



## Preparation and Curing Kinetics Investigation of Diglycidyl Ether of Bisphenol A/Liquid Crystalline Epoxy Resin Blends

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### ABSTRACT

A novel liquid crystalline epoxy resin (PHQEP) was synthesized by phase transfer catalytic method and characterized as a nematic liquid crystalline by polarized optical microscope (POM). The cure kinetics of diglycidyl ether of bisphenol A (E-51)/PHQEP blends using 4,4'-diaminodiphenylsulphone (DDS) as the curing agent was studied by non-isothermal differential scanning calorimetry (DSC) at four linearly programmed heating rates of 5, 10, 15, and 20 K/min. The apparent activation energy ( $E_a$ ) was determined by Friedman method, and kinetic model was predicted by Málek method. In the curing process of PHQEP/DDS, the  $E_a$  values decreased slowly with the conversion in the region of 0.2~0.5 for the formation of liquid crystalline phase. The  $E_a$  value of PHQEP/DDS system is generally higher than those of PHQEP/E-51/DDS and E-51/DDS systems and the  $E_a$  of PHQEP/E-51/DDS system is generally higher than that of E-51/DDS. This may imply that PHQEP is less reactive than E-51 in the curing process, since the molecular movement was limited because of the aromatic ester structure and the hydrogen bonds which were formed between the carbonyl groups of PHQEP and hydroxyl groups produced in the curing process. Furthermore, autocatalytic model was predicted to be the kinetic model of the above mentioned three systems. The predicted curves fit well with the experimentally obtained curves.

### Key Words:

liquid crystalline epoxy;  
cure kinetics;  
activation energy;  
isoconversional method;  
autocatalytic model.

### INTRODUCTION

In recent years, liquid crystalline epoxy resins have drawn much attention of the chemists because of enhanced properties such as anisotropic orientation, high modulus and tensile strength, and low coefficient of thermal expansion [1-3]. Mormann et al. [4] reported the synthesis and the phase behaviour of azomethine-linked mesogenic epoxies. Choi et al. [5] also

reported the synthesis of azomethine epoxies with central flexible spacer and twin mesogen, and the curing behaviour with a diamine curing agent. Besides, Panchaipetch et al. [6] investigated the effect of a conventional epoxy resin reacting to a diglycidyl-terminated liquid crystalline monomer. The synthesis, curing kinetics, and degree of miscibility of the resulting

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system were reported as well. It is well known that the physical properties of cured epoxy resins depend on their structures and cure degree. Thus, it is important to understand the nature of the curing process and how its kinetic parameters can be influenced by temperature and materials ratio, the structures of the cured material, etc. The cure behaviours of liquid crystalline epoxy resin [7,8] and common epoxy resin [9-11] have been largely studied and developed, respectively.

Conventional synthesis pathway of liquid crystalline epoxy resin was designed so to oxygenize the double bond terminated mesogenic monomer [12,13]. It has been impossible to obtain liquid crystalline epoxy oligoester or polymer by other means so far. In the present study, a novel liquid crystalline epoxy oligoester (PHQEP) containing ester mesogen was synthesized by using a phase transfer catalyst [14,15,16] and characterized by Fourier transformed infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), POM and DSC techniques. The cure kinetics of common epoxy resin blended with liquid crystalline epoxy resin has been seldom investigated. PHQEP and E-51 have each different curing behaviours, and the curing process of PHQEP/E-51 blend becomes relatively complex. It is important to study the curing reaction of PHQEP/E-51 blend, and then find a proper curing procedure to prepare a composite with superior properties. While DDS was used as a curing agent, the curing process of PHQEP/E-51 blend was scanned by dynamic DSC at the linear heating rates of 5, 10, 15, and 20 K/min. The curing behaviours of PHQEP/E-51/DDS were compared to the curing behaviours of PHQEP/DDS and E-51/DDS by a series of kinetic parameters such as  $E_a$ , pre-exponential factor, and exponential factor. The curing model was predicted by Málek method. It is aimed to learn the effect of liquid crystalline phase on the curing behaviour of PHQEP/DDS, and the effect of PHQEP content on the curing behaviour and curing mechanisms of PHQEP/E-51 blend.

## EXPERIMENTAL

### Materials and Methods

The epoxy resin used in this study is a commercial

grade of diglycidyl ether of bisphenol A (E-51, epoxy value = 0.51, purchased from Yueyang Chemical Plant, China). Hydroquinone (Hunan Nanhua Chemical Co., Ltd, China, analytical reagent), *p*-hydroxybenzoic acid (Sinopharm Chemical Reagent Co., Ltd, China, chemical pure) and epichlorohydrin (Chinese Pharmaceutical BLOC Shanghai Chemical Agent Co., China, chemical pure) were used as received. Curing agent, 4,4'-diaminodiphenyl sulphone (DDS) with a molar mass of 248.3 g/mol and a purity of 99% was purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Fourier transformed infrared spectroscopy (FTIR) was recorded between 4000 and 400  $\text{cm}^{-1}$  on a Nicolet 470 spectrophotometer using KBr pellets as a reference at room temperature.  $^1\text{H}$  NMR was obtained on a 400 Bruker NMR instrument using chloroform- $d$  as the solvent of PHQEP, DMSO- $d_6$  as the solvent of PHQ, and tetramethyl silane (TMS) as the internal standard. A lexica polarized optical microscope Olympus BH-2 equipped with heating stage Mettler FP82 was used to investigate the liquid crystalline morphologies of the PHQEP.

### Synthesis of PHQEP

#### *Synthesis of Di(p-hydroxyl benzoic acid) Hydroquinone Ester (PHQ)*

A 250 mL three-necked flask with a condenser, nitrogen inlet and thermometer was charged with hydroquinone (2.5 g, 22.7 mmol), *p*-hydroxybenzoic acid (7.2 g, 52.1 mmol), dibutyl phthalate (7 mL) and 4-methylbenzenesulphonic acid (0.3 g, 1.7 mmol). The mixture, under  $\text{N}_2$  atmosphere, was stirred for 3 h at 180°C, then cooled to 50°C, and poured into 100 mL of ethanol. The precipitate was collected by filtration and washed with methyl alcohol 3 times [17]. The solid product was dried at 80°C. The yield was 58 % (8 g).

#### *Synthesis of Liquid Crystalline Epoxy Resin (PHQEP)*

The synthesis of PHQEP followed a phase transfer catalytic method [18]. A mixture of PHQ (5 g, 14.5 mmol), tetrabutylammonium bromide (1.4 mg, 0.02 mmol) and epichlorohydrin (15 mL, 18.9 mmol) was refluxed until it became clear. Residual epichlorohydrin was distilled partly under a reduced pressure. The reaction continued at 80°C, and 45 wt% of NaOH

**Table 1.** EEW Analytical results of PHQHP.

Sample	W (g)	A (mL)	EEW (g/mol)
a	0.102	0.91	357.1
b	0.103	0.96	374.7
c	0.101	0.56	317.5

B = 3.71 mL, N = 0.1 mol/L

aqueous solution (1.71 mL) was added dropwise to the reaction system within 3 h under vigorously stirring, and then it lasted for further 3~6 h to complete the ring closure. After cooling, the mixture was poured into the mixed solvents of acetone and ethanol (volume ratio 2/5). The precipitate was separated by filtration, then washed by distilled water and mixed solvents in order. The final product was dried at 60°C. The yield was 4.5 g.

#### Characterization of Epoxy Equivalent Weight (EEW) of PHQEP

The EEW was estimated by HCl-THF solution (hydrochloric acid 1.5 mL and tetrahydrofuran 70 mL) method [19]. About 0.1 g of PHQEP was dissolved in a 9 mL of HCl-THF solution under stirring, and then kept for 1 h in a plugged conical flask. A sodium hydroxide standard solution (1N) was added dropwise into the conical flask using phenolphthalein as an indicator. Besides, a 9 mL of pure HCl-THF solution was titrated as a reference. The volumes of consumed NaOH standard solution were recorded. The equation for calculating the EEW of PHQEP is given as follows:

$$EEW = 1000 \times W/N(B-A) \quad (1)$$

where, W, N, B, and A are the actual weight of PHQEP (g), the concentration of NaOH standard solution (mol/L), the volume of NaOH standard solution consumed by 9 mL of HCl-THF solution (mL) and the volume of NaOH standard solution consumed by 9 mL of HCl-THF/PHQEP solution, respectively. The analytic results of three different samples are revealed in Table 1.

The EEW difference of PHQEP is related to the different lasting reaction time after dripping off 45 wt% NaOH aqueous solution in the synthesis of PHQEP.

#### Sample Preparation

PHQEP/DDS mixture was prepared by grinding PHQEP with DDS in an agate mortar time after time. The EEW of PHQEP used is 357.1 g/mol. The preparation of PHQEP/DDS/E-51 blends obeys the following procedure: PHQEP was dissolved in the heated epoxy resins (E-51, with an EEW=196.08 g/mol) while vigorously stirring. After being cooled to 50°C, the PHQEP/E-51 solution was mixed with DDS. The formulations of E-51/DDS, PHQEP/DDS and PHQEP/DDS/E-51 systems are shown in Table 2.

#### DSC Measurements

DSC is extensively used for investigating the curing reaction of thermoset polymers. Curing kinetics can be characterized with DSC by measuring the heat which were generated during curing reaction and pre-

**Table 2.** Formulations of E-51/DDS, PHQEP/DDS and PHQEP/DDS/E-51 systems.

Sample	Weight formulation			Molar ratio (amino group/epoxy group)
	E-51 (g)	DDS (g)	PHQEP (g)	
E-51/DDS	1	0.3	-	0.4738
PHQEP/DDS	-	0.164	1.0	0.4717
PHQEP(1 wt%)/E-51/DDS	1	0.3	0.01	0.4712
PHQEP(2.5 wt%)/E-51/DDS	1	0.3	0.025	0.4674
PHQEP(5 wt %)/E-51/DDS	1	0.3	0.05	0.4612
PHQEP(7.5 wt%)/E-51/DDS	1	0.3	0.075	0.4551
PHQEP(10 wt %)/E-51/DDS	1	0.3	0.1	0.4492

sented a functional relationship with temperature and time. All DSC studies of the curing behaviour were performed with the NETZSCH DSC204 differential scanning calorimeter under the nitrogen atmosphere. Pure indium was used as a standard for calorimetric calibration. All samples (= 20 mg) were contained within sealed aluminium DSC pans, and were scanned from 50 to 350°C at different heating rates (5, 10, 15, and 20 K/min). An identical empty cell was taken as reference.

### Theoretical Analysis

The basic kinetic equation [20,21] can be described as follows:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (2)$$

where,  $K(T)$ ,  $T$ ,  $f(\alpha)$ , and  $\alpha$  are the temperature dependent reaction rate constant, the absolute temperature, the function depending on the reaction mechanism, and the fractional conversion or curing degree estimated by the ratio of  $\Delta H$  against  $\Delta H_0$  respectively.

$$\alpha = \frac{\Delta H}{\Delta H_0} \quad (3)$$

where  $\Delta H$  and  $\Delta H_0$  are the released heat at certain conversion and the total heat evolution in the whole curing reaction, respectively. Reaction rate is a function of time and it can be expressed as eqn (4) [10,22,23].

$$\left(\frac{d\alpha}{dt}\right) = \frac{dH/dt}{\Delta H_0} \quad (4)$$

where,  $dH/dt$  is instantaneous heat flow. The temperature dependence of the specific rate constant  $K(T)$  is described by Arrhenius equation [24].

$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where,  $A$ ,  $R$ , and  $E_a$  are the pre-exponential factor, the universal gas constant, and the apparent activation energy, respectively.

Curing of epoxy resin involves several steps and is accompanied by a physical change of the reaction medium from low-viscosity liquids to glassy solids

[25]. The complexity of the curing process leads to a variation of the activation energy with the curing degree or curing time. Thus, the activation energy obtained in the kinetic analysis is apparent activation energy. In non-isothermal conditions when the temperature varies with time linearly, a constant heating rate ( $\beta$ ) is defined as follows:

$$\beta = \frac{dT}{dt} \quad (6)$$

By combining eqns (2) and (4)-(6), eqn (2) can be expressed as follows:

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (7)$$

$E_a$  can be calculated using various computational methods [26,27]. Iso-conversional methods are much more sensitive in detecting the curing kinetics complexity. Friedman method [28] as a typical iso-conversional method is applied to calculate the  $E_a$  values.

$$\ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (8)$$

The slope of  $\ln(d\alpha/dt)$  versus  $1/T$  for the same  $\alpha$  value gives the value of  $E_a$ . The values of  $E_a$  can then be used to find the appropriate kinetic model  $f(\alpha)$ . In the following description, it is necessary to appeal to the special functions  $y(\alpha)$  and  $z(\alpha)$  [20,29].

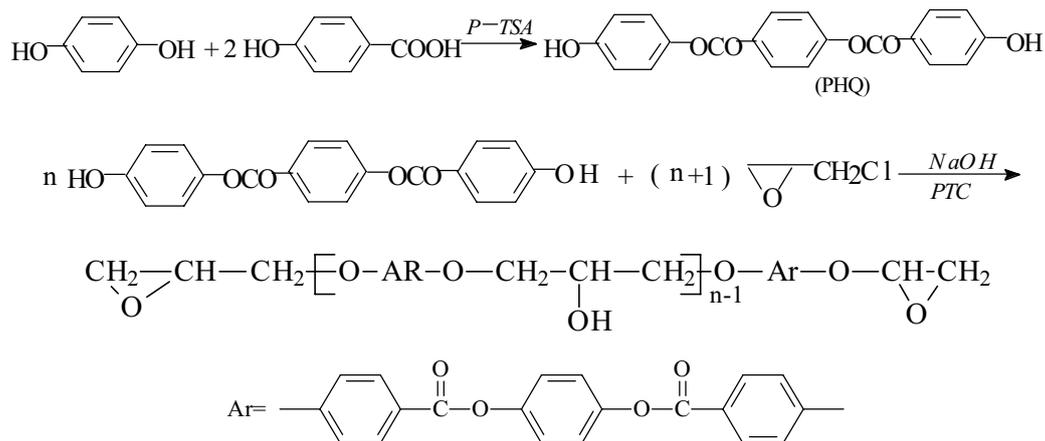
$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)e^x \quad (9)$$

$$z(\alpha) = \pi(x) \left(\frac{d\alpha}{dt}\right) \frac{T}{\beta} \quad (10)$$

Where,  $x$  and  $\pi(x)$  are reduced activation energy ( $E_a/RT$ ) and the expression of the temperature integral, respectively. As it was pointed out [21] that  $\pi(x)$  function can be well approximated using the 4th rational expression of Senum and Yang [30].

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (11)$$

The values of both  $y(\alpha)$  and  $z(\alpha)$  functions normalized within the (0,1) interval give valuable information for the determination of the most suitable kinetic



Scheme I. Synthesis pathway of PHQEP.

ic model. Knowing the value of  $E_a$  and the kinetic model function, the pre-exponential factor  $A$  is calculated according to eqn (12)[31].

$$A = -\frac{\beta x_p}{Tf'(\alpha_p)} \exp(x_p) \quad (12)$$

where,  $f'(\alpha)$  is the differential form of  $f(\alpha)$  and  $\alpha_p$  is the conversion corresponding to the maximum of heat flow on a DSC curve.

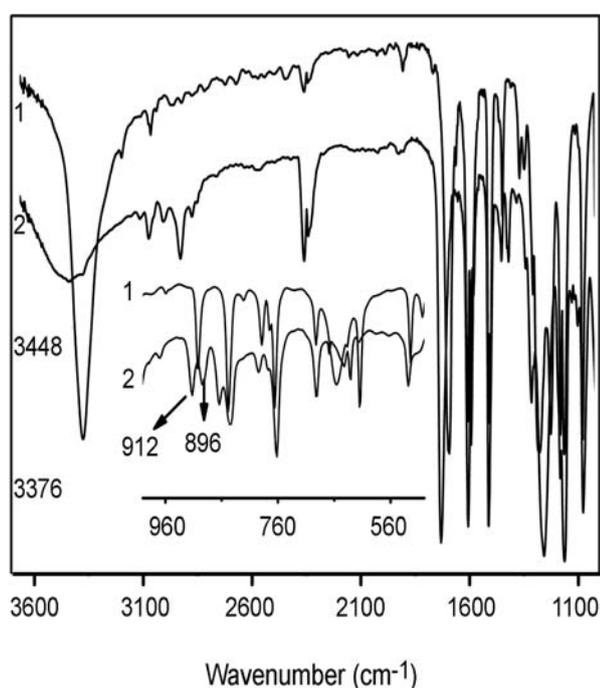


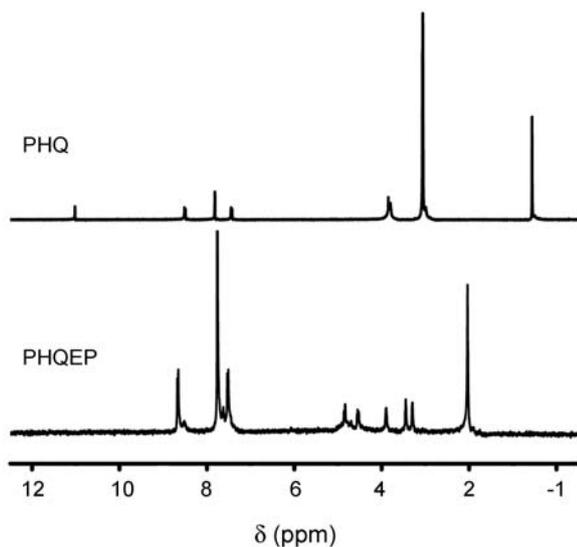
Figure 1. FTIR Spectra for (1) PHQ and (2) PHQEP.

## RESULTS AND DISCUSSION

### Structure Characterization of PHQ and PHQEP

The reaction between PHQ and epichlorohydrin is catalyzed by a phase transfer catalyst and transferred from sodium hydroxide solution to an organic phase which can reduce the reaction time and decrease the reaction temperature [32]. The expected molecular structures are shown in Scheme I. Figure 1 displays the FTIR spectra of PHQ and PHQEP. The strong absorption at  $\sim 3376 \text{ cm}^{-1}$  in PHQ is due to the stretching vibration of phenolic hydroxyl group and the wide absorption centered at  $3448 \text{ cm}^{-1}$  in PHQEP is attributed to the stretching vibration of hydroxyl groups. The characteristic bands at  $\sim 1254 \text{ cm}^{-1}$  (ph-O-C)  $\sim 2900 \text{ cm}^{-1}$  (alkoxy-ether bond), and  $\sim 896 \text{ cm}^{-1}$  and  $\sim 912 \text{ cm}^{-1}$  (epoxy group) just appearing in PHQEP indicate the existence of epoxy group.

The typical  $^1\text{H}$  NMR spectra of PHQ and PHQEP are given in Figure 2. The chemical shift at 10.6 ppm is attributed to the phenolic-OH in PHQ which is higher than the normal chemical shift of -OH because of the hydrogen bonds formation between the carbonyl groups and phenolic-OH of PHQ. The same peak is not found, however, in PHQEP spectrum, although there are not any differences in the chemical shifts around 7.1, 6.8, and 8.0 ppm (C-phenyl-H). It is illustrated that the phenolic hydroxyl groups have reacted with epoxy groups and the ester structures of PHQEP coming from PHQ are not destroyed. In the high magnetic field region, the major chemical shifts

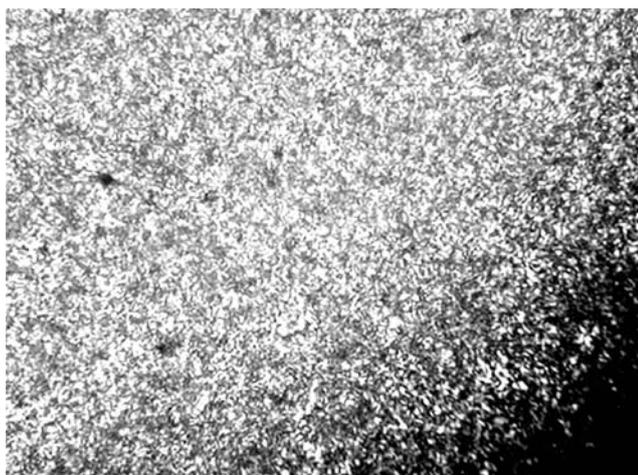


**Figure 2.**  $^1\text{H}$  NMR Spectra of PHQ (in  $\text{DMSO-d}_6$ ) and PHQEP (in  $\text{CDCl}_3$ ).

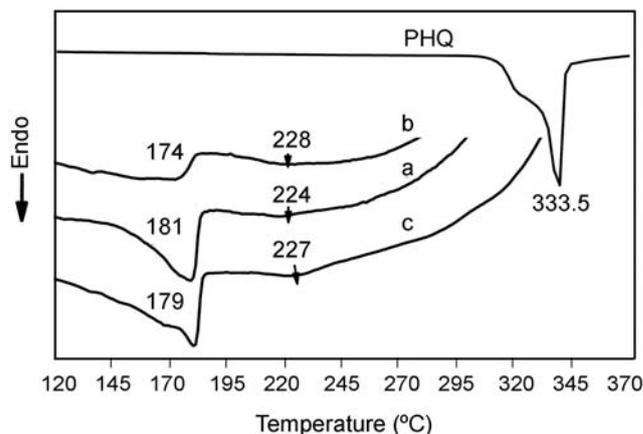
$\delta = 2.8$  and  $2.9$  ppm [ $\text{CH}_2$  of epoxy group, multiplets],  $3.4$  ppm [ $\text{CH}$  of epoxy group, multiplets],  $4.0$  ppm [ $\text{CH}_2$  of  $-\text{CH}_2$ -epoxy group],  $4.1$  ppm [ $\text{CH}$  of  $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ , multiplets],  $4.2$  ppm [ $\text{OH}$  of  $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ , singlet], and  $4.3$  ppm [ $\text{CH}_2$  of  $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ , multiplets] confirm the coexistence of epoxy groups and the ring-opening component of epoxy group.

### Thermal and Mesomorphic Properties of PHQEP

The liquid crystalline phase of PHQEP was observed



**Figure 3.** Representative polarized optical micrograph of the texture of PHQEP (with EEW of  $357.1$  g/mol, obtained at  $185^\circ\text{C}$ , magnification  $\times 200$ ).



**Figure 4.** The DSC curves of PHQ and PHQEP (EEW: (a)  $357.1$ ; (b)  $374.7$ ; (c)  $317.5$  g/mol).

by POM when the thermal properties of PHQEP oligomers were characterized by DSC. As PHQEP was heated to  $180^\circ\text{C}$ , a nematic texture appeared and became clearer as the temperature elevated. The POM micrograph taken at  $185^\circ\text{C}$  was displayed in Figure 3. While being consecutively heated to  $225^\circ\text{C}$ , the nematic texture disappeared gradually. The temperature range in which PHQEP displayed nematic texture is nearly consistent with the DSC scanning result in Figure 4. There appeared two endothermic peaks which are centered at  $\sim 180^\circ\text{C}$  and  $\sim 225^\circ\text{C}$ , respectively. The former is due to the first transition endothermic from solid to liquid crystalline phase and the latter is the result of the second transition from liquid crystalline phase to isotropic state. The repeating rigid segments of PHQEP chain which originated from PHQ showed a melting point of  $333.5^\circ\text{C}$ . It can be seen that PHQ did not show the liquid crystalline phase transition endothermic behaviour below  $300^\circ\text{C}$ . The flexible hydroxyl ether group ( $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ ) embedded in PHQEP decreases the molecular interactions, crystalline degree, and melting temperature. The temperature range of liquid crystalline phase is smaller than that reported by Liu [19]. This may be due to the different synthesis methods which lead to different molecular weights and PHQEP structures.

### Curing Kinetic Analysis

Non-isothermal DSC measurement curves are shown in Figures 5a-5c. The distinctions between PHQEP/DDS heat flow curves and the other two sys-

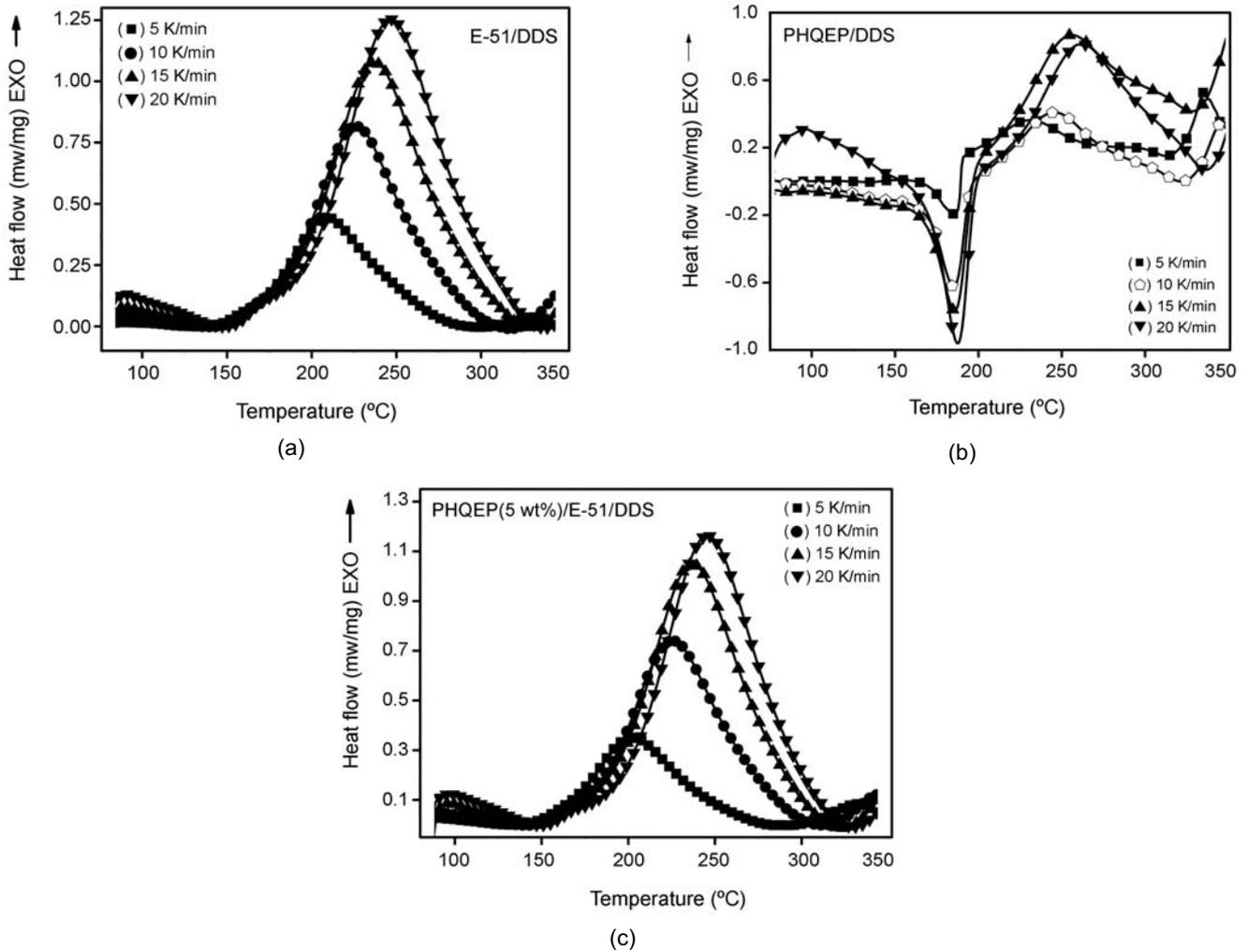


Figure 5. DSC Curves recorded for PHQEP/DDS, E-51/DDS, and PHQEP/E-51/DDS systems for different heating rates.

Table 3. Curing characteristics of the PHQEP/DDS, E-51/DDS, and PHQEP/DDS/E-51systems.

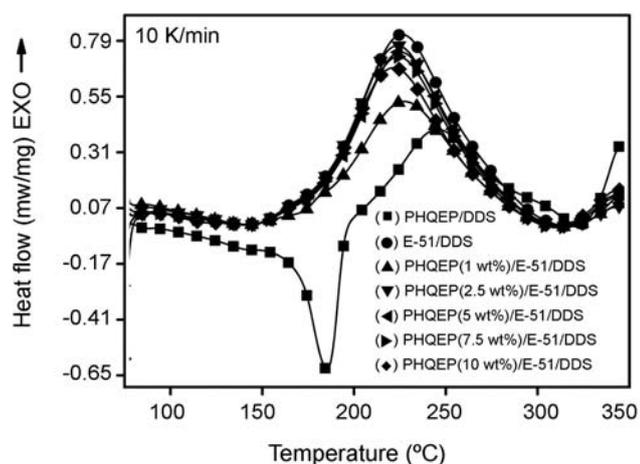
Sample	$\beta$ (K/min)	$T_p$ (°C)	$T_i$ (°C)	$T_f$ (°C)	Curing range (°C)	Curing time (min)	$\Delta H$ (J/g)
PHQEP/DDS	5	231.0	195.0	285.5	90.5	18.1	143.7
	10	245.6	197.3	321.3	124.0	12.4	145.9
	15	256.2	201.3	327.8	126.5	8.4	152.9
	20	261.9	203.0	334.5	131.5	6.6	145.3
E-51/DDS	5	201.6	135.4	291.9	156.5	31.3	303.9
	10	226.7	145.0	310.0	165.0	16.5	326.8
	15	237.6	147.1	325.1	178.0	11.9	304.2
	20	247.4	149.1	333.1	184.0	9.2	274.0
PHQEP/ E-51/DDS*	5	203.0	133.9	281.2	147.3	29.5	252.2
	10	226.1	145.2	309.2	164.0	16.4	286.4
	15	237.9	146.8	315.8	169.0	11.3	278.7
	20	246.8	150.1	325.1	175.0	8.8	234.4

(\*) PHQEP content is 5 wt%.

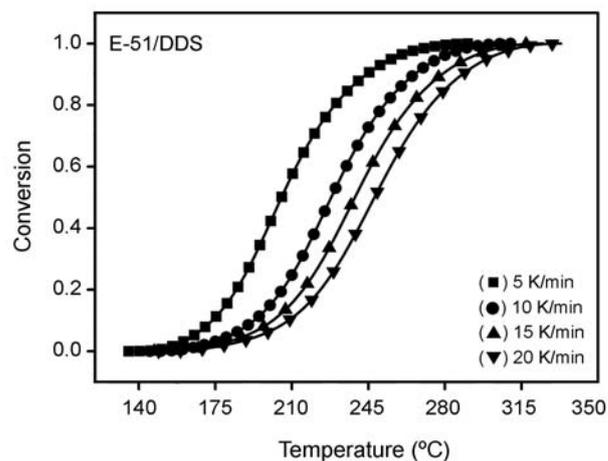
tems are that two peaks appeared in PHQEP/DDS system, but only one appeared in both E-51/DDS and PHQEP/E-51/DDS blend system, respectively. For PHQEP/DDS system, endothermic and exothermic peaks appeared successively, where the former is ascribed to the melting of PHQEP/DDS and the transition from solid state to liquid crystalline phase and the latter ascribed to the curing reaction of PHQEP with DDS. As for PHQEP/E-51/DDS blend system, just an exothermic peak is observed since PHQEP was dissolved in E-51 matrix before the addition of DDS and DDS dissolved in E-51 at 130°C.

From Figure 5 and Table 3, it can be clearly seen that the heating rate ( $\beta$ ) influenced the curing process to a certain extent. As heating rate has been increased from 5 K/min to 10 K/min or other higher values, all peaks are transferred towards higher temperature range, as did the corresponding peak temperature ( $T_p$ ), initial temperature ( $T_i$ ), and the end temperature ( $T_f$ ). Furthermore, the curing range was widened with the increase of heating rate, though the curing time was shortened. The temperature location of exothermic peak for PHQEP/DDS at 10 K/min is higher than that of other two systems in Figure 6, as the cure reaction of PHQEP mainly took place above the melting temperatures of PHQEP and DDS. However, the shape of exothermic peak for all the epoxy systems is similar, which is an indication of similar reaction mechanisms involved in PHQEP and E-51 against DDS.

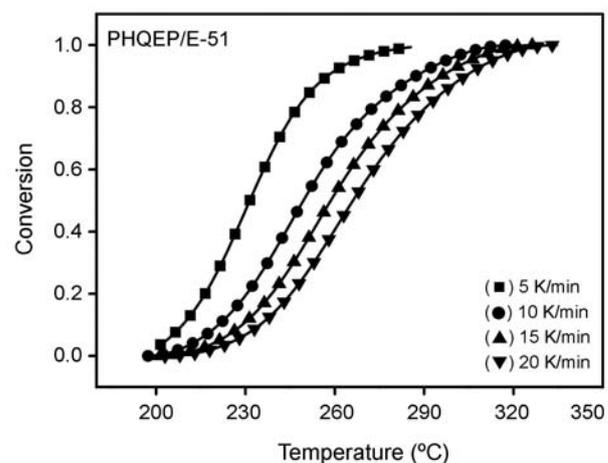
Figures 7a-7c show the variations of fractional



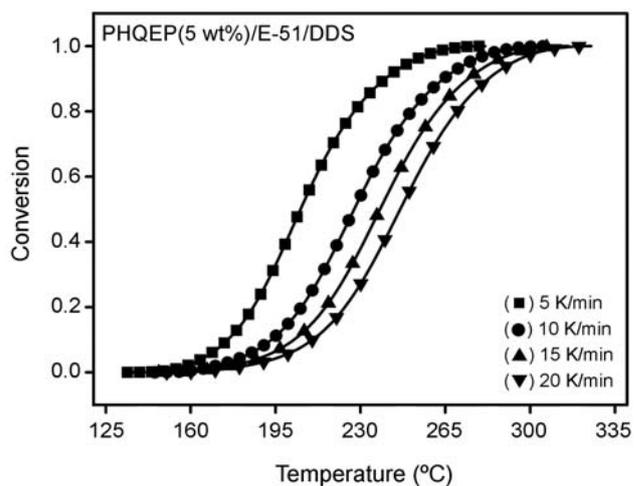
**Figure 6.** Heat flow versus temperature plot for various formulations of epoxy system at a heating rate of 10 K/min.



(a)

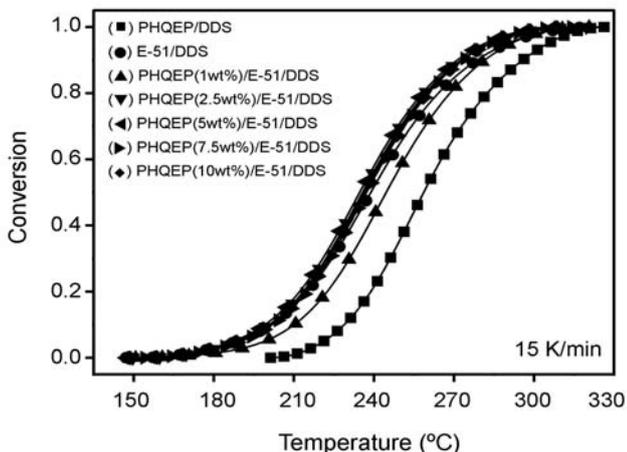


(b)



(c)

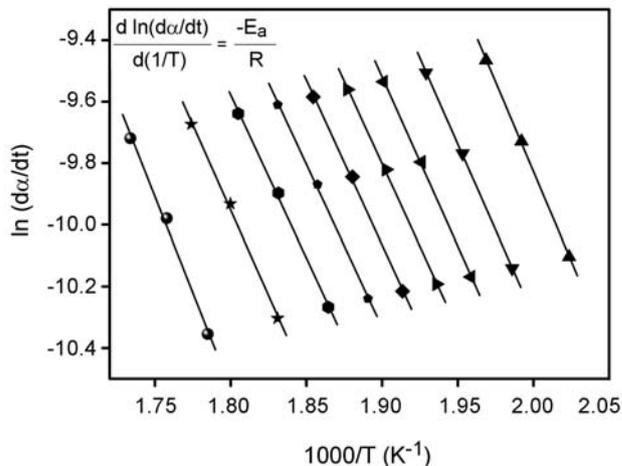
**Figure 7.** Representation of fractional conversion in relation to the temperature for PHQEP/DDS, E-51/DDS, and PHQEP(5 wt%)/E-51/DDS systems for different heating rates.



**Figure 8.** Conversion versus temperature plots for various formulations of epoxy systems at a heating rate of 15 K/min.

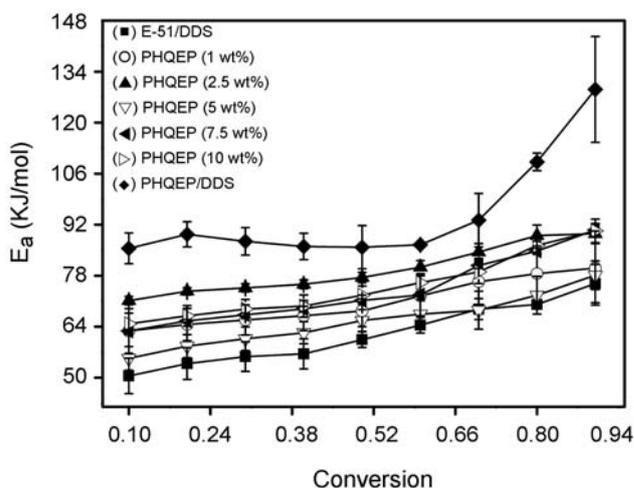
conversion ( $\alpha$ ) as a function of temperature at various heating rates for the PHQEP/DDS, E-51/DDS, and PHQEP(5wt%)/E-51/DDS systems. It can be seen that all  $\alpha$  values have increased very slowly at the beginning. When the temperature is high enough, the  $\alpha$  values are raised rapidly over 90%, and then they are leveled off. Moreover, the temperatures at the same conversion increased with the increase of heating rate. A similar conversion change trend versus temperature was found in PHQEP/DDS, E-51/DDS and PHQEP/E-51/DDS blend systems under the heating rate of 10 K/min in Figure 8.

The activation energy of every sample is estimated from the slope of  $\ln(d\alpha/dt)$  versus  $1/T$  at the same conversion in Figure 9 and the  $E_a$  values versus fractional conversion curves are given in Figure 10. It can be observed that on the whole the values of  $E_a$  approximately increased with the increase of conversion. At the later curing stage ( $\alpha > 0.8$ ) the rapid increase of  $E_a$  with conversion may have been the result of the transition of overall reaction rates from homopolymerization to etherification reactions [33,34]. For PHQEP system, the  $E_a$  values decreased slightly within 0.2~0.5 conversion range. This decrease has been proved to be correlated with the formulation of liquid crystalline phase by Vyazovkin et al. [35]. However, this decrease has not appeared in the PHQEP/E-51/DDS system, as it is presumably due to the low quantity of PHQEP contained in PHQEP/E-51 system. In fact, the  $E_a$  values of PHQEP/DDS system are generally above the values



**Figure 9.** Determination of  $E_a$  values for PHQEP/DDS system at 10, 15, and 20 K/min by Friedman method (the symbols represent 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.6, 0.7, 0.8, 0.9 beginning from the right, the regression coefficient is above 0.99).

of PHQEP/E-51/DDS and E-51/DDS systems, of which the values of E-51/DDS are the lowest at the same conversion condition. It is revealed that PHQEP is not, however, as reactive as E-51 when reacting with DDS. The EEW of PHQEP is larger than that of E-51 and the corresponding space volume of PHQEP is bigger than that of E-51 as well. For this reason, more energy is needed to promote the motion of PHQEP compared to E-51. Moreover, the formation of hydrogen bonds between the carbonyl groups of



**Figure 10.** Dependence of  $E_a$  values on conversion for various formulations of epoxy systems.

**Table 4.** The curing parameters evaluated for PHQEP/DDS, E-51/DDS and PHQEP/E-51/DDS systems.

Sample	$\beta$ (K/min)	$E_a$ (kJ/mol)	$\alpha_p$	$\alpha_p^\infty$	$\alpha_M$	n	m	lnA
E-51	5	56.92±7.50	0.447	0.471	0.217	1.600	0.442	13.17
	10		0.485	0.485	0.260	1.525	0.534	13.18
	15		0.495	0.503	0.262	1.545	0.549	13.27
	20		0.491	0.518	0.270	1.540	0.571	13.31
PHQEP	5	88.05±5.17	0.501	0.479	0.200	1.490	0.370	19.90
	10		0.438	0.464	0.168	1.670	0.338	19.91
	15		0.462	0.462	0.165	1.540	0.304	19.83
	20		0.437	0.468	0.164	1.730	0.339	19.93
PHQEP(5 wt%)/E-51	5	63.89±5.23	0.468	0.451	0.207	1.560	0.407	14.93
	10		0.481	0.497	0.240	1.390	0.438	14.88
	15		0.496	0.511	0.251	1.380	0.463	14.92
	20		0.511	0.526	0.248	1.420	0.469	14.88

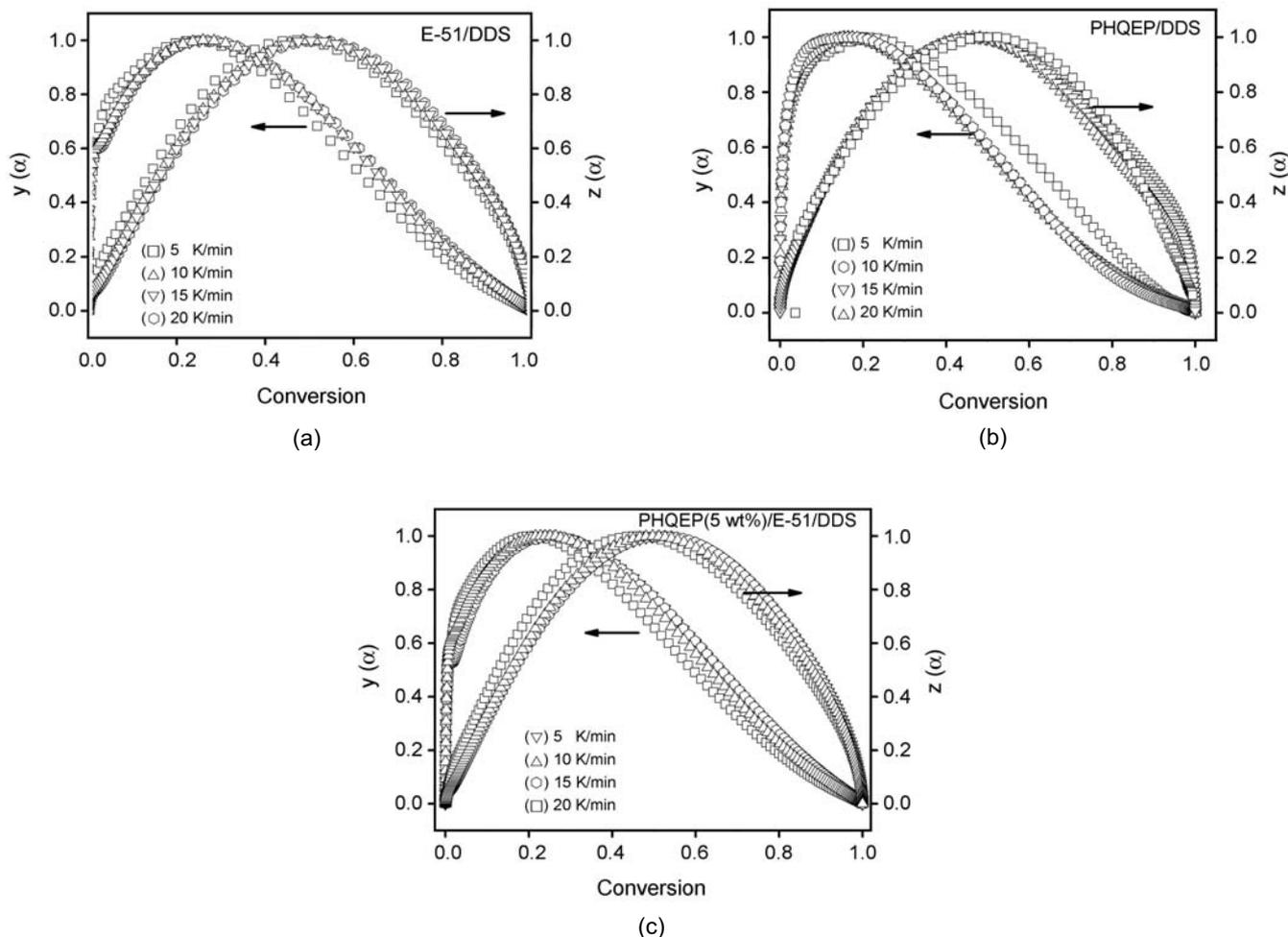
PHQEP and the hydroxyl groups that are formed in the curing process is another factor to limit the motion of PHQEP.

The apparent incremental tendency of  $E_a$  value with PHQEP content for PHQEP/E-51/DDS blend system is not obtained, which is an indication of the complexity of reaction mechanism. In the conversion interval of 0.2~0.7, the relative error in respect to Figure 10 is within 8.5%, and the maximal deviation of the mean value is 9.70 kJ/mol. The mean  $E_a$  values are used to calculate  $y(\alpha)$  and  $z(\alpha)$  according to eqns (8) and (9), respectively. The values of  $y(\alpha)$  and  $z(\alpha)$  have been normalized in the range of 0~1. The variation of  $y(\alpha)$  and  $z(\alpha)$  values with conversion is

shown in Figure 11. The  $y(\alpha)$  exhibits maximum at  $\alpha_M$ , and  $z(\alpha)$  exhibits maximum at  $\alpha_p^\infty$ . The values of  $\alpha_M$ ,  $\alpha_p^\infty$ , and  $\alpha_p$  (the conversion degree corresponding to the peak temperature of each DSC heat flow curve) for PHQEP/DDS, E-51/DDS and PHQEP(5wt%)/E-51/DDS systems at various heating rates are listed in Table 4, and the mean values of four heating rates for all samples are listed in Table 5. Both  $\alpha_M$  and  $\alpha_p^\infty$  help to decide the choice of the kinetic model [26,29]. As was noted, the fluctuations of  $\alpha_M$ ,  $\alpha_p^\infty$ , and  $\alpha_p$  values in Table 4 with heating rate are negligible. It can be said that  $\alpha_M$ ,  $\alpha_p^\infty$ , and  $\alpha_p$  are independent of heating rate. Simultaneously, the values of  $\alpha_M$  are lower than the values of  $\alpha_p$ ,

**Table 5.** The mean value of kinetic parameters for various epoxides formulations.

Sample	$E_a$ (kJ/mol)	$\alpha_p$	$\alpha_M$	$\alpha_p^\infty$	n	m	lnA (min <sup>-1</sup> )
E-51	56.9 ± 7.50	0.478	0.252	0.494	1.55 ± 0.05	0.52 ± 0.08	13.23 ± 0.08
PHQEP	88.0 ± 5.17	0.460	0.174	0.468	1.61 ± 0.12	0.34 ± 0.03	19.89 ± 0.06
PHQEP(1wt%)/E-51	69.1 ± 7.25	0.487	0.230	0.495	1.62 ± 0.20	0.49 ± 0.20	16.10 ± 0.30
PHQEP(2.5wt%)/E-51	77.7 ± 6.76	0.456	0.180	0.499	1.69 ± 0.10	0.37 ± 0.02	18.38 ± 0.10
PHQEP(5 wt %)/E-51	63.9 ± 5.23	0.489	0.237	0.496	1.44 ± 0.10	0.44 ± 0.04	14.90 ± 0.03
PHQEP(7.5wt%)/E-51	71.0 ± 9.70	0.479	0.205	0.500	1.59 ± 0.20	0.41 ± 0.01	16.65 ± 0.07
PHQEP(10wt %)/E-51	72.2 ± 6.84	0.491	0.203	0.502	1.58 ± 0.20	0.40 ± 0.02	16.95 ± 0.09



**Figure 11.** Variation of  $y(\alpha)$  and  $z(\alpha)$  vs. conversion for all epoxy systems at different heating rates.

while the values of  $\alpha_p^\infty$  are lower than 0.632. These remarks indicate that the studied curing processes can be described using two-parameter autocatalytic kinetic model of Šesták-Berggren (eqn(13)) [27].

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{13}$$

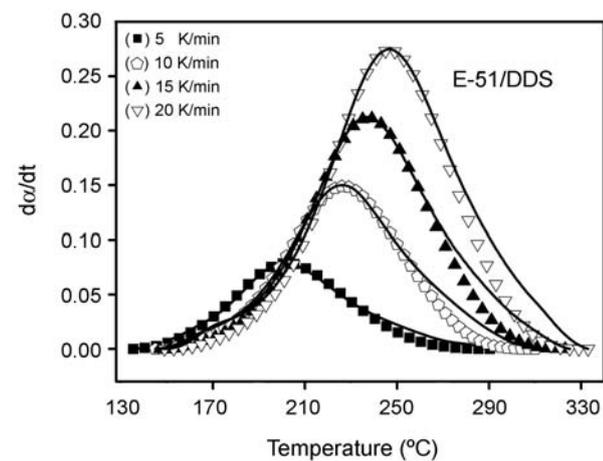
where,  $m$  and  $n$  are the kinetic exponents.

The kinetic exponent  $n$  is obtained by the slope of a linear dependence of  $\ln[(d\alpha/dt)e^x]$  versus  $\ln(\alpha^p(1-\alpha))$  and  $m=n \times p$ , where  $p = \alpha_m / (1-\alpha_m)$ . The values of  $n$ ,  $m$ , and calculated  $\ln A$  at each heating rate are listed in Table 4. Apparently, the influence of heating rate on  $n$ ,  $m$ , and  $\ln A$  is very small and can be neglected. The mean values obtained from four different heating rates are listed in Table 5. The impact of

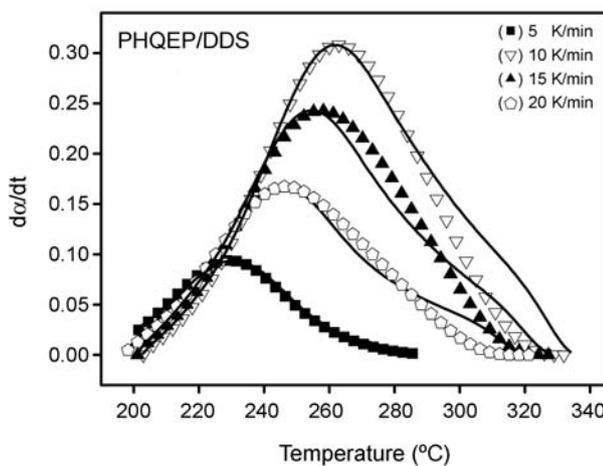
PHQEP content on  $n$ ,  $m$ , and  $\ln A$  is similar to the effect of PHQEP content on  $E_a$  values. PHQEP/DDS system owns higher  $n$  and  $\ln A$  value than the other systems. After blending PHQEP with E-51,  $n$  and  $\ln A$  reach higher values relative to the values of E-51/DDS system. However, the deviation from the average values of blend systems is low. The similarity of  $n$  and  $m$  for PHQEP/DDS, E-51/DDS and PHQEP/E-51/DDS systems indicates the similarity of curing reaction mechanisms.

$$d\alpha/dt = \exp(\ln A - E_a/RT) \alpha^m(1-\alpha)^n \tag{14}$$

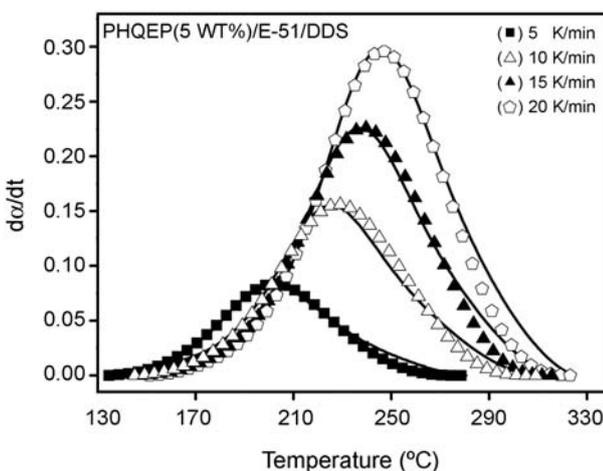
Figures 12 and 13 give the comparisons of the experimental and calculated (from eqn (14)) rate-temperature curves. It can be seen that the calculated rate-temperature curve agrees well with the experimental



(a)

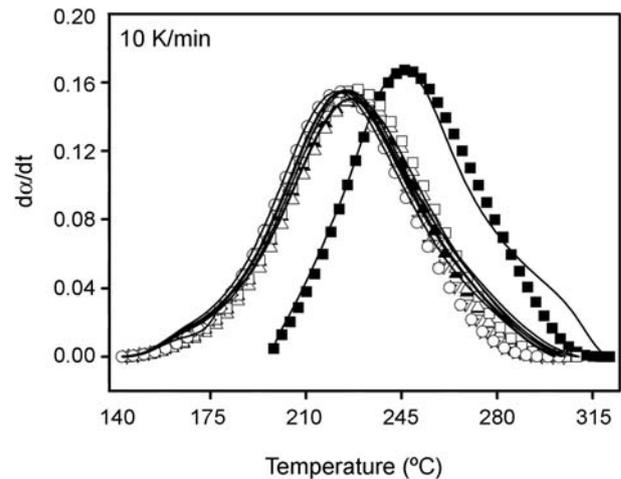


(b)



(c)

**Figure 12.** Comparison of experimental (solid line) and calculated (symbols) rates curves vs. temperature at different heating rates.



(■) PHQEP/DDS (▽) PHQEP (2.5 wt%)/E-51/DDS  
 (▲) E-51/DDS (△) PHQEP(1 wt%)/E-51/DDS  
 (□) PHQEP(5 wt%)/E-51/DDS (★) PHQEP (7.5 wt%)/E-51/DDS  
 (○) PHQEP(10 wt%)/E-51/DDS.

**Figure 13.** Comparisons of experimental (solid line) and calculated (symbols) rate-temperature curves at a heating rates of 10 K/min.

one in most part of the temperature region. This proves that the autocatalytic model is a proper selection to describe the whole curing process.

## CONCLUSION

A novel Liquid crystalline epoxy oligoester PHQEP containing ester mesogen was synthesized by a phase transfer catalytic method, characterized as a type of nematic liquid crystalline. The temperature region of 180~220°C is where PHQEP shows the nematic texture. The cure kinetics behaviours of diglycidyl ether of bisphenol A (E-51), liquid crystalline epoxy resin PHQEP and PHQEP/E-51 blend with DDS as the hardener were studied by means of non-isothermal DSC. By comparing the kinetic parameters of the three curing systems and the PHQEP content effect on the curing behaviour of PHQEP/E-51 blends, it can be concluded that PHQEP hindered the curing reaction of epoxy group to some extent. The activation energy  $E_a$  determined by isoconversional method, exponential factor  $\ln A$  calculated by autocatalytic model for PHQEP/DDS system are generally higher than that for PHQEP/DDS and PHQEP/E-

51/DDS systems. The cure behaviour difference of PHQEP towards E-51 arises by the formations of liquid crystalline phase, aromatic ester structure, and the hydrogen bonds between carbonyl groups of PHQEP and hydroxyl groups that are formed in the curing process. The curing behaviour of PHQEP/E-51/DDS system is closed to that of E-51/DDS because of the low content of PHQEP.

The two-parameter autocatalytic model is established to be suitable for the description of the studied curing process. Furthermore, the calculated rate-temperature curve is in agreement with the one that has been experimentally determined.

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