Nonisothermal Cure of Bisphenol Epoxy Resin with a Nonlinear Aliphatic Polyamine Hardener

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ABSTRACT: The amino terminated polypropylenimine dendrimer (DAB-dendri-$(NH_2)_4$) was employed as a new nonlinear aliphatic curing agent for diglycidyl ether of bisphenol A (DGEBA). Nonisothermal curing reaction kinetics of DGEBA/DAB was investigated with a differential scanning calorimeter (DSC). The apparent reaction activation energy E_a is about 56.7 kJ/mol determined using the Kissinger equation, and a two-parameter (m, n) autocatalytic model ([icirc]Sesták–Berggren equation) was confirmed to be able to well simulate the reaction kinetics in the light of the Málek method. In addition, the relation between reaction activation energy E_a and curing degree α was obtained by applying model-free isoconversional analysis with the Kissinger-Akahira-Sunose (KAS) method. As α increases, E_a reduced quickly from >80 kJ/mol to ≈60 kJ/mol up to $a \approx 15\%$, then decreased slowly to 55 kJ/mol till $a \sim 75\%$, and finally dropped to 44 kJ/mol at full conversion. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1147–1152, 2012

Key words: differential scanning calorimeter; epoxy resin; curing kinetics; KAS method; SB (m, n); model

INTRODUCTION

Epoxy resins, as one of the most important thermosetting polymers, have been widely used in many fields such as protective coatings, adhesives, high-performance composites, insulating materials, and so on, and the uncured epoxy resins are composed of oligomers or monomers, which can be cured to be a network.[1–8] To obtain excellent overall properties, epoxy resins must be transformed into a crosslinked network by curing reactions in the presence of curing agents. Thus, exploiting a novel curing agent is one of main and effective ways of improving the specific properties of cured epoxy resins at the molecular level. In the past decades, great efforts have been paid to improving thermal resistance, mechanical strength, and flame retardancy of epoxy resins with aromatic amine curing agents. However, aromatic amine curing agents can hardly cure epoxy resins to an acceptable extent under room-temperature range, which limits their applications in some areas. On the other hand, aliphatic amine-based curing agents can generally well solidify epoxy resins at room temperature, which results in their extensive applications in protective and industrial coatings, high-performance adhesives, and so on. On the other

hand, cure behavior of thermosetting polymers plays an extremely important role in determining their curing and processing condition and further affect end-use properties.[9–12] However, curing kinetic analysis of epoxy–new aliphatic amine reaction system is still seldom concerned in open literature to date.[13–19]

In this article, we first, systematically investigate nonisothermal curing of bisphenol-A epoxy resin with a new nonlinear aliphatic amine, which has a branched molecular structure and a great number of functional groups, by applying standard model-fitting and model-free isoconversional methods.

## EXPERIMENTAL

Materials

Shown in Scheme 1 is the molecular structure of the curing agent with butanediamine as the core (DAB-dendri-$(NH_2)_4$), which was purchased from Aldrich and dehydrated in vacuum at 100°C for 2 h before use, and its main properties were listed in Table I (data from the literature[20]). Diglycidyl ether of bisphenol A (DGEBA) was obtained from Heli Resin, Co., Ltd., Suzhou, China, with epoxy equivalent weight of 196 g/equiv. and dehydrated in vacuum prior to use.

Differential scanning calorimeter measurement

A Perkin–Elmer differential scanning calorimeter (DSC-7) was used to measure the curing reaction of DGEBA/DAB. Stoichiometric DAB and DGEBA (NH : EP = 1 : 1) were mixed quickly at room
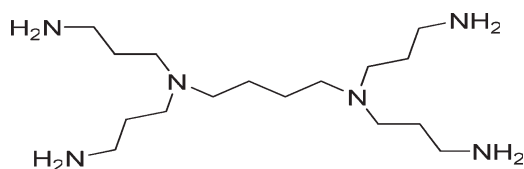
Scheme 1. Molecular structure of DAB-dendri-$(NH_2)_4$.

temperature to obtain a transparent solution. Then, the mixture was sealed in an aluminum DSC pan with mass of about 10 mg and subjected the dynamic temperature scan at heating rates of 5, 10, 15, and 20°C/min under N_2 purge (20 mL/min) in the temperature ranges from 25 to 250°C.

RESULTS AND DISCUSSION

Nonisothermal cure

Nonisothermal curing behavior of DGEBA/DAB is examined with a dynamic DSC technique at the various heating rates, and DSC thermographs are illustrated in Figure 1. With the increasing heating rates, the exothermic peak position shifts gradually to a higher temperature, and the peak becomes more and more broad. In addition, only a single exothermic peak appears in every curing curve without any shoulders, which likely suggests that the whole reaction only experiences a single kinetic process. The characteristic parameters of the onset cured temperature (T_{onset}), peak temperature (T_p), and reaction enthalpy at various heating rates were listed in Table II. The heating rate has little influence on the reaction enthalpy ($\Delta H = 496$–512 J/g), which suggests that the nonisothermal reaction of DGEBA/DAB can achieve an identical absolute reaction degree.

The DSC curve of the cured epoxy resin at the heating rate of 10°C/min was shown in Figure 2. Obviously, the curve shows a glass transition without any exothermic peak, which indicated that the epoxy resin could be fully cured with DAB in the previous heating run. In addition, the glass transition temperature is 116.6°C, which illustrates that the DGEBA/DAB has good thermal resistance to meet the requirement from many applications.

Apparent reaction activation energy

The Kissinger equation[21,22] was used to estimate global activation energy of the nonisothermal curing

TABLE I
The Main Properties of DAB-dendri-$(NH_2)_4$

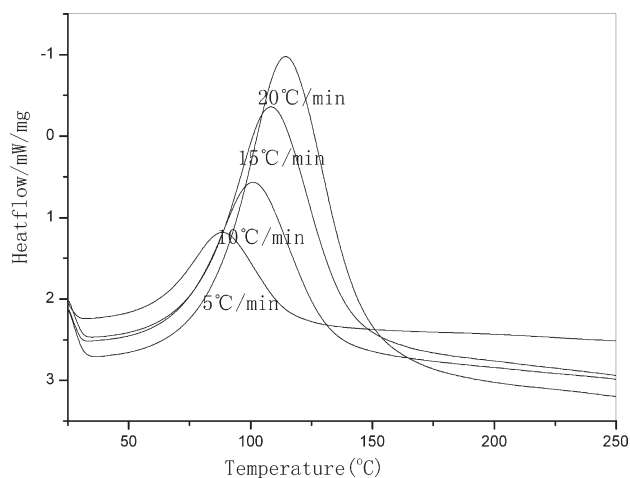| Molecular weight (g/mol)	Intrinsic viscosity 25°C/THF (d/g)	Appearance	T_g onset (°C)
317	0.026	Light yellow oil	−107.15

Figure 1 Curing curves of DGEBA/DAB at the different heating rates.

reaction of DGEBA/DAB. According to the Kissinger equation [eq. (1)], $\ln(\beta/T_p^2)$ against $1/T$ is plotted in Figure 3, which shows an excellent linear correlation ($R = 0.99986$). As a result, the reaction activation energy of nonisothermal cure can be estimated from the slope of the corresponding straight line, and the obtained value (56.7 kJ/mol) is in a good agreement with typical value (50–70 kJ/mol)[14] of the reaction activation energy of many epoxy–amine polymerizations.

$$\ln\left(\frac{\beta}{T_p^2}\right) = C - \frac{E_a}{RT_p}. \qquad (1)$$

In eq. (1), C is the constant, β is the heating rate, T_p is the exothermic peak temperature, R is the universal gas constant, and E_a is the apparent activation energy.

Kinetic modeling

In general, there are two main kinetic methods which have been frequently cited and derived to study the reaction kinetics of epoxy resins: the model-fitting method and the model-free isoconversional method. To avoid randomly selecting a kinetic

TABLE II
Characteristic Parameters for Nonisothermal Curing Reaction of DGEBA/DAB at Different Heating Rates of 5, 10, 15, and 20°C/min

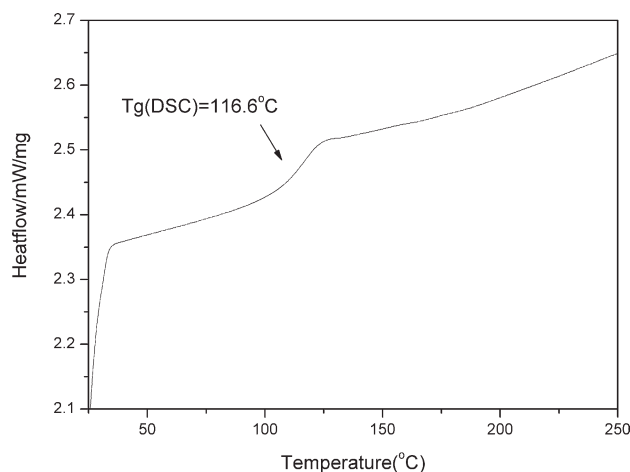| Heating rate (°C/min)	T_{onset} (°C)	T_p (°C)	ΔH (J/g)
5	59.78	88.65	495.86
10	69.47	101.13	508.31
15	76.33	108.45	503.23
20	81.36	114.47	512.13

Figure 2 DSC curve of the cured DGEBA/DAB at the heating rate of 10°C/min.

model and estimating the involved model parameters, method proposed by Málek,[23–25] is used to select a suitable reaction model and evaluate the involved model parameters in the present work. According to this method, E_a, da/dt, T, and β are introduced into the two special functions $y(\alpha)$ and $z(\alpha)$, eqs. (2)–(5) can be defined as the diagnostic signatures for determination of reaction models and for calculation of model parameters.

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp(x), \quad (2)$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta}, \quad (3)$$

$$x = \frac{E_a}{RT}, \quad (4)$$

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (5)$$
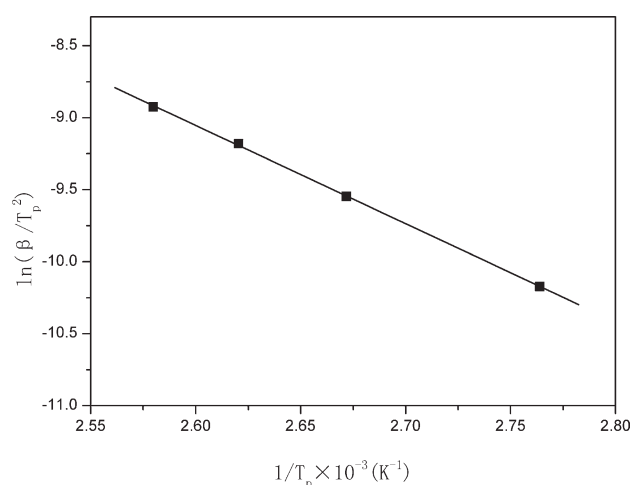

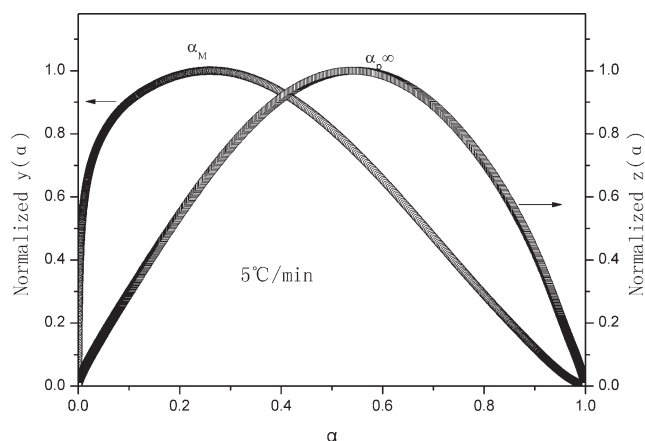**Figure 3** The plot of $\ln(\beta/T_p^2)$ against $1/T$ according to the Kissinger equation.

Figure 4 The normalization function curves of $y(\alpha)$ and $z(\alpha)$ by the Málek equation.

In the equations above, x is the reduced activation energy, $d\alpha/dt$ is the curing reaction rate, T is the absolute temperature, and $\pi(x)$ is the function of temperature integral which can be numerically approximated with sufficient accuracy using a fourth-order rational equation derived by Senum and Yang.[26]

The function curves of $y(\alpha)$ and $z(\alpha)$ can be determined by introducing the calculated values of E_a, $d\alpha/dt$, β, and T into eqs. (3)–(5) as shown in Figure 4. A suitable kinetic model can be chosen based on the maximum conversion rate (α_m) value of $y(\alpha)$ function and the maximum value (α_p^∞) of $z(\alpha)$ function. Furthermore, other model parameters can be determined, and finally, a explicit kinetic rate equation also can be established.

The typical function curves of $y(\alpha)$ and $z(\alpha)$ at the heating rate of 5°C/min are illustrated in Figure 4. These curves show that the conversion for the maximum value of $y(\alpha)$ function (α_m) is about 0.26, whereas that for the maximum value of $z(\alpha)$ function (α_p^∞) is about 0.54; meanwhile, the experimental rate-peak conversion (α_p) is about 0.52. Apparently, the values of α_m, α_p, and α_p^∞ can be simultaneously satisfied with the conditions about $\alpha_m < \alpha_p < \alpha_p^\infty$ and $\alpha_p^\infty \neq 0.632$. The same conclusions also can be obtained from the other heating rates, as indicated in Table III. According to the criteria proposed by Málek,[25] therefore the autocatalytic îSesták–Berggren model (SB (m, n))[27] (Eq 6) is an optimal choice to be used

TABLE III
Characteristic Parameters Obtained by the Málek Method

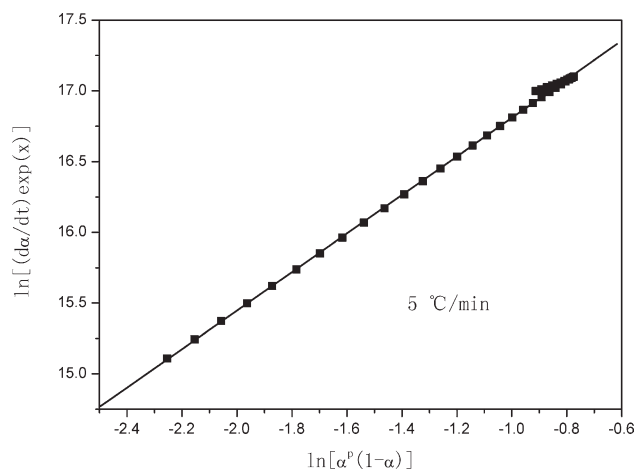| β	α_m	α_p	α_p^∞	R
5°C/min	0.2599	0.5204	0.5421	0.9997
10°C/min	0.2502	0.5166	0.5408	0.9997
15°C/min	0.2574	0.5063	0.5342	0.9996
20°C/min	0.2613	0.5067	0.5350	0.9995

Figure 5 The plot of $\ln[(d\alpha/dt)\exp(x)]$ against $\ln[\alpha^p (1 - \alpha)]$.

to describe the nonisothermal reaction rate of DGEBA/DAB:

$$\frac{d\alpha}{dt} = A \exp(-\frac{E\alpha}{RT})\alpha^m(1 - \alpha)^n, \qquad (6)$$

where m and n are the reaction orders and a is the pre-exponential factor.

Here eq. (6) can be easily transformed into eq. (7):

$$\ln\left[\left(\frac{d\alpha}{dt}\right)\exp(x)\right] = \ln A + n \ln[\alpha^p(1 - \alpha)], \qquad (7)$$

where p is defined as followed.

$$p = m/n = a_M/(1 - a_M). \qquad (8)$$

According to Eq. 7, $\ln[(d\alpha/dt)\exp(x)]$ against $\ln[a^p(1 - \alpha)]$ can be fitted to a straight line. Then, reaction order n can be determined from the slope of this straight line and pre-exponential factor A can be obtained from the intercept of the linear plot. In the end, the whole SB (m, n) model parameters were obtained.

A plot of $\ln[(d\alpha/dt)\exp(x)]$ against $\ln[\alpha^p(1 - \alpha)]$ is presented in Figure 5 at the heating rate of 5°C/min, which shows an excellent linear correlation. Consequently, the slope and the intercept of the straight line can be used to calculate m, n, and $\ln A$ at the various heating rates, and the results are summar-

TABLE IV
The Kinetic Parameters for SB (*m*, *n*) Model

β	m/n	ln A	n	m	R
5°C/min	0.3511	18.1723	1.3628	0.4784	0.9997
10°C/min	0.3337	18.1121	1.3740	0.4585	0.9997
15°C/min	0.3466	18.2065	1.4553	0.5043	0.9996
20°C/min	0.3537	18.2548	1.5371	0.5437	0.9995

ized in Table IV. Obviously, the heating rates affect slightly these model parameters, without the variation exceeding 10% of their mean values.

Reaction rate equation can be obtained by introducing the calculated averaged values of ln A, m, n, and E_a into eq. (6), as indicated in eq. (9)

$$\frac{d\alpha}{dt} = 7.91 \times 10^7 \exp(-\frac{56702}{RT})\alpha^{0.50}(1 - \alpha)^{1.43}. \qquad (9)$$

Then, the model predicated result from eq. (9) is compared with the experimental results at the different heating rates in Figure 6, where a good agreement was observed. Moreover, the relationship between the reaction rate and conversion at different reaction temperatures can be predicated according to eq. (9), as shown in Figure 7. Obviously, increasing the reaction temperature leads to the increased reaction rate at the same conversion. Note that the maximum reaction rate appears at an essentially
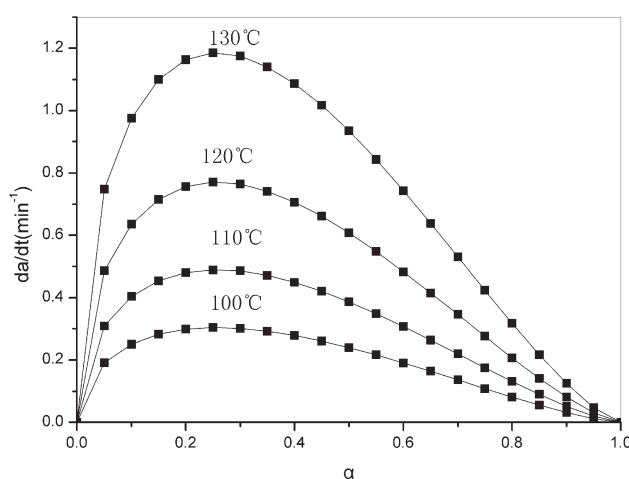

Figure 6 Comparison between the experimental and model predicated rate at the various heating rates.

Figure 7 Reaction rate $d\alpha/dt$ as a function of conversion α at various temperatures.
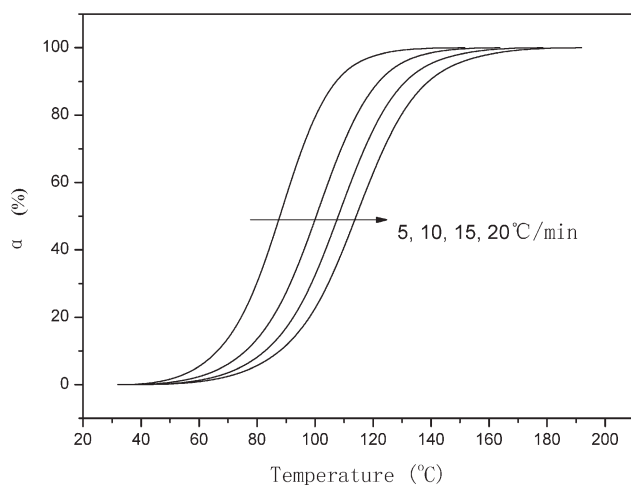
Figure 8 The relationship curve of conversion of epoxy groups and temperature.

Figure 9 Plots of $\ln(\beta/T^2)$ against $1/T$ at different fractional conversions by KAS method.

constant conversion of about 0.3 independent of the reaction temperature, which can justify that the reaction of DGEBA/DAB is autocatalytic reaction.[28]

The relationship of reaction activation energy and fractional conversion with isoconversional principle

The rate equation [eq. (9)] is able to well describe the curing process of DGEBA/DAB in a global manner, but, in fact, reactions of epoxy resins are extremely complicated processes involving various possible elementary reaction pathways, complex mass transfer processes, and a number of physico-chemical transitions.[14,29] Therefore, using a single reaction rate equation to accurately untangle these complexities often yield very limited understanding about the reaction mechanisms. For this reason, the isoconversional Kissinger-Akahira-Sunose (KAS) method[22,30] was used to analyze the curing processes in more detail, whereby one can determine the activation energy value for each conversion. The KAS models are based on the assumption that the activation energy remains constant for a given cure degree independent of the heating rate applied, which is expressed by eq. (10). In this work, the KAS method was used to determine the activation energy as a function of cure degree for DGEBA/DAB over the whole conversion range investigated.

$$\ln \frac{\beta}{T_\alpha^2} = \ln\left[\frac{A_\alpha R}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{RT}, \qquad (10)$$

where A_α is the pre-exponential factor, E_α is the activation energy for α, T_α is the temperature for α, and $g(\alpha)$ is the temperature integral.[31]

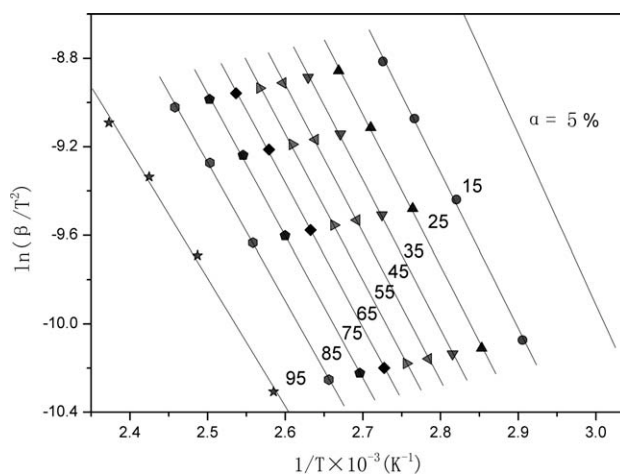The relationship between conversion of epoxy groups and temperature of the nonisothermal reac-

tion of DGEBA/DAB at different heating rates is shown in Figure 8. As seen, with increasing the heating rates, the conversional curves shift toward a higher temperature region; namely, the reaction rate is an increasing function of the temperature.

For a given heating rate, each curing degree is associated with a single temperature (T_a; seen in Fig. 8), and thus the corresponding activation energy (E_α) can be determined from the slope of the fitted straight line of $-\ln \beta/T_\alpha^2$ versus $1/T_\alpha$, as shown in Figure 9. The shape of E_α as a function of α can provide us a valuable perspective of the change in reaction mechanisms in the curing process of DGEBA/DAB, as shown in Figure 10. With the increased of the conversion, the reaction activation energy decreases from >80 KJ/mol to $\approx$ 60 KJ/mol up to $\alpha \approx 15\%$, which may imply the change of cure reaction mechanisms.[32] The following two reasons may account for this observation.[14,15] First, the secondary —OH functionalities generated during the epoxy–amine addition can greatly catalyze there main
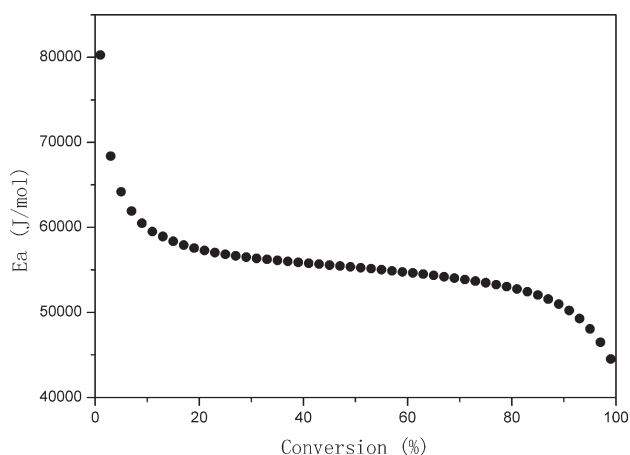

Figure 10 Activation energy as a function of fractional conversion by KAS method.

epoxy–amine reaction via a trimolecular transition state, particularly an activated epoxy–amine–hydroxyl complex. Second, the viscosity of the reaction mixture decreases dramatically with increasing the temperature at this stage, which promotes diffusion of the reactive species easier. As a result, the energetic barriers for the reaction itself and the diffusion are decreased simultaneously, hence lowering overall E_a at the early reaction stage. At the middle conversion stage (15–75%), the value of apparent activation keeps a relative stability about 55–60 kJ/mol, which implies little change involved in reaction mechanism. Finally, as there action progresses in the deep conversion range ($\alpha > 0.75$), E_a decreases abruptly to 44 kJ/mol. This fact implies the rate-determining step of the reaction generally changing from the reaction control to the diffusion limitation.[33,34]

CONCLUSIONS

The curing reaction kinetics of the DGEBA/DAB-dendri-$(NH_2)_4$ system was studied by using the dynamic DSC in this article. The curing curves showed only a single exothermic peak and reaction enthalpy appear at 496–512 kJ/mol at different heating rates. Increasing the heating rate led to the reaction shifting toward a high-temperature range with increasing the heating rate. The value of activation energy was used to calculate about 56.7 kJ/mol determined by the Kissinger method. The reaction rate equation was established, which could well simulate the process of curing reaction. The relationships of the activation energy and the conversion obtained from the KAS method analysis showed that the reaction mechanism was extremely complicated. At the early stage of curing reaction, the reaction rate was initially controlled by the reaction-controlled, but it was controlled by the diffusion-controlled in the later stage. From the analysis above, it is concluded that anticipated that DAB has a promising potential to be used as an epoxy curing agent with high reactivity and good thermal properties. In our further work, the isothermal cure of bisphenol epoxy resin with a nonlinear aliphatic polyamine hardener will be discussed in detail.

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