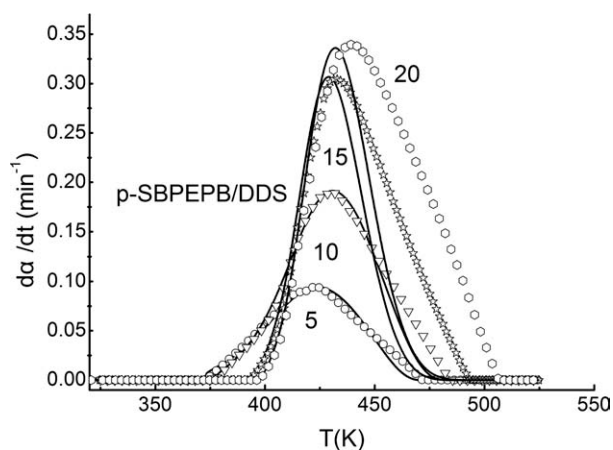


Figure 5 Experimental (symbols) and calculated (full lines) DSC curves of the *p*-SBPEPB/DDS systems (where *t* is time).

As seen from Figure 6, for $\alpha \ll \alpha_c$, $k_e = k_c$, $f'(\alpha)$ was approximately equal to unity, and the effect of diffusion was negligible so that the reaction was kinetically controlled. When α approached α_c , $f'(\alpha)$ began to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$. Beyond that point, it continued to decrease and approached zero, which meant that the reaction became very slow and effectively stopped. As seen also from Figure 6, α_c approached unity when the heating rate was lower. This result was different from some isothermal processes, in which it α_c is usually lower than unity.^{28,29} This was related to the increasing temperature, and it could reach a higher α in a nonisothermal process.

From eq. (10), we obtained

$$-\ln\left[\frac{1}{f'(\alpha)} - 1\right] = C\alpha_c - C\alpha \quad (11)$$

where C and α_c were obtained from the slope and the intercept of plot of $-\ln[1/f'(\alpha) - 1]$ versus α , as

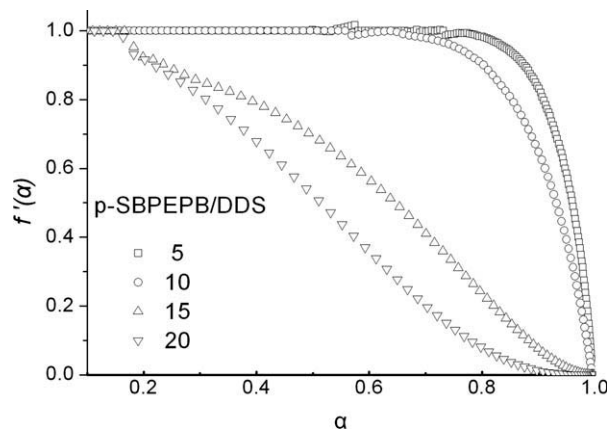


Figure 6 $f'(\alpha)$ versus α for the *p*-SBPEPB/DDS cured systems.

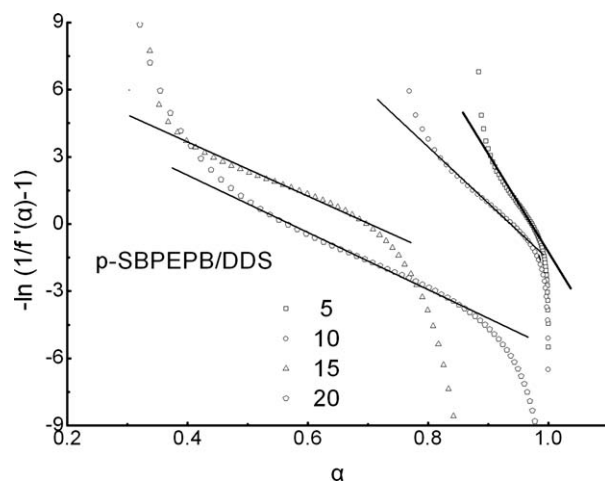


Figure 7 Plot of $-\ln[1/f'(\alpha) - 1]$ versus α for the *p*-SBPEPB/DDS system at different heating rates.

seen in Figure 7 at different heating rates. The linear correlation was good when the curing extent was relatively lower, but it had an obvious deviation in the final stage of the reaction. The calculated C and α_c at different heating rates are tabulated in Table III. As seen from Table III, the diffusion effect was smaller at lower heating rates.

With the diffusion effect taken into consideration, the modified S-B equation can be expressed in the following form:

Heating rate (K/min)	α_c	C
5	0.961	61.71
10	0.933	37.38
15	0.652	16.21
20	0.510	26.72

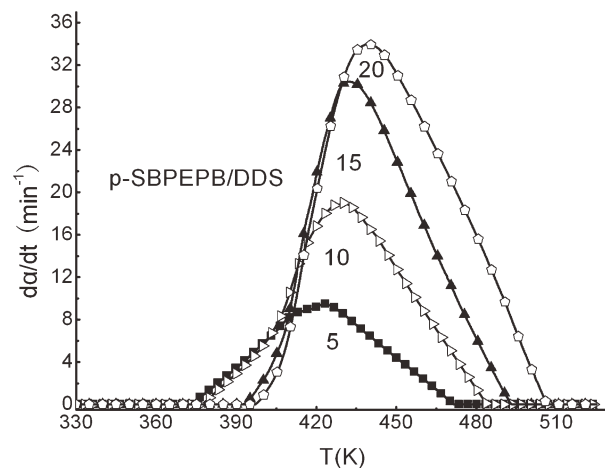


Figure 8 Comparison of the experimental values and values obtained from eq. (12) for the *p*-SBPEPB/DDS system (where *t* is time).

$$\frac{d\alpha}{dt} = K\alpha^m(1 - \alpha)^n \times \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (12)$$

Figure 8 shows the comparison between the experimental curves and the simulation curves obtained from eq. (12). The simulation curves agreed very well with the experimental curves, even at fast heating rates. Therefore, we could employ the modified S–B model to predict and describe the nonisothermal curing reactions.

CONCLUSIONS

1. The nonisothermal curing kinetics of *p*-SBPEPB/DDS could all be described by the Ozawa equation and the two-parameter autocatalytic kinetic model of S–B. The DSC experimental results had some deviation with those simulations in the last stage of the curing reaction at higher heating rates.
2. The molecular structure and order of LCERs had an effect on the reaction kinetics. The even reaction orders *m* and *n* and ΔS (J K⁻¹ mol⁻¹) for *p*-SBPEPB/DDS were 0.33, 2.40, and –74.50, respectively.
3. $f(\alpha)$ was proposed and introduced into the S–B equation. With the modified model, the simulations values agreed very well with the experiment data. So the modified S–B equation was better for describing and predicting the nonisothermal curing reaction of the epoxy resin.

References

1. Yu, Y.; Gan, W.; Liu, X.; Li, S. *J Appl Polym Sci* 2008, 109, 2964.
2. Harada, M.; Sumitomo, K.; Nishimoto, Y.; Ochi, M. *J Polym Sci Part B: Polym Phys* 2009, 47, 156.
3. Ren, S.; Liang, L.; Lan, Y.; Lu, M. *J Appl Polym Sci* 2007, 106, 2917.
4. Liu, G. D.; Zhou, B.; Zhao, D. M.; Li, Q.; Gao, J. G. *Macromol Chem Phys* 2008, 209, 1160.
5. Xu, G.; Shi, W. F.; Shen, S. J. *J Polym Sci Part B: Polym Phys* 2004, 42, 2649.
6. Xie, H.; Liu, B.; Yuan, Z.; Shen, J.; Cheng, R. *J Polym Sci Part B: Polym Phys* 2004, 42, 3701.
7. Evrikleia, G.; Karayannidou, D. S.; Achilias, I.; Sideridou, D. *Eur Polym J* 2006, 42, 3311.
8. Vyazovkin, S.; Sbirrazzuoli, N. *Macromolecules* 1996, 29, 1867.
9. Kamal, M. R. *Polym Eng Sci* 1974, 14, 23.
10. Ma, Z.; Gao, J. *J Phys Chem B* 2006, 110, 236.
11. Seung, H.; Hog, Y.; Kwang, S. S.; Whan, G. K.; Tak, J. M. *J Polym Sci Part A: Polym Chem* 1999, 37, 713.
12. Šesták, J.; Berggren, G. *Thermochim Acta* 1971, 3, 1.
13. Rosu, D.; Mititelu, A.; Cascaval, C. N. *Polym Test* 2004, 23, 209.
14. Lin, Q.; Yee, A. F.; Sue, H. J.; Earls, J. D.; Hefner, R. E., Jr. *J Polym Sci Part B: Polym Phys* 1997, 35, 2363.
15. Huo, L.; Gao, J.; Du, Y.; Chai, Z. *J Appl Polym Sci* 2008, 110, 3671.
16. Huo, L.; Gao, J.; Zhang, X. *J Appl Polym Sci* 2009, 113, 3639.
17. Ozawa, T. *J Therm Anal* 1979, 2, 301.
18. Zhang, Y.; Vyazovkin, S. *J Phys Chem B* 2007, 111, 7098.
19. Zheng, Y. Q.; Shen, M. M.; Lu, M. G.; Ren, S. P. *Eur Polym J* 2006, 42, 1735.
20. Sbirrazzuoli, N.; Vyazovkin, S.; Mititelu, A.; Sladic, C.; Vincen, L. *Chem Phys* 2003, 204, 815.
21. Ehers, J. E.; Rondan, N. G.; Huynh, L. K.; Pham, H.; Marks, M.; Truong, T. N. *Macromolecules* 2007, 40, 4370.
22. Lee, J. Y.; Jang, J. *Polymer* 2006, 47, 3036.
23. Si, A.; Majid, K. *Thermochim Acta* 1998, 317, 183.
24. Gao, J.; Zhang, X.; Huo, L. *Iran Polym J* 2010, 19, 731.
25. Gao, J.; Zhang, X.; Huo, L. *Int Polym Mater* 2008, 57, 925.
26. Rosu, D.; Cascaval, C. N.; Mustata, F.; Ciobanu, C. *Thermochim Acta* 2002, 383, 119.
27. Chern, C. S.; Poehlein, G. W. *Polym Eng Sci* 1987, 27, 782.
28. Li, Y.; Shen, S.; Liu, Y.; Gao, J. *J Appl Polym Sci* 1999, 73, 1799.
29. Gao, J.; Zhao, H.; Li, Y. *Polym Int* 2002, 51, 1422.