



Thermal properties and cure kinetics of a liquid crystalline epoxy resin with biphenyl-aromatic ester mesogen

Yin-Ling Liu, Zhi-Qi Cai*, Xiufang Wen, Pihui Pi, Dafeng Zheng, Jiang Cheng, Zhuoru Yang

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:

Received 7 August 2010

Received in revised form 7 November 2010

Accepted 8 November 2010

Available online 16 November 2010

Keywords:

Liquid crystalline epoxy resin

Cure kinetics

Thermal property

Differential scanning calorimetry (DSC)

Thermoset

ABSTRACT

A liquid crystalline epoxy resin diglycidyl ether of 3,3',5,5'-tetramethylbiphenyl-4,4'-diyl bis(4-hydroxybenzoate) (DGE-TMBPBHB) was synthesized and its thermal properties were studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Thermal history markedly affected liquid crystalline (LC) phase behaviors. The peak values of the isotropized temperature (T_i), crystallized temperature (T_c) and enthalpy change (ΔH_i) caused by the transition from the LC phase to the isotropic state of DGE-TMBPBHB decreased slightly during repetitive heat-cool cycles. Two liquid crystalline thermosets were prepared based on the epoxy monomer with two different curing agents, 4,4'-diaminodiphenyl methane (DDM) and 4,4'-diaminodiphenyl sulfone (DDS), respectively. Cure kinetics of mixtures of DGE-TMBPBHB/DDM and DGE-TMBPBHB/DDS were investigated by DSC under nonisothermal processes.

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1. Introduction

In the past few years, widely-held interests have been focused on liquid crystalline epoxy resins (LCERs) [1–3]. In general, LCER is composed of an aromatic mesogenic group and a pair of reactive oxirane rings [4], which can react with a curing agent by a ring-opening reaction. Ordered, anisotropic network structures have brought LCERs into many potential applications such as wave-guides, electronic packaging, matrix materials and optional switches for high performance composites [5].

Cure kinetics and thermal properties of different LCERs have been performed by various researchers [6–10]. Vyazovkin proposed an advanced isoconversional method (AICM) conveniently to investigate phase behaviors of epoxy resin at different curing stages [11–14]. AICM provides the probabilities to the researchers to reveal a variation of the effective activation energy of the monomer at different conversion and to avoid using explicit kinetic models. Lee et al. synthesized a series of LCERs based on biphenol mesogen and studied the effect of mesogenic length on the curing behavior and properties of LCERs [15–18].

* Corresponding author at: School of Chemistry and Chemical Engineering, South China University of Technology, Rm. 511B, Bd #16, 381 Wushan Rd., Tianhe District, Guangzhou 510640, Guangdong Province, China.

Tel.: +86 20 8711 4639x606; fax: +86 20 8711 2057x804.

E-mail address: cezqcai@scut.edu.cn (Z.-Q. Cai).

The level of order of a cured thermoset network can be strongly affected by the nature of a liquid crystalline epoxy compound and physical properties of the cured material. In order to obtain LCER with high thermal properties, Sun et al. synthesized a novel rigid-rod epoxy monomer containing the long mesogenic unit of biphenyl and aromatic ester group, diglycidyl ether of 3,3',5,5'-tetramethylbiphenyl-4,4'-diyl bis(4-hydroxybenzoate) (DGE-TMBPBHB) recently [7]. DGE-TMBPBHB has a higher decomposition temperature than flexible epoxies and better thermal resistance than other rigid-rod epoxies. They further investigated the liquid crystalline phase behavior and curing kinetics of DGE-TMBPBHB with curing agent diaminodiphenylsulfone (DDS) by AICM [6].

In this study, an efficient and economic synthetic pathway to synthesize DGE-TMBPBHB is described which required only two reaction steps. Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were used to study the thermal properties and LC phase transition behavior of DGE-TMBPBHB. Interestingly, LC phase transition of DGE-TMBPBHB was different from the observation described earlier in the scientific literatures [6,7]. We found that thermal history of the sample had a sound influence on the thermal properties. In order to study this phenomenon more thoroughly, we used two different aromatic diamine curing agents 4,4'-diaminodiphenyl methane (DDM) and DDS to examine the cure kinetics of DGE-TMBPBHB/DDM and DGE-TMBPBHB/DDS mixtures. The thermal properties of two different thermosets prepared from the mixtures were also compared.

2. Experimental

2.1. Materials

4-Hydroxybenzoic acid (HBA), *p*-toluene sulfonic acid (*p*-TSA) and epichlorohydrin (EC) were purchased in analytical grade from the chemical agent company in Guangzhou, China. Sulfolane, 4,4'-diaminodiphenyl methane (DDM), and 4,4'-diaminodiphenyl sulfone (DDS) were purchased in analytical grade from Aladdin (Shanghai, China). 3,3'-5,5'-Tetramethyl-4,4'-dihydroxybiphenyl (TMDHBP) was a gift from Ao Kai Chemical Engineering Co. (Lanzhou city, Gansu province, China).

2.2. Measurement

¹H NMR and ¹³C NMR spectra were recorded by a Bruker Avance-400 spectrometer with CDCl₃ or dimethyl sulfoxide (DMSO-*d*₆) as a solvent and tetramethylsilane (TMS) as the internal standard. Infrared spectra were obtained with a Nicolet 380 Fourier transform infrared (FT-IR) spectrophotometer. Mass spectra were recorded with a Bruker Esquire HCT plus mass spectrometer. Elementary analysis was recorded on Elementar Vario EL III. Calorimetric studies were performed using Netzsch DSC 204 F1 Phoenix with N₂ as purge gas with the flow rate of 70 ml min⁻¹ by dynamic and isothermal scanning. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 C thermogravimetric analyzer under N₂ atmosphere at a heating rate of 10 °C min⁻¹ up to 800 °C. The textures of the mesophase were observed with a polarized optical microscopy Olympus BX41 equipped with a THMS 600 hot stage and a TMS 94 Temperature Controller (Scheme 1).

2.3. Synthesis of DGE-TMBPBHB

A mixture of TMDHBP (0.05 mol, 12.1 g), HBA (0.2 mol, 27.6 g), sulfolane (50 ml) and *p*-TSA (5 mmol, 0.9 g) was stirred at 180 °C for 4 h. The crude product was washed with cool water and ethanol to give 19.3 g of 3,3',5,5'-tetramethylbiphenyl-4,4' diyl bis(4-hydroxybenzoate) (TMBPBHB) [19,20]. Then, a mixture of TMBPBHB (10.5 mmol, 5.1 g), EC (0.42 mol, 39.2 g) and isopropyl alcohol (0.32 mol, 19.1 g) was stirred at 50 °C for 0.5 h. After that, the aqueous solution of NaOH (30 wt%, 8.5 ml) was added dropwise into the mixture in 1 h. The mixture was again stirred at 60 °C for 4 h. After cooling, a white precipitate was recrystallized several times with CH₂Cl₂/CH₃OH to give 4.59 g of DGE-TMBPBHB as white powder. Yield: 73.5%. FT-IR (KBr, ν, cm⁻¹): 2922 (C–H), 1729 (C=O), 1510 cm⁻¹ (C–H), 1480 (C–H), 1090 cm⁻¹ (C–O), 1258, 1167, 917 and 841 (oxirane). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.20 (d, *J*=8.8 Hz, 4H, Ar), 7.26 (s, 4H, Ar), 7.02 (d, *J*=8.8 Hz, 4H, Ar), 4.36–4.33 (m, 2H, CH), 4.04–4.00 (m, 2H, CH), 3.40–3.39 (m, 2H, CH), 2.94 (t, *J*=4.8 Hz, 2H, CH), 2.80–2.78 (m, 2H, CH), 2.22 (s, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 164.12, 162.78, 147.83, 138.45, 132.38, 130.64, 127.43, 122.10, 114.53, 68.95, 49.95, 44.61, 16.61. MS (APCI) calcd for C₃₆H₃₄O₈ 594.2, found 595.7. Anal. Calc. for C₃₆H₃₄O₈: C, 72.71; H, 5.76. Found: C, 72.50; H, 5.79.

2.4. Curing processes of DGE-TMBPBHB

DGE-TMBPBHB and a curing agent, DDM or DDS, were pestled in an agate mortar and mixed together in a stoichiometric ratio. The DSC experiments were conducted with different heating rates of 5, 10, 15 and 20 °C min⁻¹ under N₂ for DGE-TMBPBHB/DDM and DGE-TMBPBHB/DDS mixtures.

2.5. Theory of the cure kinetics

The curing of DGE-TMBPBHB/DDM and DGE-TMBPBHB/DDS mixtures was studied by DSC. The DSC curves were analyzed on the basis of the following assumptions: the area under the curves was proportional to the conversion α , whereas the extent of reaction during the mixing of epoxy resin and diamine was neglected. The conversion α at any time could be defined as:

$$\alpha = \frac{H_t}{H_{\text{total}}} \quad (1)$$

where H_t is the partial heat of reaction at time t , and H_{total} is the total heat of curing reaction. For a thermosetting resin, the rate of curing da/dt is usually obtained by:

$$\frac{da}{dt} = \frac{dH/dt}{H_{\text{total}}} \quad (2)$$

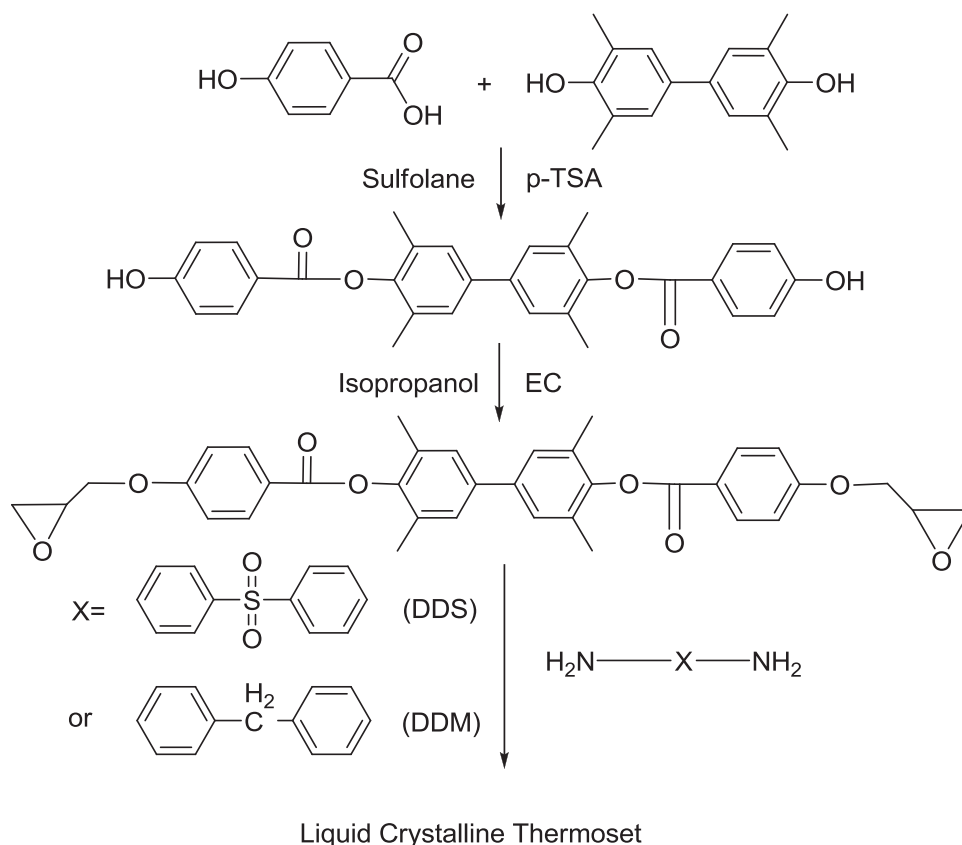
where dH/dt is the heat flow at time t in curing reaction.

3. Results and discussion

3.1. LC phase transition behavior of DGE-TMBPBHB

Thermal programs consisting of repetitive ramps – a ramp heating scan and a 2-min isothermal step, followed by cooling and a 2-min isothermal step – were used to study the thermal properties of the epoxy monomer DGE-TMBPBHB. Fig. 1a shows the thermograms of DGE-TMBPBHB with a constant heating rate of 20 °C min⁻¹ in the temperature range between 100 °C and 280 °C. The thermal transition temperatures and the corresponding enthalpy changes of the liquid crystalline monomer collected from repetitive heat-cool scans are summarized in Table 1. As shown in Fig. 1a, an endothermic peak at 245.1 °C was observed upon the first heating which could be attributed to the isotropization ($T_i = 245.1$ °C). During the first cooling run, a blunt peak was observed at around 220.4 °C, which indicated the phase behavior of DGE-TMBPBHB from the isotropic phase to liquid crystal phase. With the reduction of temperature, the sample began to crystallize at 164.3 °C ($T_c = 164.3$ °C). When we ran the heat-cool cycle a second and a third time, the peak values of the T_i and T_c slightly shifted towards lower temperatures. Enthalpy change caused by the transition from solid phase to isotropic state (ΔH_i) decreased during repetitive heat-cool cycles, which changed from 70.9 to 65.4, and to 56.5 J g⁻¹. Fig. 1b shows the thermograms when heating of the sample was conducted at a heating rate of 10 °C min⁻¹ in each heat-cool ramp. A decrease of T_i , T_c and ΔH_i was also observed. The small blunt peak practically disappeared on the third cooling. Obviously, the liquid crystalline behavior changed at different heating rates.

In order to corroborate that the decrease of enthalpy in DSC thermograms were not due to the degradation of the monomer, thermogravimetric analysis of DGE-TMBPBHB was performed. The result revealed a very small (1.2%) weight loss of the DGE-TMBPBHB at 280 °C. Thus, degradation did not occur at the temperature used in the DSC experiment [21,22]. Actually, the enthalpy decrease and the non-reproducibility of DSC thermograms during repetitive heating and cooling ramps were also observed by some other authors [22–24]. Percec and coworkers [25,26] found that the heat and temperature of isotropization, ΔH_i and T_i , were remarkably affected by the preceding thermal treatment. We assumed that two main factors were responsible for the non-reproducibility. For one thing, thermal history markedly affected LC phase behaviors. The experimental conditions, specifically heating and cooling rates used in DSC had a significant impact on enthalpic relaxation [27] since enthalpic signal were believed to arise from a competition among kinetic and thermodynamic factors. For another, the cure behavior and thermal properties of LCERs were affected by the



Scheme 1. Synthetic pathway of liquid crystalline thermosets.

structure of the aromatic mesogenic group and the length of the flexible spacer which decouples the reactive end-functional group from the rigid-rod mesogenic group [28]. Due to the steric hindrance between the hydrogen atoms in the two benzene rings in DGE-TMBPBHB, the biphenyl moiety had greater effect on the liquid crystal phase formation than the phenyl group [21]. From this point, we assumed that the long mesogenic unit in DGE-TMBPBHB and molecular interactions played a major role in thermal transition temperature and the corresponding enthalpy change [24,29].

Polarized optical microscopy was applied to identify the mesophases of DGE-TMBPBHB. The samples were prepared by sandwiching a tiny powder between two glass plates. Fig. 2 shows the POM photographs of DGE-TMBPBHB at different temperatures ($200\times$ magnification). When DGE-TMBPBHB was heated to 250°C , the sample began to melt. The texture color changed with increasing temperature and disappeared at 265°C (Fig. 2a). With the reduction of temperature, the isotropic state changed to LC phase and the texture of DGE-TMBPBHB exhibited obvious birefringence (Fig. 2b, 224°C). The sample began to crystallize when the temperature dropped further. Fig. 2 shows the isotropic state, liquid

crystalline state, and the crystalline state of the DGE-TMBPBHB, respectively. Birefringence was only observed during the cooling process and it confirmed that DGE-TMBPBHB is a typical monotropic liquid crystal. This was consistent with the results obtained by DSC.

3.2. Cure kinetics of DGE-TMBPBHB with DDM and DDS

The curing behavior of DGE-TMBPBHB/DDM was examined using DSC. Fig. 3 shows the curing curves of DGE-TMBPBHB/DDM system at the heating rates of 5, 10, 15 and $20^\circ\text{C min}^{-1}$, respectively. It exhibits typical DSC curves for the curing reaction of DGE-TMBPBHB and DDM as a function of heating rate. Before the beginning of the cure, there was an endothermic peak around 91°C in 5°C min^{-1} curve which was assigned to the melting of DDM. Following the endothermic peak, an exothermal curing peak was observed at about 161.9°C . With increasing the heating rate, the endothermic peak shifted slightly towards a higher temperature. At the same time, the temperature range of DGE-TMBPBHB/DDM curing reaction became broader and the initial

Table 1
Thermal transitions and corresponding enthalpy changes in repetitive heat-cool cycles.

Heat-cool cycles	Heating rates ($^\circ\text{C min}^{-1}$)	Heating scan		Cooling scan	
		Enthalpy changes (J g^{-1})	Transition temperature ($^\circ\text{C}$) ^a	Enthalpy changes (J g^{-1})	Transition temperature ($^\circ\text{C}$) ^a
Fig. 1a-1	20	70.9	245.1	-3.4, -54.8	220.4, 164.3, 148.9
Fig. 1a-2	20	65.4	245.3	-3.6, -48.4	207.4, 143.8
Fig. 1a-3	20	56.5	243.4	-2.1, -43.8	200.4, 137.1
Fig. 1b-1	10	73.0	243.4	-3.6, -49.9	218.8, 158.9, 150.2
Fig. 1b-2	10	65.9	242.8	-2.0, -42.3	205.1, 144.3
Fig. 1b-3	10	56.1	240.9	-38.5	139.8

^a Peak temperatures were taken as phase transition temperatures.

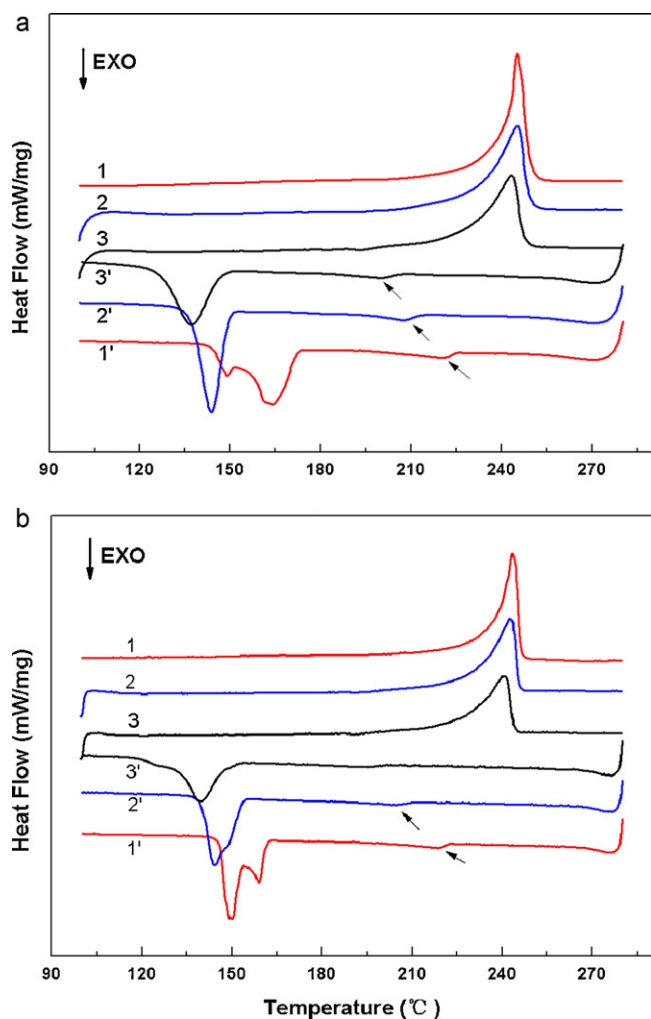


Fig. 1. DSC curves of repetitive heat-cool cycles for DGE-TMBPBHB: (a) 20 °C min⁻¹, (b) 10 °C min⁻¹.

curing temperature (T_i), the peak temperature (T_p) and the finishing temperature (T_f) were all increased with the increasing heating rate. The mean thermal exothermic effect, which characterized the reaction between DGE-TMBPBHB and DDM, might be due to the errors connected with methods used to estimate the baseline [30].

To study the cure kinetics of the curing systems, the relation of the extent of conversion (α) and the curing time under different heating rates was obtained from DSC. Fig. 4 presents the plots of the extent of conversion versus the temperature of DGE-TMBPBHB/DDM system at different heating rates.

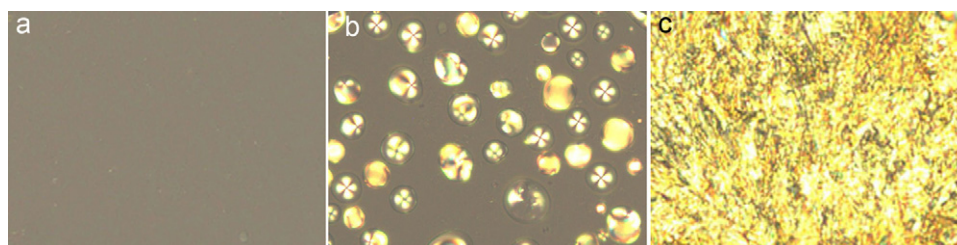


Fig. 2. POM photographs of DGE-TMBPBHB at different temperatures (200×).

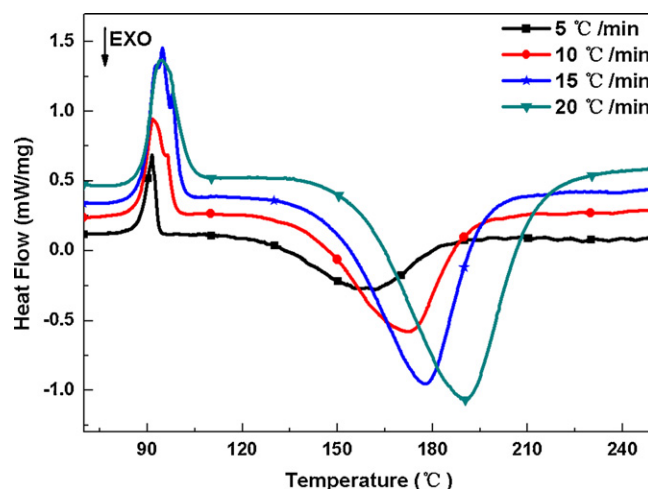


Fig. 3. DSC curves for the curing reaction of DGE-TMBPBHB with DDM.

If one assumes that the curing rate is only a function of conversion and temperature T , the da/dt can be also described as:

$$\frac{da}{dt} = k(T)f(a) = A \exp\left(\frac{-E_a}{RT}\right) f(a) \quad (3)$$

or:

$$\frac{d \ln(da/dt)}{dT^{-1}} = \frac{-E_a}{R} \quad (4)$$

where A is the frequency factor; E_a is the effective activation energy; $f(a)$ is the reaction model; R is the gas constant. From Eq. (4), a plot of $\ln(da/dt)$ versus $1/T$ at the same time α from a series of DSC curves with various heating rates would result in a straight line with a slope of $-E_a/R$. Repeating this procedure, the relationship between E_a and α can be obtained, which is called isoconversional method (ICM). This method has been successfully applied to study the curing process since it allowed for evaluating E_a as a function of the extent of reaction α without assuming a particular form of the reaction model [14].

The values of E_a obtained at different conversions are shown in Fig. 5. In DGE-TMBPBHB/DDM system, the initial curing stages had an E_a around 46 kJ mol⁻¹. Then the E_a increased in the range of 55–75 kJ mol⁻¹ of typical epoxy-amine curing reaction. The value of E_a decreased quickly from ≈ 67 to ≈ 30 kJ mol⁻¹ at conversions above 0.8. A decrease in E_a associated with the diffusion control has been reported in a number of papers following the original paper by Vyazovkin and Sbirrazzuoli [31]. Generally, kinetic-controlled reaction dominated the polymerization in the early stage, while as the reaction proceeded towards gelation and vitrification, diffusion control became dominative and the E_a value gradually decreased [13]. The values of E_a obtained for the curing reaction of DGE-TMBPBHB/DDS system are also plotted in Fig. 5.

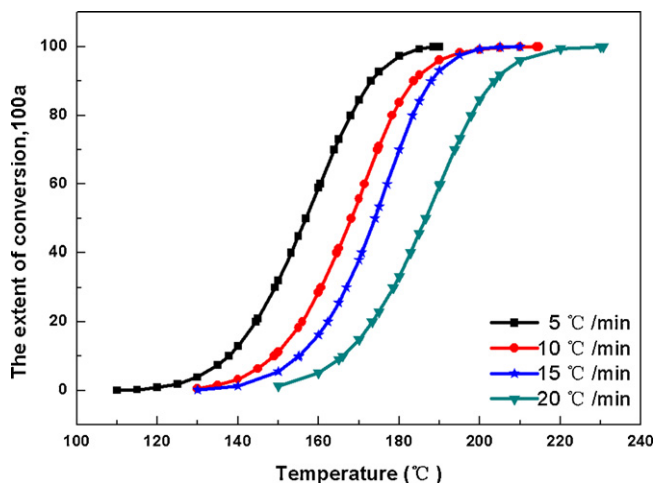


Fig. 4. α - T curves of DGE-TMBPBHB/DDM cured system.

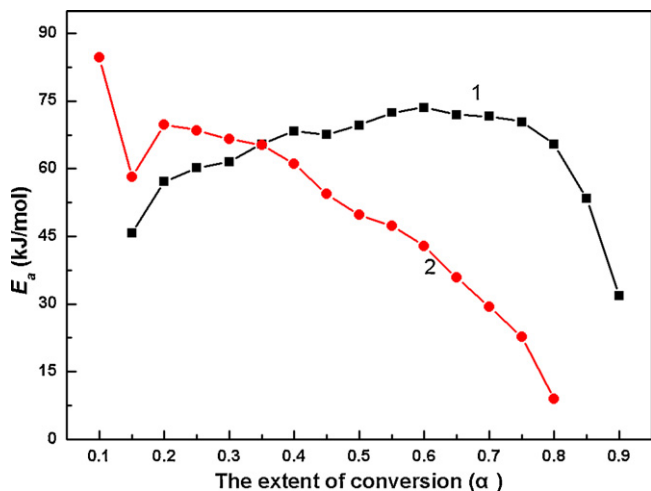


Fig. 5. Plots of E_a versus α of cured system: (1) DGE-TMBPBHB/DDM; (2) DGE-TMBPBHB/DDS.

3.3. Thermal properties of DGE-TMBPBHB cure systems

The glass transition temperature (T_g) is an important parameter in connection with structures and properties. The T_g values of the cured materials, DGE-TMBPBHB/DDM or DGE-TMBPBHB/DDS, which formed after completion of the first curing process were investigated. For each of the LCER cure systems, we cured the sample at the same heating and cooling rate and the glass transition temperature were collected upon the second heating. Table 2 shows the glass transition temperature of DGE-TMBPBHB/DDM and DGE-TMBPBHB/DDS systems under the heating rate of 10, 15, 20 °C min⁻¹, respectively. Practically, a slow heating rate for epoxy-amine curing system is often used in industry to avoid the heat aggregation and heat stress in the resultant materials because of the decomposition of part of polymer chains and untimely relax-

ation of the polymer chains under a fast heating rate [32]. From Table 2 it can be learned that the T_g values of DGE-TMBPBHB/DDS systems were higher than those of cured DGE-TMBPBHB/DDM thermosets since the melting point of DDS was a little higher than DDM.

4. Conclusions

A liquid crystalline epoxy resin DGE-TMBPBHB was synthesized by a highly efficient and economical method. The epoxy monomer could be obtained from several common primary materials and thus the procedure was much more effective when the mesogen was used for mass production in industry. Then, we studied the LC phase transition behavior of DGE-TMBPBHB and found that thermal history had a significant influence on the thermal properties of the epoxy monomer. The peak values of the T_i and T_c in DGE-TMBPBHB decreased slightly during the second and the third heat-cool cycle. Enthalpy change caused by the transition from the LC phase to the isotropic state (ΔH_i) also decreased during repetitive heat-cool cycles. The cure kinetics of DGE-TMBPBHB/DDM and DGE-TMBPBHB/DDS mixtures was studied. The T_g values of DGE-TMBPBHB/DDS systems were higher than those of cured DGE-TMBPBHB/DDM thermosets.

Acknowledgements

We are appreciating the DSC measurement for Mr Jiwen Chen and Mr Guoming Zhong from Guangdong Test Center of Product Quality Supervision (Shunde, Guangdong Province). The authors also thank Dr. Yanbin Jiang for the POM observation in this work. Financial support from the *Natural Science Foundation of South China University of Technology* (Grant No. x2hge5090490) is gratefully appreciated.

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Table 2

T_g (°C) values of cured system under different heating rates.

Thermoset	10 (°C min ⁻¹)	15 (°C min ⁻¹)	20 (°C min ⁻¹)
DGE-TMBPBHB/DDM	135.1	122.9	149.0
DGE-TMBPBHB/DDS	166.1	176.9	188.6

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