

# Reaction Kinetics, Thermal Properties of Tetramethyl Biphenyl Epoxy Resin Cured with Aromatic Diamine

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**ABSTRACT:** Epoxy resins, 4, 4'-diglycidyl (3, 3', 5, 5'-tetramethylbiphenyl) epoxy resin (TMBP) containing rigid rod structure as a class of high performance polymers has been researched. The investigation of cure kinetics of TMBP and diglycidyl ether of bisphenol-A epoxy resin (DGEBA) cured with *p*-phenylenediamine (PDA) was performed by differential scanning calorimeter using an isoconversional method with dynamic conditions. The effect of the molar ratios of TMBP to PDA on the cure reaction kinetics was studied. The results showed that the curing of epoxy resins contains different stages. The activation energy was dependent of the degree

of conversion. At the early of curing stages, the activation energy showed the activation energy took as maximum value. The effects of rigid rod groups and molar ratios of TMBP to PDA for the thermal properties were investigated by the DSC, DMA and TGA. The cured 2/1 TMBP/PDA system with rigid rod groups and high crosslink density had shown highest  $T_g$  and thermal degradation temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2611–2620, 2007

**Key words:** resins; kinetics (polym); activation energy; differential scanning calorimetry (DSC)

## INTRODUCTION

Epoxy resins have been widely used as high performance materials in many fields, such as adhesive, coating, laminating capsulation, electrical insulation, and composite applications.<sup>1–4</sup> The epoxy resins have exhibited good thermal properties, chemical resistance, and electric insulation through a crosslinking reaction with a curing agent to make the three-dimensional network structure. These properties of cured epoxies depend on the structures of epoxy resins and curing agents.

Recently, epoxy resins containing rigid rod structure have been synthesized as a new class of high performance polymers.<sup>5–7</sup> A rigid rod material typically has a rigid rod segment in the polymer chain either on the polymer backbone or on the side chain. Rigid rod epoxy resins have been developed as a high performance polymer for electronic and aerospace applications because of their good thermal stability and unique physical properties. Rigid rod epoxy resins in particular offer potentially enhanced thermal stability and dielectric properties over conventional epoxy resin.<sup>6–11</sup>

Because of the rigid rod structure containing four methyl groups, 4, 4'-diglycidyl (3, 3', 5, 5'-tetramethylbiphenyl) epoxy resin (TMBP) will reduce its moisture absorption.<sup>12–14</sup> It has great advantage for good adhesion, high toughness, and the feasibility of high

filler loading. Su et al.<sup>8–11</sup> cured epoxy monomers bearing biphenol rigid rod group with aromatic diamine, anhydride, and phenol novolac, respectively. The cured epoxies have exhibited good thermal and electrical properties.

It is well known that the properties of the cured epoxy resins depend on their structure,<sup>15,16</sup> the extent of cure,<sup>17</sup> the reaction kinetics such as the curing conditions<sup>18,19</sup> and the time the temperature of cure.<sup>20</sup> For this reason, it is necessary to know and to understand the relationships between the structure of the networks and the final properties, to obtain resins with high performance applications.<sup>21,22</sup>

Many equations were developed to investigate the cure kinetics of the epoxy system, including the *n*-order reaction model, the autocatalytic reaction model, and the diffusion control model.<sup>23–26</sup> All kinetic studies can start with the basic equation as follow:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

or in the integrated form

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{-\infty}^t kdt \quad (2)$$

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

For the nonisothermal conditions, when the temperature varies with time with a constant heating rate,  $q = dT/dt$ , the equation is represented as follows:

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$$\frac{d\alpha}{dT} = \frac{A}{q} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

where  $T$  is the temperature (K),  $E$  is the activation energy,  $R$  is the universal gas constant (8.314 J/mol K),  $A$  is the pre-exponential factor.

Iso-conversional kinetic analysis offers a viable alternative in this situation. The basic idea of the type of analysis is that  $f(\alpha)$  has the same form regardless of the temperature for the same degree of conversion  $\alpha$ , or say, the reaction rate at a constant conversion depends only on the temperature. It is more convenient to use the integral forms of equation. The derivative modes from Ozawa, Flynn, Wall, Kissinger and Doyle<sup>26-32</sup> can be used to give the  $E_\alpha$  from the plot  $\ln(q_i/T_{\alpha,i}^2)$  or  $\ln q_i$  versus  $T_{\alpha,i}^{-1}$  (here  $i$  is ordinal number of DSC runs performed at different heating rate,  $q_i$ ). By using the Coats-Redfern<sup>27</sup> approximation for the resolution of eq. (3) and considering  $2RT/E \ll 1$ , we can rewrite this equation as follows:

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{qE} \right] - \frac{E}{RT} \quad (4)$$

For a given kinetic model, the linear representation of  $\ln[g(\alpha)/T^2]$  versus  $T^{-1}$  makes it possible to determine  $E$  (apparent  $E$  value) and  $A$  from the slope and the ordinate at the origin. In this work, the kinetic model that had the best linear correlation in the Coats-Redfern equation and that had an  $E$  value similar to that obtained isoconversionally (considered to be the effective  $E$  value) was selected.

By reordering eq. (4), we can rewrite the equation as followed:

$$\ln \frac{q}{T^2} = \ln \left[ \frac{AR}{g(\alpha)E} \right] - \frac{E}{RT} \quad (5)$$

The linear representation of  $\ln[q/T^2]$  versus  $1/T$  makes it possible to determine  $E$  and the kinetic parameter  $\ln[AR/g(\alpha)E]$  for every value of  $\alpha$ . So the Coats-Redfern mode can be used to obtain the relationship of  $E_\alpha \sim \alpha$ .

$$\ln \left( \frac{q_i}{T_{\alpha,i}^2} \right) = \ln \left[ \frac{RA}{E_{\alpha,i} g(\alpha)} \right] - \frac{E_{\alpha,i}}{R} \frac{1}{T_{\alpha,i}} \quad (6)$$

The activation energy can be obtained during the curing process at different conversion. This is more precise than the assumption of constant activation energy for the whole polymerization.

The curing reaction of TMBP and PDA was seldom researched. The study was performed in parallel with two types of epoxies: tetramethyl biphenol epoxy, and a flexible bisphenol-A epoxy. The effects of chemical structure changes on the properties of epoxies cured with the same curing agent could be investigated.

In this study, the cure reaction kinetics of epoxy monomer (TMBP) cured with aromatic diamine (PDA) at various molar ratios was also investigated. To estimate the total curing heat, activation energy were calculated and reported by the Coats-Redfern method. In the process study, a design of experiments was performed so that the most important curing parameters could be identified. The effects of the curing process and different molar ratios for the thermal properties of the cured epoxy resin, which were characterized by DSC, DMA, and TGA, have been investigated.

## EXPERIMENTAL

### Materials

The epoxy monomer, 4, 4'-diglycidyl (3, 3', 5, 5'-tetramethylbiphenyl) epoxy resin (TMBP) with an epoxy equivalent of 177 used in this study was synthesized according to our previously reported procedure.<sup>33-35</sup> The diglycidyl ether of bisphenol-A epoxy resin (DGEBA, trade name E-51) was obtained from Wuxi Resin Factory with the epoxy equivalent weight of 196.08. The curing agent, *p*-phenylenediamine (PDA), a solid difunctional aromatic amine with a molecular weight of 114 g/mol, was purchased from Shangyu Lixing Chemical Limited Company, which was used without further purification. The chemical structures of the epoxy monomers and the curing agent are shown in Figure 1.

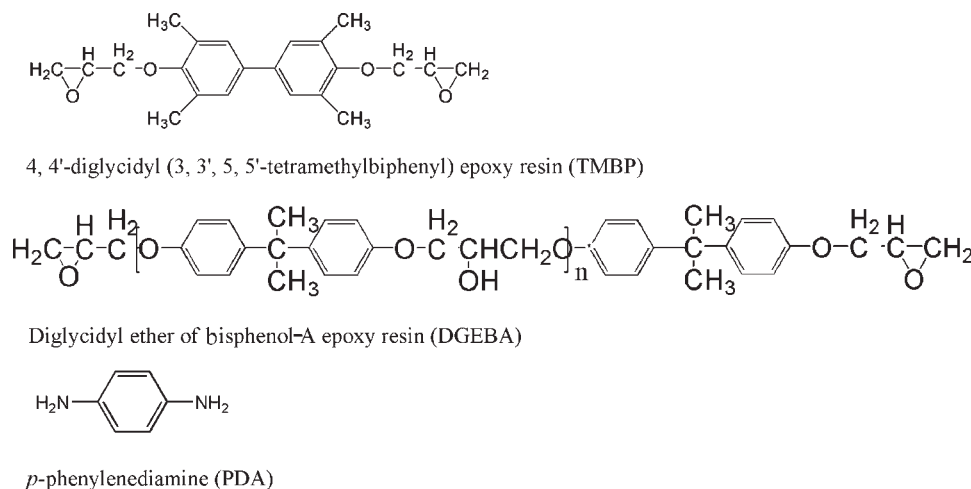
### Sample preparation

The samples of TMBP/PDA and DGEBA/PDA were prepared in the same way.

TMBP or DGEBA monomers were put into tetrahydrofuran (THF) and heated until a clear solution was obtained. The solution was cooled to the room temperature, and a stoichiometric amount of PDA were added and stirred for about 3 min. The solution was poured on a glass plat and dried in a vacuum oven at 25°C for 2 days to remove the solvent. The power mixtures were stored at room temperature and measured within 3 days.

### Curing kinetics of the curing process by DSC measurement

Calorimetric measurements were performed using a METTLER TOLEDO instruments differential scanning calorimeter (DSC 821<sup>e</sup>), which was calibrated with the temperature region of 25 to 250°C at different heating rates of 5, 10, 15, and 20°C/min under nitrogen gas at a flow rate of 200 mL/min. The conversion degrees were considered as 0% at the beginning of exothermic peaks and 100% at the end of exothermic peaks in DSC curves. The conversion degrees



**Figure 1** Chemical structures of 4, 4'-diglycidyl (3, 3', 5, 5'-tetramethylbiphenyl) epoxy resin (TMBP), Diglycidyl ether of bisphenol-A epoxy resin (DGEBA) and *p*-phenylenediamine (PDA).

and kinetics of the process were obtained from the Star<sup>e</sup> software.

### Thermal analysis

Differential Scanning Calorimetry (DSC) thermograms were recorded using METTLER TOLEDO DSC 821<sup>e</sup> operating from 25 to 250°C at a heating rate of 10°C/min under a nitrogen flow of 200 mL/min. It was used to determine the glass transition temperatures ( $T_g$ ) of cured samples. An empty aluminum pan was used as a reference.

Dynamic Mechanical Analysis (DMA) was performed using a three-point bending mode over a temperature range of 80–250°C at a heating rate of 5°C/min and a frequency of 1 Hz using a TA DMA Q800 dynamic mechanical analyzer. The samples were both in the form of specimens  $\approx$  15 cm long,  $\approx$  10 mm wide, and  $\approx$  3 mm thick. The glass transition temperatures ( $T_g$ ) of the samples were determined by the peak of  $\tan \delta$  of DMA thermograms.

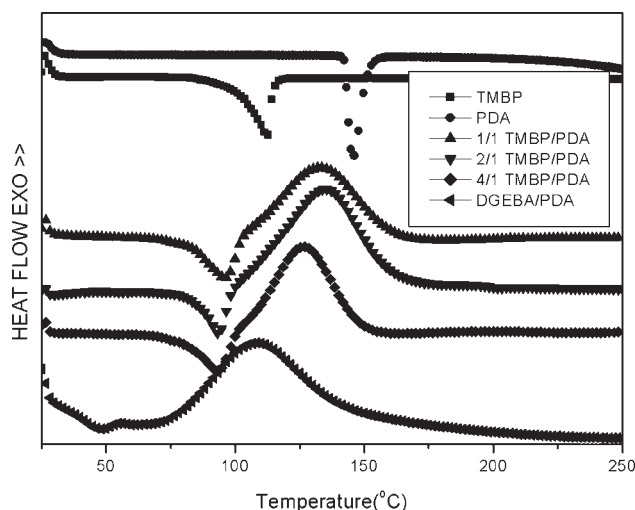
A Pyris 1TGA (Perkin-Elmer) TGA was employed to study the thermal degradation temperatures and thermal stability of the samples. About 5–10 mg samples of epoxy cured with PDA were heated from 50 to 700°C at a heating rate of 10°C/min under air atmosphere, the temperature at which 10% weight loss was recorded for each material.

## RESULTS AND DISCUSSION

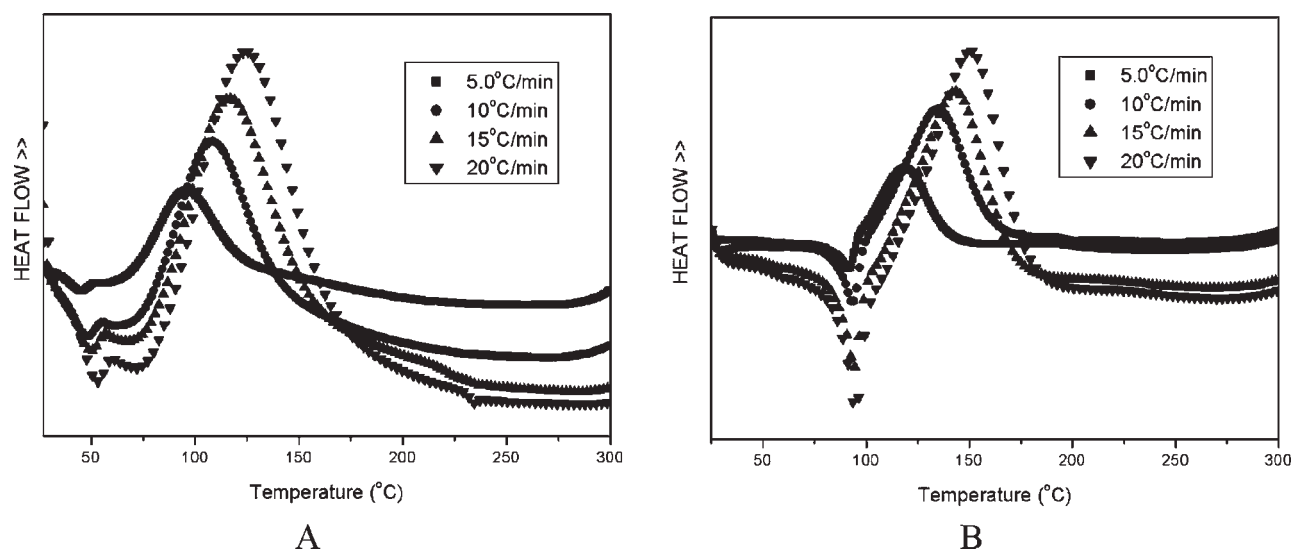
### DSC measurements

Figure 2 shows the results of dynamic DSC curves for TMBP, PDA, 1/1 TMBP/PDA system, 2/1 TMBP/PDA system, 4/1 TMBP/PDA system, and DGEBA/PDA system from room temperature to 250°C at 10°C/min. The TMBP curve showed an endothermic peak which was the melt point of the TMBP at about

105°C, and the PDA curve also showed a melting endothermic peak of the PDA at about 150°C. The curves of TMBP/PDA systems all contained an endothermic peak and an exothermic peak. The endothermic peak at around 95°C was attributed to the eutectic property between TMBP and PDA. The eutectic peak showed the well miscibility between epoxy and diamine monomers. The peak temperature of exothermic peak of the curve of 2/1 TMBP/PDA system was higher than those of the others, which showed that the cure reaction between TMBP and PDA monomers of 2/1 TMBP/PDA system needed more energy. It might be because of the large steric hindrance of structure and the increasing crosslink density when reactions have taken place in a high extent that hindered the diffusion of functional groups. The curves of DGEBA/PDA systems contained two endothermic



**Figure 2** DSC curves for TMBP, PDA, 1/1 TMBP/PDA system, 2/1 TMBP/PDA system, 4/1 TMBP/PDA system and DGEBA/PDA system at 10°C/min from room temperature to 250°C.

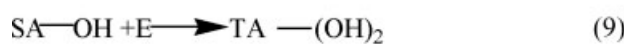


**Figure 3** Dynamic DSC curves at different heating rates for (A) the DGEBA/PDA and (B) TMBP/PDA system.

peaks and an exothermic peak, respectively. The endothermic peaks were at around 50 and 70°C, respectively. The temperature of the exothermic peak at 110°C was lower than those of the TMBP/PDA systems. It might be because that the DGEBA was liquid state at room temperature and the effective collision between the DGEBA and PDA needed low energy.

The dynamic DSC curves at different heating rates for the DGEBA/PDA system and TMBP/PDA system with molar ratio of 2/1 at the heating rates of 5, 10, 15, 20°C/min are shown in Figure 3. In the dynamic DSC curves for DGEBA/PDA system, all curves showed two endothermic peaks and an exothermic peak. For TMBP/PDA system, all curves showed one endothermic peaks and an exothermic peak. Regardless of the heating rate, the exothermic peak at all curves shifted to the high temperature with increasing heating rates. The exothermic curve for all curves in Figure 3(A) increased slowly after the monomer melting and then showed a rapid increase with temperature. This means that at the early stage of cure reaction, newly molten monomers might need high activation energy for reaction.

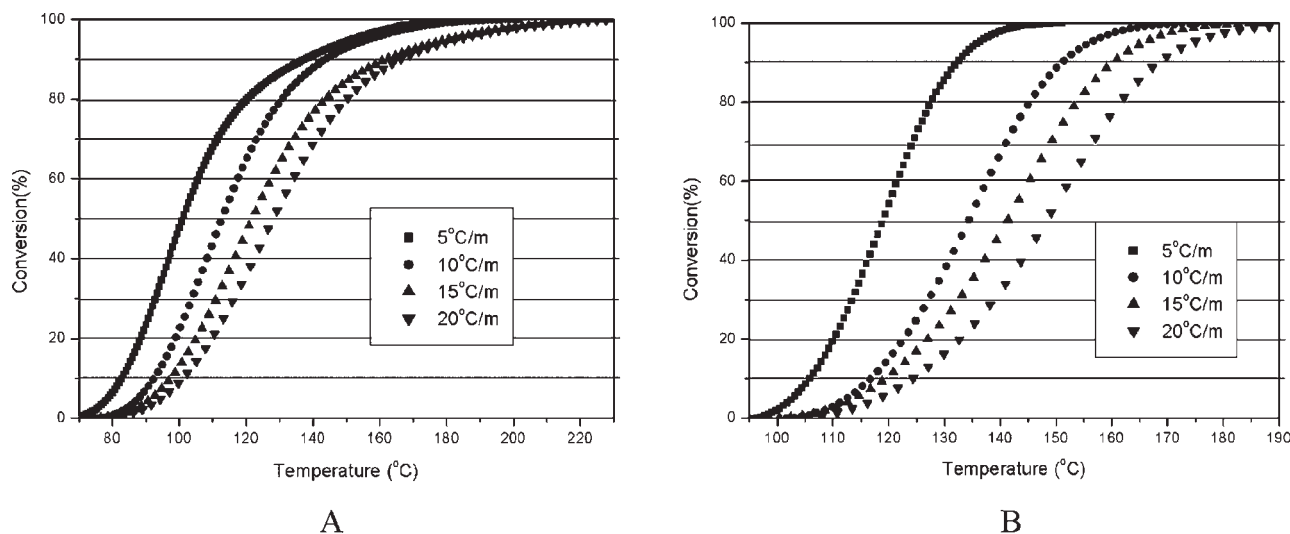
The main elementary reactions in the epoxy-amine compound are followed<sup>36</sup>:



where PA, SA, and TA designate the primary, secondary, and tertiary amines, respectively: E repre-

sents the epoxide; and —OH is the hydroxyl group attached to the SA or TA. Equations (7), (9), and (11) are autocatalytic reactions and eqs. (8) and (10) are catalytic reactions. Each elementary reaction has a different rate constant, and these reactions take place competitively and serially in the same reactant mass. For a single step process,  $E_\alpha$  is independent of  $\alpha$  might have the meaning of the intrinsic activation energy. Multi-step processes reveal the dependence of  $E_\alpha$  and  $\alpha$ , the analysis of which helps not only to disclose the complexity of a process but also to identify its kinetic scheme,<sup>37</sup> so the activation energy is useful in predicting behavior of thermoset in real processes.

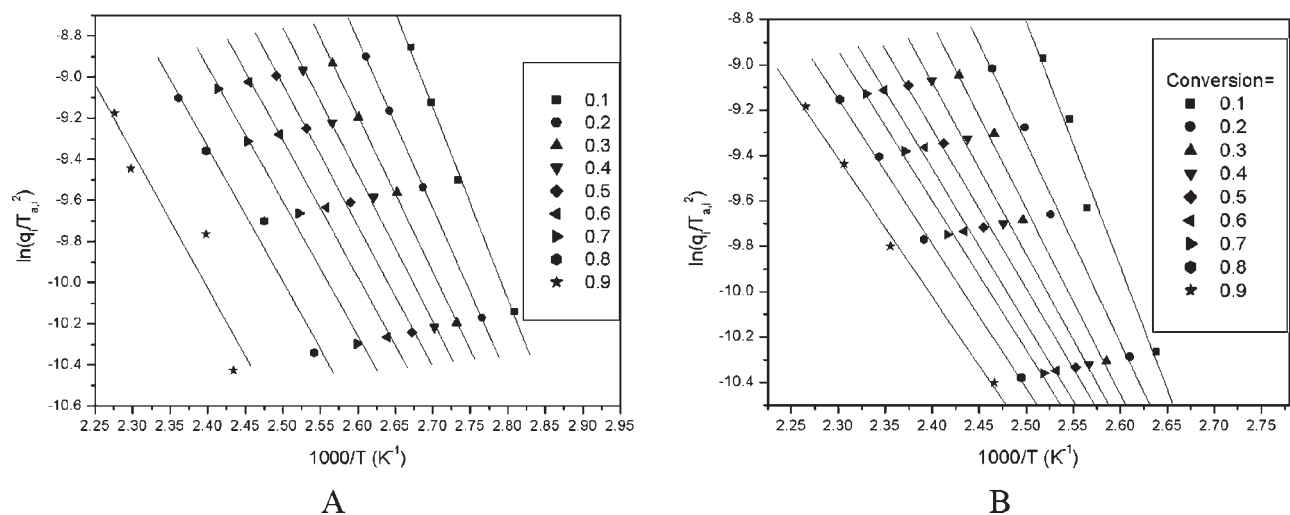
Figure 4 shows the fractional conversions as a function of temperature for various heating rates for the DGEBA/PDA and TMBP/PDA systems. It could be seen that the isoconversional temperature increased with the heating rate at the same conversion for both systems. The isoconversional plots by Coats-Redfern mode are given in Figure 5, and the dependence of  $E_\alpha$  calculated by eq. (6) and  $\alpha$  for the epoxy/PDA systems are presented in Table I. As can be seen, the values of activation energy were not a constant, as supposed in many works throughout the whole curing process.<sup>37,38,49</sup> According to the cure mechanism of epoxy resin-diamine hardener,<sup>40</sup> as shown in Figure 6, at the early stage of cure reaction, the reaction between epoxy ring and primary amine had occurred until most of the hydroxyl groups were formed. The activation energy took as maximum value as shown in Figure 6(2) where nonautocatalytic reaction occurred. The hydroxyl groups which could catalyze the reaction formed during the curing facilitated ring opening. It was reasonable to expect a reduction in  $E$  in comparison with that at the very beginning of the cure. The activation energy was decreased greatly at this stage until the active hydroxyl groups were



**Figure 4** Fractional conversions as a function of temperature for various heating rates for the (A) DGEBA/PDA and (B) TMBP/PDA systems.

enough for next reaction as shown in Figure 6. So with the increasing active hydroxyl groups, the activation energy of the reaction between secondary amine and epoxy ring was decreasing. Therefore, as the reaction conversion increased the activation energy decreased. The activation energy at  $\alpha = 0.1$  of TMBP/PDA system was 151.4 kJ/mol and higher than that of DGEBA/PDA system. This was because TMBP monomers had rigid rod groups and the freely diffused functional groups needed higher energy at the early reaction stage. After  $\alpha = 0.2$ , the activation energies were similar, which showed the rigid rod groups at TMBP had no influence for the activity of epoxy group. With the increasing of hydroxyl groups which could catalyze the cure reaction, the activation energies decreased until the end of reaction.

The effects of molar ratios of TMBP to PDA for cure mechanisms had been investigated. Figure 7 shows dynamic DSC curves at different heating rates for the 1/1 and 4/1 TMBP/PDA systems with different molar ratios of TMBP to PDA. The activation energy calculated by eq. (6) through the fractional conversions as shown in Figures 8 and 9 of the 1/1 TMBP/PDA and 4/1 TMBP/PDA systems has been listed in Table I. The activation energy of the 1/1 TMBP/PDA and 4/1 TMBP/PDA systems decreased with the increasing reaction conversion. At  $\alpha = 0.1 \sim 0.4$ , the value of activation energy of the 1/1 TMBP/PDA and 4/1 TMBP/PDA systems were both lower than those of the 2/1 TMBP/PDA system. It was due to the fact that the effective collision between TMBP and PDA at 1/1 TMBP/PDA and 4/1 TMBP/PDA systems,



**Figure 5** Iso-conversional plots of (A) DGEBA/PDA and (B) 2/1 TMBP/PDA systems.

**TABLE I**  
**Activation Energy ( $E_{\alpha}$ ) as Calculated by Iso-Conversional Method**

Conversion	TMBP/PDA 1/1	TMBP/PDA 2/1	TMBP/PDA 4/1	DGEBA /PDA
	$E_{\alpha}$ (kJ/mol)	$E_{\alpha}$ (KJ/mol)	$E_{\alpha}$ (KJ/mol)	$E_{\alpha}$ (KJ/mol)
0.1	76.44	151.4	74.71	132.4
0.2	68.69	104.8	71.96	106.0
0.3	64.24	89.5	68.80	87.4
0.4	61.38	75.7	67.00	75.1
0.5	59.05	63.1	65.64	68.9
0.6	56.57	58.0	63.42	64.5
0.7	55.06	51.7	61.60	58.0
0.8	53.50	46.0	60.16	53.3
0.9	52.82	38.2	58.28	51.7
Average	60.86	50.2	65.73	77.5

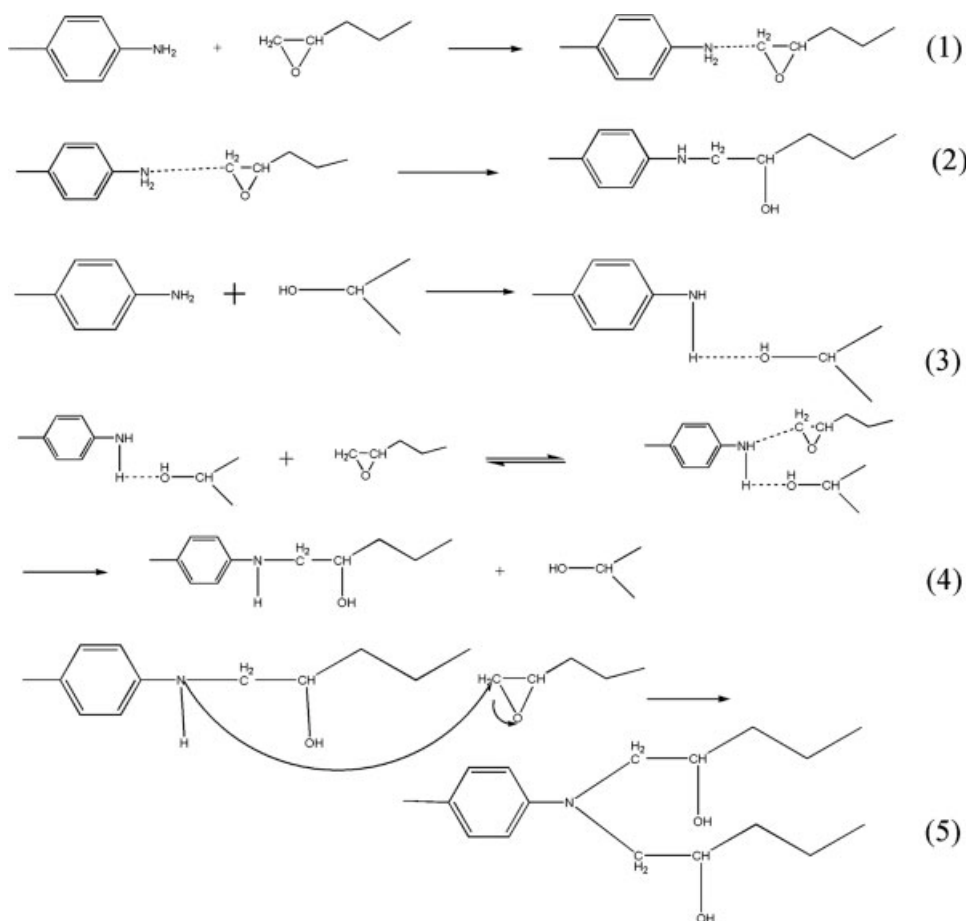
which had excess epoxies or amine groups could easily occur. After  $\alpha = 0.5$ , the value of activation energies of the 1/1 TMBP/PDA and 4/1 TMBP/PDA systems were both larger than those of the 2/1 TMBP/PDA system because more hydroxyl groups formed in 2/1 TMBP/PDA system.

At  $\alpha = 0.1 \sim 0.9$ , the activation energy of the 1/1 TMBP/PDA were both lower than those of the 4/1 TMBP/PDA system, which showed that the freely

diffusion of the TMBP molecule with rigid rod groups need higher energy.

### Thermal properties

It is well known that the process of the curing reaction between epoxy monomer and the curing agent is trapeziform curing temperature in the current technochemistry.<sup>8-11,34,35</sup> The different temperatures



**Figure 6** Chemical reactions mechanism of epoxy resin (TMBP) with diamine (PDA).

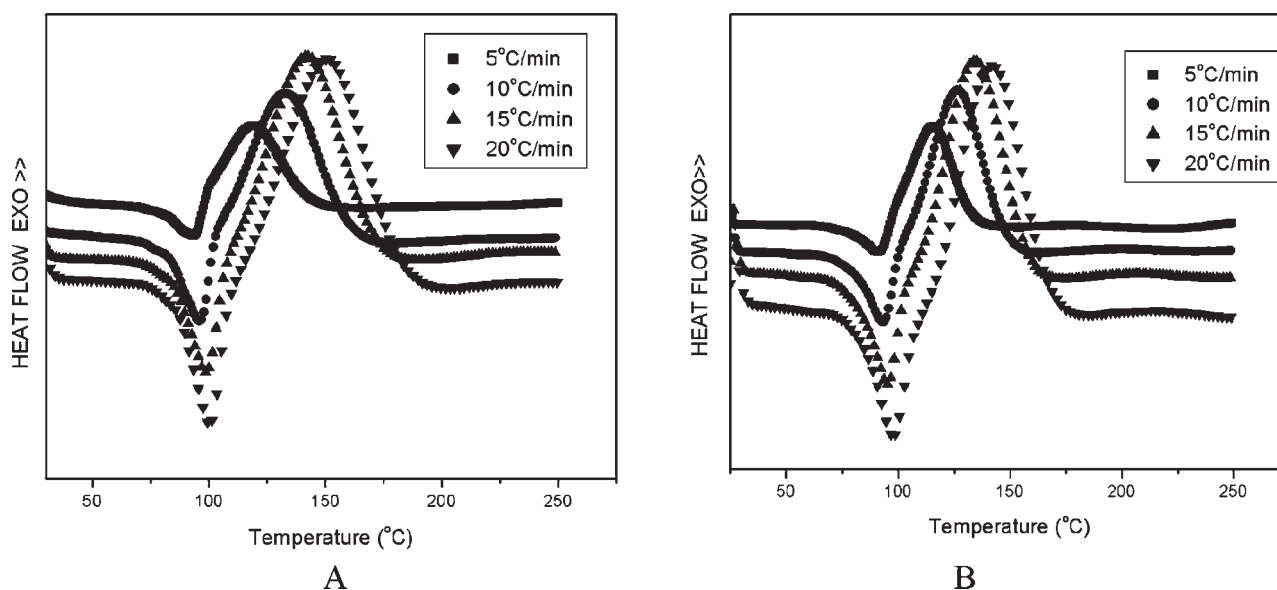
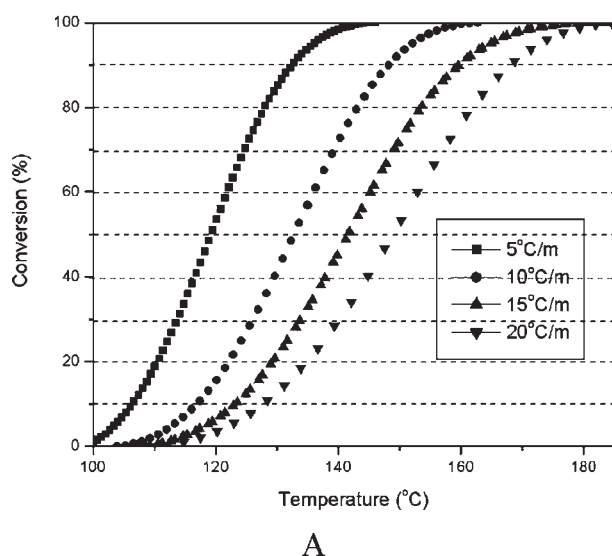


Figure 7 Dynamic DSC curves at different heating rates for the (A) 1/1 and (B) 4/1 TMBP/PDA systems.

for precure steps can be obtained from the different  $T_x$ s when the heating rate is  $0^\circ\text{C}/\text{min}$  and the temperature for postcure steps is obtained from the final peak temperature at heating rate of  $20^\circ\text{C}/\text{min}$  for each system. The temperatures of  $T_x$ s in the exothermic peaks at different heating rates for TMBP/PDA systems are shown in the Table II. The stepwise, isothermal process of curing would be derived from the dynamic curing curves. The curing process of DGEBA/PDA system is shown as follow:

Precure:  $60^\circ\text{C}$  for 1 h,  $85^\circ\text{C}$  for 2 h,  $130^\circ\text{C}$  for 2 h, and Postcure:  $190^\circ\text{C}$  for 1 h.



The curing process of 1/1 TMBP/PDA system is shown as follow:

Precure:  $90^\circ\text{C}$  for 1 h,  $108^\circ\text{C}$  for 2 h,  $138^\circ\text{C}$  for 2 h, and Postcure:  $190^\circ\text{C}$  for 1 h.

The curing process of 2/1 TMBP/PDA system is shown as follows:

Precure:  $85^\circ\text{C}$  for 1 h,  $105^\circ\text{C}$  for 3 h,  $143^\circ\text{C}$  for 2 h, and Postcure:  $210^\circ\text{C}$  for 1 h.

The curing process of 4/1 TMBP/PDA system is shown as follows:

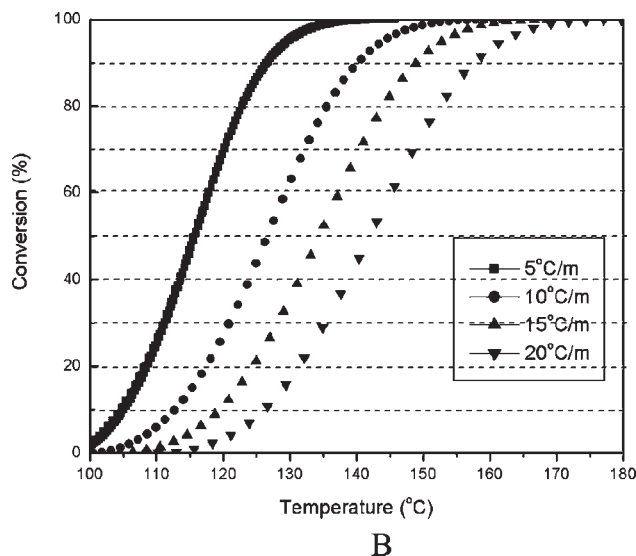
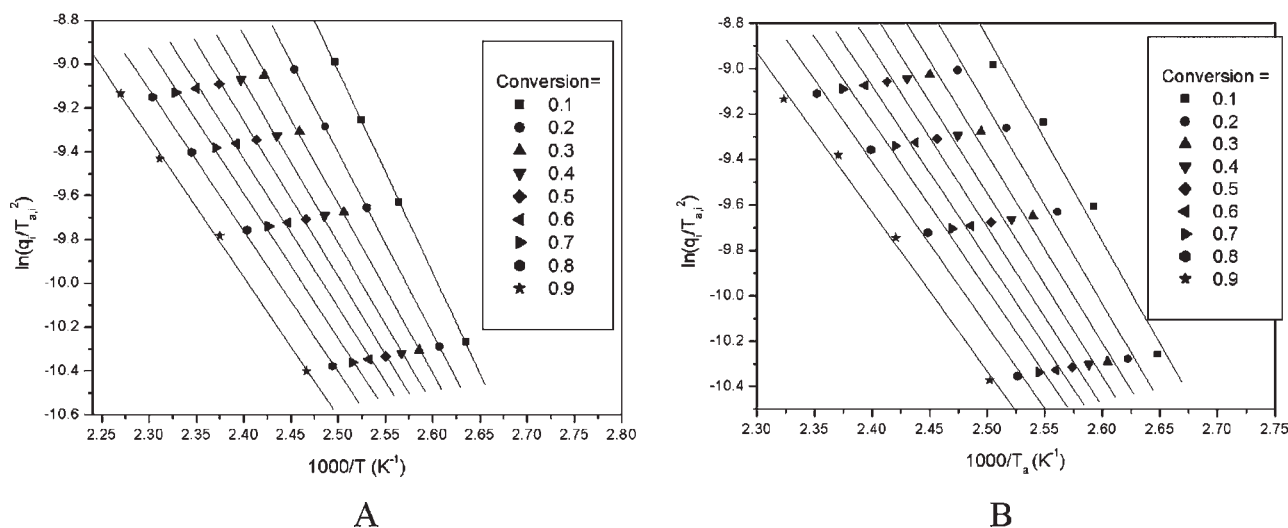


Figure 8 Fractional conversions as a function of temperature for various heating rates for the (A) 1/1 and (B) 4/1 TMBP/PDA systems.



**Figure 9** Iso-conversional plots of (A) 1/1 TMBP/PDA and (B) 4/1 TMBP/PDA systems.

Precure: 88°C for 1 h, 105°C for 2 h, 125°C for 2 h, and Postcure: 175°C for 1 h.

The data shows that 2/1 TMBP/PDA system took more time or higher temperature to be fully cured than flexible DGEBA epoxy. The results indicated that the rigid rod epoxies had a slower curing rate than that of flexible epoxy due to the slow molecular motions of rigid rod structure in the rigid rod epoxies. 2/1 TMBP/PDA system also took more time or higher temperature to be fully cured than other TMBP/PDA system, which might be due to the structure of tetramethyl groups on biphenyl main chain and additional crosslink between epoxy and amine. The theoretical structures of cured TMBP/PDA systems are shown in Figure 10.

Through the curing processes of different systems as shown above, the cured epoxy samples could be obtained. The thermal properties of the cured DGEBA/PDA system and TMBP/PDA systems were studied by DSC, DMA and TGA. The glass transition temperatures ( $T_g$ ) of the cured samples were measured by using DSC and DMA. The DSC is a general method to obtain the  $T_g$  of the different cured epoxy/PDA systems. But the DSC method is not very sensitive in detecting the glass transition of crosslinked polymer due to the small conformational changes in crosslinked polymer upon heating, so the DMA- $T_g$  is obtained by the maximum peak value of  $\tan\delta$ . The different chemical structure changes could occur with the epoxy cured with different contents of the curing agent. With the increasing degree of cure, the  $T_g$  will increase due to the most crosslinked density. Table III shows that all of the  $T_g$  measured by DMA was about 5°C lower than the  $T_g$  obtained from the DSC method in two epoxy/PDA systems.  $T_g$  obtained by DSC or DMA of 2/1 TMBP/PDA system was highest than that of other systems.

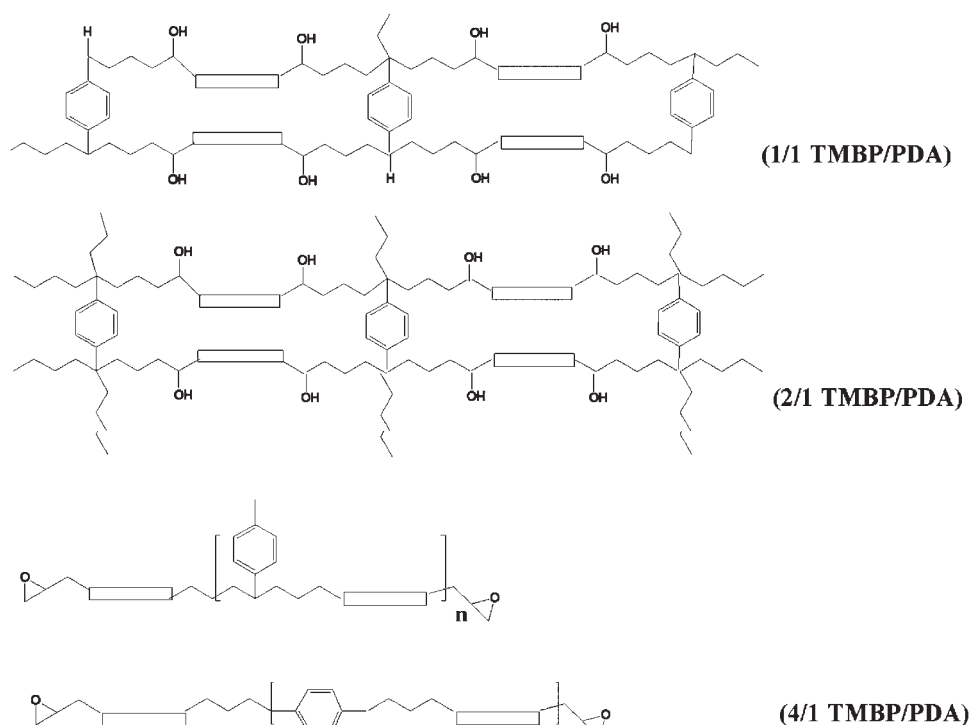
Figure 11 shows TGA curves of different cured epoxy/PDA systems under the air atmosphere flow. The weight-loss curves for cured samples of 1/1, 2/1 TMBP/PDA, and DGEBA/PDA systems implied a two-step degradation mechanism, but that for cured samples of 4/1 TMBP/PDA system implied three-step degradation, which might be due to the two structures formed as shown in Figure 10. Table IV shows the thermal degradation temperatures and stability properties of different epoxy/PDA systems. The value of  $T_{d10}$  (the temperature of degradation at which the weight loss is 10%) for different cured TMBP/PDA systems and DGEBA/PDA system was

**TABLE II**  
Heating Rate's Influence on Temperature  
T of Curing Reaction

TMBP/PDA	$q$ (°C/min)	$T_i$ /°C	$T_p$ /°C	$T_f$ /°C
1/1	5	97	118	150
	10	102	132	169
	15	106	141	184
	20	110	151	192
2/1	5	95	119	144
	10	100	134	168
	15	103	144	180
	20	107	150	201
4/1	5	96	114	136
	10	100	125	156
	15	105	131	165
	20	109	141	178
DGEBA/PDA	5	64	95	132
	10	68	108	150
	15	79	117	177
	20	83	124	194

$T_i$  is the temperature where the instant conversion rate is initial at each heating rate;  $T_p$  is the temperature where the instant conversion rate is maximum at each heating rate;  $T_f$  is the temperature where the instant conversion rate is final at each heating rate.





**Figure 10** The theoretic structures of the cured TMBP/PDA systems.

330, 333, 290, and 319°C, respectively. The char yields of 2/1 TMBP/PDA system at different temperatures were higher than others because of the higher functionality that gave a higher crosslinked density.

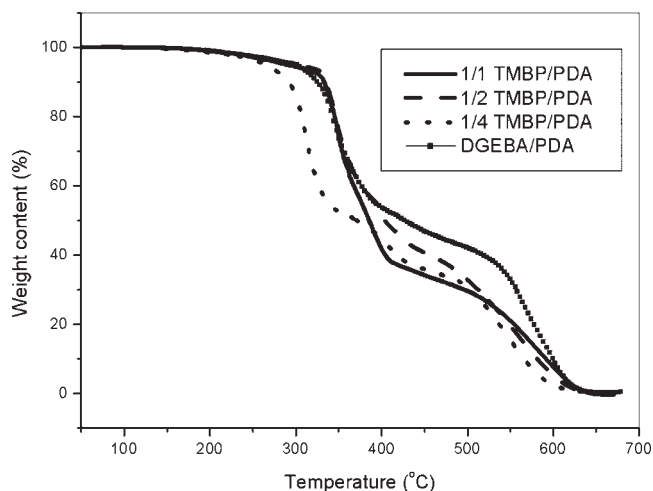
The data showed that the thermal properties of 2/1 TMBP/PDA system were better than those of DGEBA/PDA because of the rigid rod groups and bulky methyl substitutions of TMBP. The different thermal properties of different cured TMBP/PDA systems were due to the large steric hindrance effects of tetramethyl groups on biphenyl epoxy main chains and the cured crosslinked density of different systems because of the different amount of the diamine in the epoxy as showed in Figure 10. The best thermal properties of the sample of cured 2/1 TMBP/PDA system was due to the large steric hindrance effects of tetramethyl groups and highest crosslinked density, which hindered the move of the molecular chain.

**TABLE III**  
List of Glass Transition Temperatures of Different TMBP/PDA Systems and DGEBA/PDA System

TMBP/PDA	DSC- $T_g$ (°C)	DMA- $T_g$ (°C)
1/1	100	95
2/1	120	115
4/1	90	81
DGEBA/PDA	101	95

## CONCLUSIONS

The cure kinetics of TMBP/PDA and DGEBA/PDA were investigated by differential scanning calorimeter (DSC) using an isoconversional method under dynamic conditions. The results showed the activation energy was a dependent of the conversion. The reaction process was affected by the molar ratios of epoxy resin to curing agent. Because of the rigid rod groups, large steric hindrance effects, and the increase



**Figure 11** Thermograms of thermal gravimetric analysis of the cured TMBP/PDA systems and DGEBA/PDA system.

**TABLE IV**  
**TGA Results of the Cured Different Epoxy/PDA Systems**

TMBP/PDA	Temperature at 10 wt % loss (°C)	Char yield (%)		
		300°C	400°C	500°C
1/1	330	94	41	29
2/1	333	95	51	32
4/1	290	86	44	30
E-51/PDA	319	89	47	36

of crosslinked density, the 2/1 TMBP/PDA system possesses optimal thermal properties, including the highest glass transition and characteristic thermal degradation temperatures among all epoxy systems studied in the present article.

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