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Curing reaction characteristics and phase behaviors of biphenol type epoxy resins with phenol novolac resins

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Abstract

Diglycidyl ether of 4,4′-dihydroxybiphenol (BPDGE) is a liquid crystalline epoxy. The biphenyl epoxy (diglycidyl ether of 3,3′,5,5′-tetramethyl-4,4′-biphenyl, TMBPDGE) has found great applications in plastic encapsulated semiconductor packaging. Phenol novolac (PN) was used as curing agent. The reaction kinetics of BPDGE/PN and TMBPDGE/PN systems in the presence of triphenylphosphine (TPP) were characterized by an isoconversional method under dynamic conditions using differential scanning calorimetry (DSC) measurements. The results showed that the curing of epoxy resins involves different reaction stages and the values of activation energy are dependent on the degree of conversion. The effects of curing temperature on their phase structure have been investigated with polarized optical microscopy and Wide-angle X-ray diffraction. With proper curing process, BPDGE showed a nematic phase when cured with PN.

Keywords: Liquid crystalline epoxy resin; Curing kinetics; Phase behaviors

1. Introduction

In recent years, many investigations concerning the synthesis, optical and thermal properties of liquid crystalline epoxy resins have been reported [1–5]. As compared to ordinary epoxies, after cured, LCERs exhibit higher toughness due to the retardation of the crack propagation by the formation of many LC domains in the cured networks [6–8]. Diglycidyl ether of 4,4′-dihydroxybiphenol (BPDGE) is a typical kind of liquid crystalline epoxy. The phase structure, thermal and dynamical mechanical properties of its cross-link network with different curing agents have been widely investigated [9,10,11]. Diglycidyl ether of 3,3′,5,5′-tetramethyl-4,4′-biphenyl (TMBPDGE) is a commercial epoxy which can be applied as encapsulation material because of the good adhesion, low viscosity, high filler loading [12]. The similar chemical structure in both BPDGE and TMBPDGE made them interested for electronic application.

For thermosets, it is necessary to conduct the systematic studies to optimize the resin composition, processing condition, and to find out the relationship between structure and property for the final industry applications. Many studies have been done to clarify the reaction between epoxides and phenols in the presence of catalyst. Seung Han and his coworkers reported the curing reactions between TMBPDGE and three different phenolic-functional hardeners, such as phenol novolac, xylok, and dicyclopentadiene type phenolic resin, in the presence of TPP and the curing reaction of TMBP using phenol novolac as a hardener (0.5 phr TPP) proceeds through an autocatalytic kinetic mechanism similar to that of phenol novolac-cured *o*-cresol novolac epoxy resin [13]. In the other previous studies, the influences of the catalyst types on the curing reactions between TMBPDGE [14] and the effects of TPP concentration on the isothermal curing reactions of biphenyl epoxy/phenol novolac system were reported [15]. All studies were performed by a differential scanning calorimeter using an isothermal approach. Kim et al. studied the reaction kinetics of a biphenyl epoxy/polyol system in the presence of benzyldimethylamine used as a catalyst by an isoconversional method under dynamic conditions [16]. Ochi and

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his coworkers investigated the optical and thermal and mechanical properties of BPDGE with different phenolic curing agents. They made a conclusion that when phenol novolac was used to cure BPDGE, the active hydrogens are distributed in a random direction. As a result, the biphenol groups in the epoxy molecules could not be oriented in the networks [17,18].

However, we have found that the BPDGE cured with PN could form a nematic phase and be fixed in the cross-link network with proper curing process [19].

In addition, the curing reaction of BPDGE and PN in the presence of triphenylphosphine (TPP) was seldom researched, and the most of previous works analyzed the reaction kinetics by the homogeneous reaction model, normally using autocatalytic or an *n*-order equation. In this model, the whole reaction of curing was only considered as a single kinetic process, regardless of the different reactive processes or the different stages evolved in the system. In this article, polarized optical microscopy was used to determine the texture. The curing behaviors of BPDGE/PN/TPP and TMBPDGE/PN/TPP were investigated using an isoconversional method that does not require the knowledge of a reaction rate equation, and can give the curing behavior at a different content of conversion.

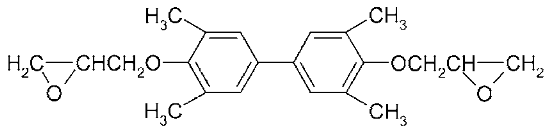
2. Experimental

2.1. Materials

The general synthesis of BPDGE, TMBPDGE and phenol novolac have been described in literature [19]. Their chemical structures are shown in Fig. 1. Triphenylphosphine (TPP) was used as an accelerator purchased from Shanghai Chemical Reagent Co., Ltd.

2.2. Sample preparation

The samples of BPDGE/PN and TMBPDGE/PN were prepared as the same way. The BPDGE or TMBPDGE was dissolved in tetrahydrofuran (THF). Then stoichiometric amounts of hardeners were added in the system. The solution was cooled down and 1 phr TPP was added to the blend system. The mixture solution was stirred till the solvent was dried and subsequently evaporating the solvent at room temperature under vacuum for 24 h. Each sample was stored in a freezer at −20 °C.



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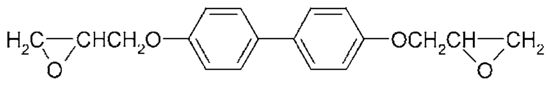
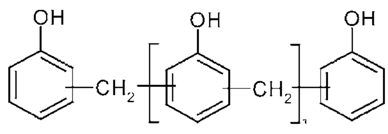


diglycidyl ether of 4,4’-dihydroxybiphenol



phenol novalac

Fig. 1. Chemical structures of epoxy monomer and curing agents.

2.3. Measurements

Calorimetric measurements were performed using a Perkin-Elmer Diamond DSC type calorimeter, under nitrogen atmosphere to measure the heat flow under non-isothermal conditions. The mass of samples was about 10–15 mg. The dynamic DSC tests were conducted from 50 to 300 °C at several heating rates under nitrogen atmosphere: 2.5, 5, 10, 20 °C/min.

The textures of the mesophases were observed with a polarizing microscope (AXIOLAB Zeiss). When BPDGE was cured with PN (1 phr TPP), the mixtures were first heated above their melting points. Second, they were quickly brought to room temperature (within approximately 5 min). Then, POM was conducted to observe the phase structure of this pre-polymer. Finally, this pre-polymer was cured at 120 °C for 5 h, and its textures were also observed by POM.

The textures of the mesophases were observed with a polarizing microscope (AXIOLAB Zeiss). Wide-angle X-ray diffraction (WAXD) studies were conducted on a D/max 200 X-ray.

3. Results and discussion

3.1. Cure kinetics

Curing kinetics was investigated by non-isothermal DSC at different heating rates and analyzed using isoconversion method.

For non-isothermal conditions, when the temperature varies with time at a constant heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$ the basic equation for non-isothermal conditions is presented as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{E_\alpha}{RT}\right) f(a) \tag{1}$$

where A is the pre-exponential factor, T is the absolute temperature (K), E_a is the activation energy, R is the universal gas constant (8.3 J/mol/K), and $f(\alpha)$ is a model function that depends on the reaction mechanism.

Isoconversional kinetic analysis offers a viable alternative in this situation [20–22]. The basic idea of this type of analysis is that the reaction rate at constant extent of conversion is only a function of the temperature,

$$-\frac{E_\alpha}{R} = \left[\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}T^{-1}}\right]_\alpha \tag{2}$$

where E_a is the effective activation energy at a given conversion. This makes it equally effective for both the *n*th order and the autocatalytic reactions. The integration of Eq. (2) gives

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\alpha = \mathrm{const} - \frac{E_\alpha}{RT} \tag{3}$$

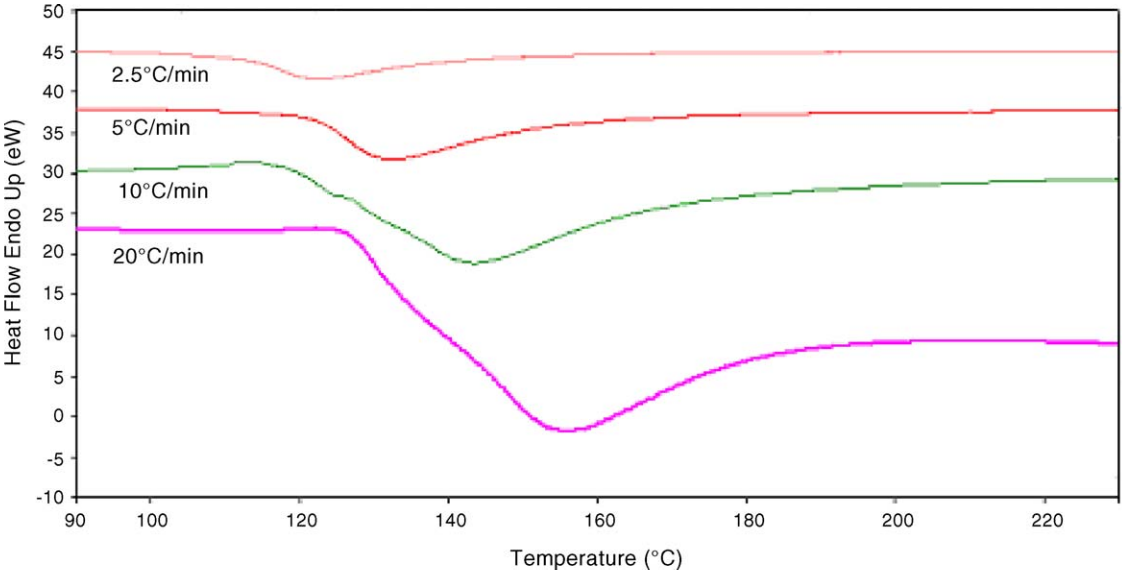


Fig. 2. DSC cure exotherms of BPDGE/PN/TPP at different scan rates.

which is the basis of the differential isoconversional method of Friedman [23]. In practice, it is more convenient to use the integral forms of Eq. (1). The derivative methods from Flynn, Wall and Ozawa [24,25] can be used to give the E_a from the plot $\ln \beta_i$ versus $T_{\alpha,i}^{-1}$ (here i is ordial number of DSC runs performed at different heating rate, β_i). The Kissinger method was used to obtain the relationship of $E_a \sim \alpha$ [26,27]. Both the value of E obtained by Kissinger and Ozawa methods are an overall value representing all complex reactions that occur during curing.

For instance, the use of Kissinger method allows one to arrive at Eq. (4)

$$\ln \frac{\beta_i}{T_{\alpha,i}^2} = \ln\left[\frac{RA}{E_{\alpha,i}\, g(\alpha)}\right] - \frac{E_{\alpha,i}}{R}\frac{1}{T_{\alpha,i}} \qquad (4)$$

where

$$g(\alpha) \equiv \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)}$$

is the integral form of the reaction model. The activation energy changes during the curing process, this is more precise than the assumption of constant activation energy for the whole polymerization. It seems reasonable to assume constant activation energy only for a certain conversion.

The non-isothermal thermogram of BPDGE/PN/TPP is shown in Fig. 2 and a similar thermogram for TMBPDGE/PN/TPP in Fig. 3. The peak exotherm temperatures shift to the higher value as the heating rate increased. However, there is a small difference between Figs. 2 and 3. All curves show only one sharp exothermic peak for BPDGE/PN/TPP in

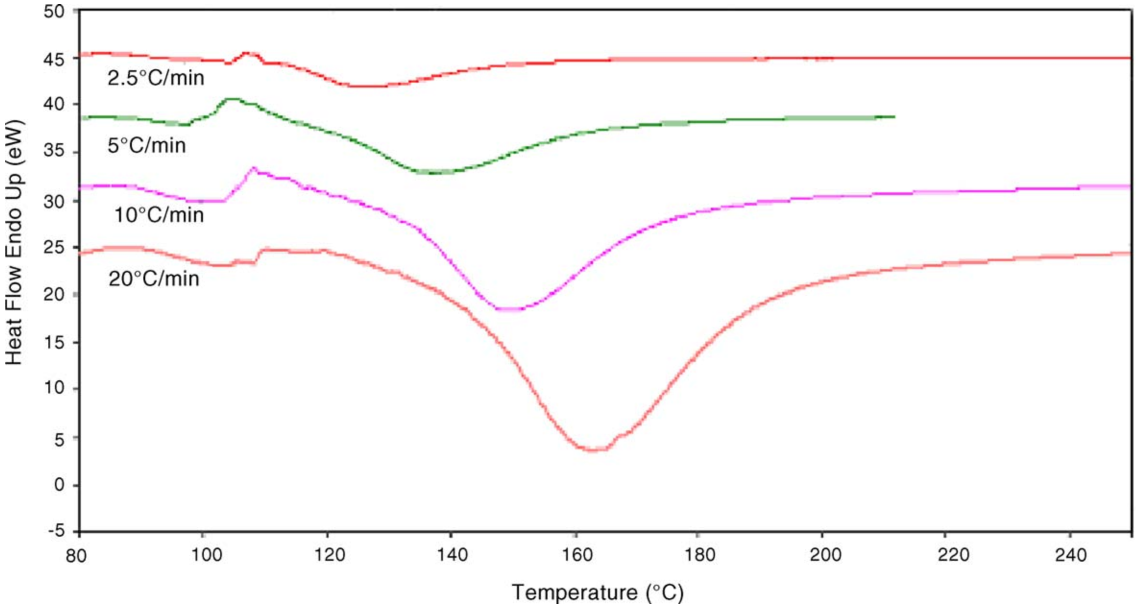


Fig. 3. DSC cure exotherms of TMBPDGE/PN/TPP at different scan rates.

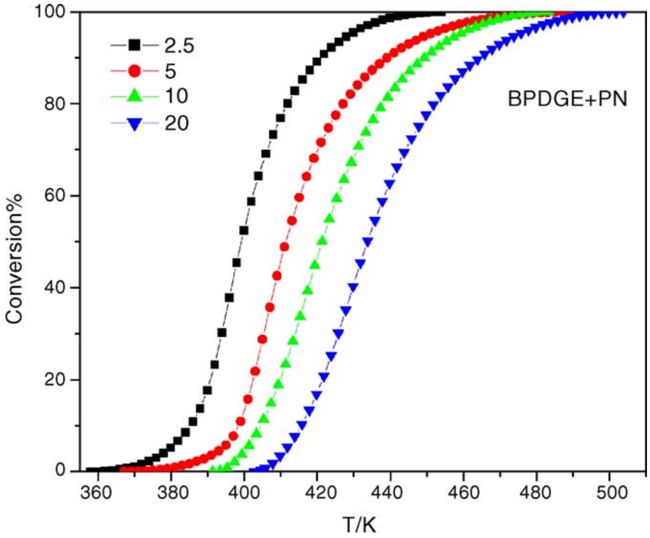


Fig. 4. α as a function of the temperature of BPDGE/PN/TPP at various rates.

Fig. 2, regardless of the heating rate. This means that the curing reaction takes place before the melting of the LCE monomers. There are an endothermal peak and an exothermal peak in each DSC curve for TMBPDGE/PN/TPP in Fig. 3. The endothermal peak at around 108 °C corresponded to the melting of TMBP and the curing reaction mainly takes place after the melting of the non-LCE monomers. The H_{tot} is calculated from the total area under the dynamic scan of curing thermogram at 10 K/min. The corresponding value for the BPDGE/PN/TPP system is 209 J/g, the TMBPDGE/PN/TPP is 191 J/g. Figs. 4 and 5 plot the conversion percent against the dynamic cure temperature for BPDGE/PN/TPP and TMBPDGE/PN/TPP for various heating rates, respectively. It can be seen that at the same conversion, the isoconversion temperature T_i for both two systems increase with the heating rate.

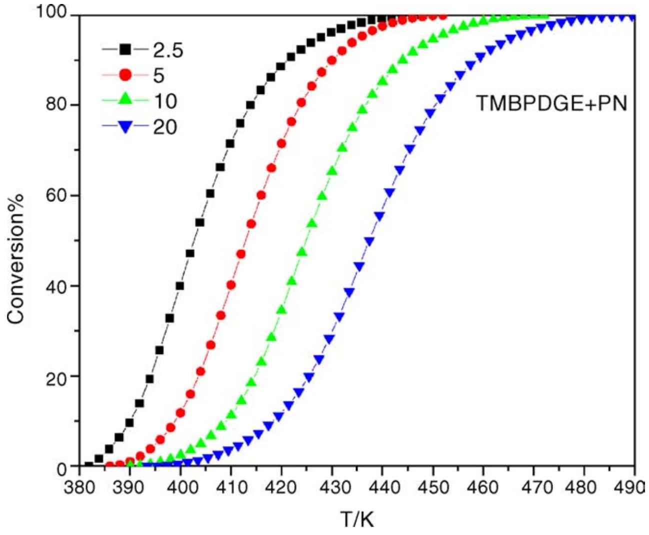


Fig. 5. α as a function of the temperature of TMBPDGE/PN/TPP at various heating rates.

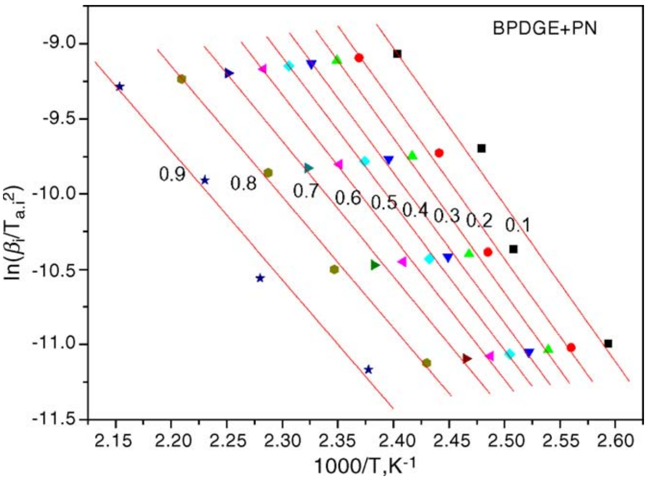


Fig. 6. Isoconversional plots of BPDGE/PN/TPP from different heating rates (the numbers in these plots refer to the conversion fraction).

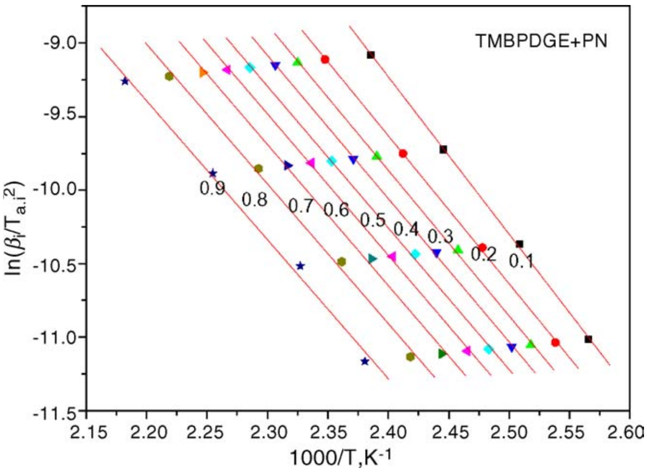


Fig. 7. Isoconversional plots of TMBPDGE/PN/TPP from different heating rates (the numbers in these plots refer to the conversion fraction).

Figs. 6 and 7 are the plots of $\ln(\beta_i/T^2_{\alpha,i})$ versus $1000/T_{\alpha,i}$ for BPDGE/PN/TPP and TMBPDGE/PN/TPP, respectively. The values of E at certain conversions obtained for them are presented in Table 1. As can be seen, the values of activation energy are not a constant, as supposed in many works throughout the whole curing process. At the early stage of cure reaction, the activation energy takes a maximum value, then decreases sharply,

Table 1
Activation energy (E_a) as calculated by isoconversional methods

Conversion	BPDGE/PN/TPP	TMBPDGE/PN/TPP
	E_a (kJ/mol)	E_a (kJ/mol)
0.1	86.6	88.7
0.2	85.7	83.4
0.3	85.3	82.2
0.4	82.7	80.9
0.5	80.8	79.9
0.6	78.6	79.8
0.7	74.6	79.6
0.8	72.2	78.8
0.9	71.2	78.4
Average	79.7	81.3

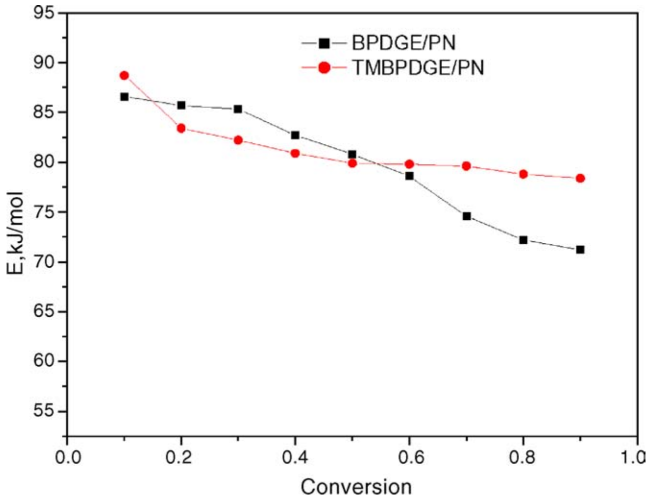


Fig. 8. The relationship between activation energy and the fractional conversion.

and finally remains practically constant. However, a systematic error is unavoidable in this simple isoconversional method that use the integrated form of the rate equation for estimating E_a and needs to be studied further.

Fig. 8 plots the values of the activation energy of BPDGE/PN and TMBPDGE/PN in the presence of TPP obtained by the Kissinger method varied with the conversion from 10 to 90%. It can be seen from Table 1 and Fig. 8 that the dependence of activation energy on conversion clearly revealed the autocatalytic reaction that occurred in these systems. At the initial stage of curing, the phenol hydroxyls addition was predominant. Etherification occurred only at elevated temperatures once most phenol hydroxyls were exhausted. Therefore, a high E value at a lower conversion (86.6 kJ/mol at $\alpha = 0.1$ for BPDGE/PN and 88.7 kJ/mol at $\alpha = 0.1$ for TMBPDGE/PN) was attributed to the phenol hydroxyls addition. This value was higher than the average one, which was supposed to be constant throughout the entire curing process [28]. Because the hydroxyl groups 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. Therefore, the constant E value of 85 kJ/mol for BPDGE/PN and 79 kJ/mol for TMBPDGE/PN were associated with the autocatalytic reaction. It starts at a conversion of around 0.3 and 0.6 for BPDGE/PN and TMBPDGE/PN, respectively. In the previously works [29], a diffusion-control process was observed for a conventional bisphenol A epoxy/amine system at the final stage of curing ($\alpha > 0.6$) where the activation energy started to decrease deeply. There is a small difference between the BPDGE/PN/TPP and conventional epoxy/amine (include bisphenol A and TMBPDGE/PN). It may be associated with

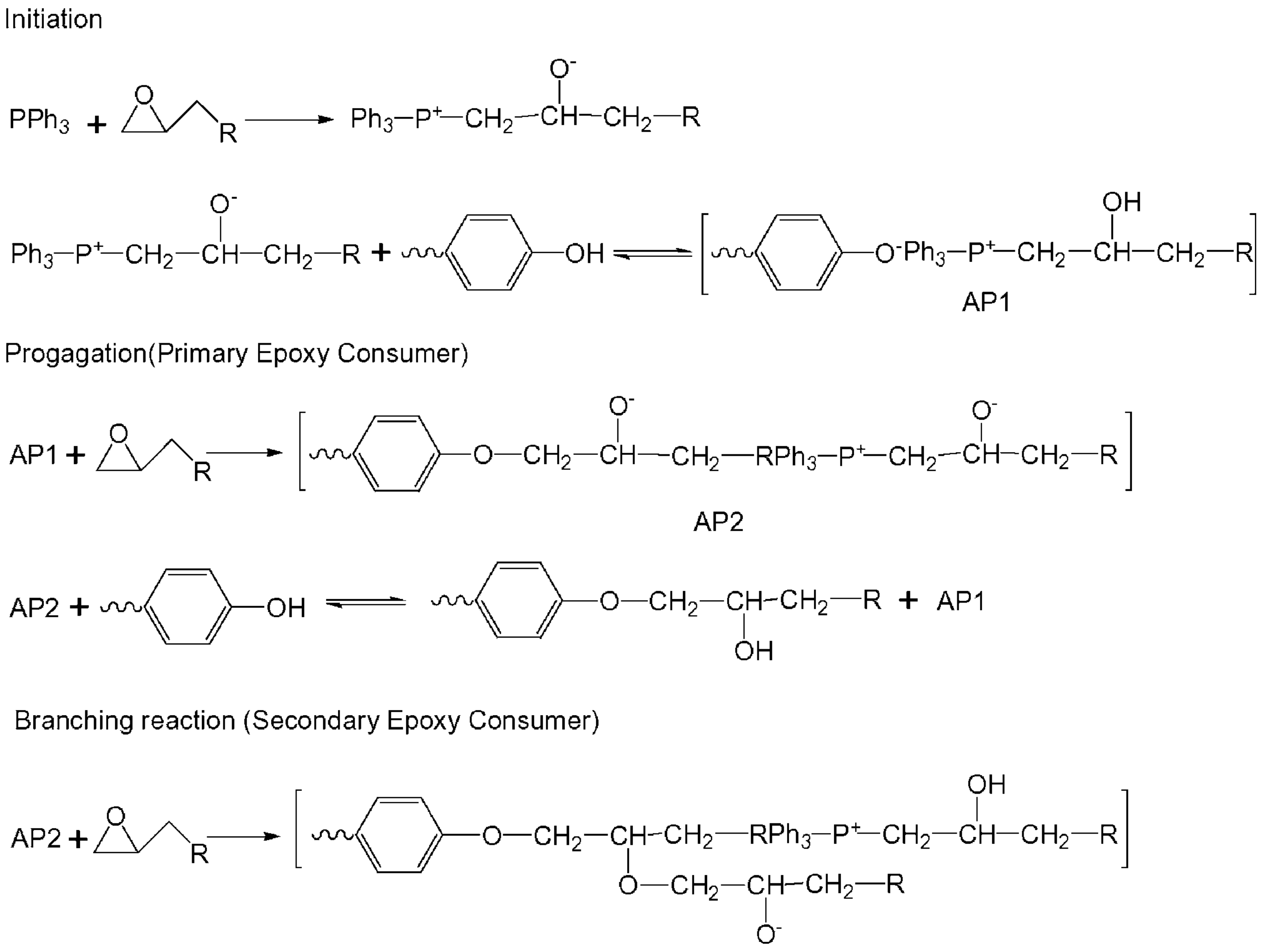


Fig. 9. Cure mechanism of biphenyl epoxy resin-phenol novolac hardener with TPP.

the formation of the liquid crystalline phase for BPDGE/PN. It has been reported that the liquid crystalline phase facilitates the reduction of the viscosity (e.g., retarding gelification) [9].

The chain-wise polymerization mechanisms of epoxies/PN/TPP can be divided into three main steps including: initiation, propagation, and branching reaction steps. According to the cure mechanism of biphenyl epoxy resin–phenol novolac hardener with TPP [13], as shown in Fig. 9, at the initial stage of cure, TPP opens the ring of the oxirane by generating a zwitter ion. In the presence of a phenol group, a rapid proton transfer from the phenol to the secondary hydroxyl occurred. The phenol hydroxyl-epoxy reaction was predominant at this stage until most phenol hydroxyls were exhausted. Then the primary epoxies were consumed quickly and a great of hydroxy groups formed during the cure facilitate ring opening. It is a decrease in the activation energy compared with the very beginning of the cure where non-autocatalytic reaction occurs. The activation energy was decreased greatly at this stage until the active hydroxy groups of the PN were consumed completely. Then branching reaction was started, and secondary epoxy reacted with the new hydroxy groups that came from the primary epoxy. The blends became gelification, vitrification, and the viscosity increased dramatically. The activation energy decreased quickly and the curing reaction was controlled by diffusion at last. Our E_a values obtained are in reasonable agreement with results of Seung Han et al. for TMBP/PN (various concentration of TPP) using isothermal method [15]. Their E_{a_1} values are ranging from 67 to 70 kJ/mol, and E_{a_2} alues are ranging from 80 to 86 kJ/mol. The E_a calculated for the system investigated here are similar with the activation energies for the catalyzed reaction E_{a_2} from isothermal kinetics.

Therefore, in a more pragmatic sense the activation energy is a time temperature factor, and as such it is useful in predicating behavior of thermosets in real processes. In other kinetic models, the epoxy addition was considered as a single step so that the activation energy was supposed to be a constant. This does not correspond to the autocatalytic mechanism of process.

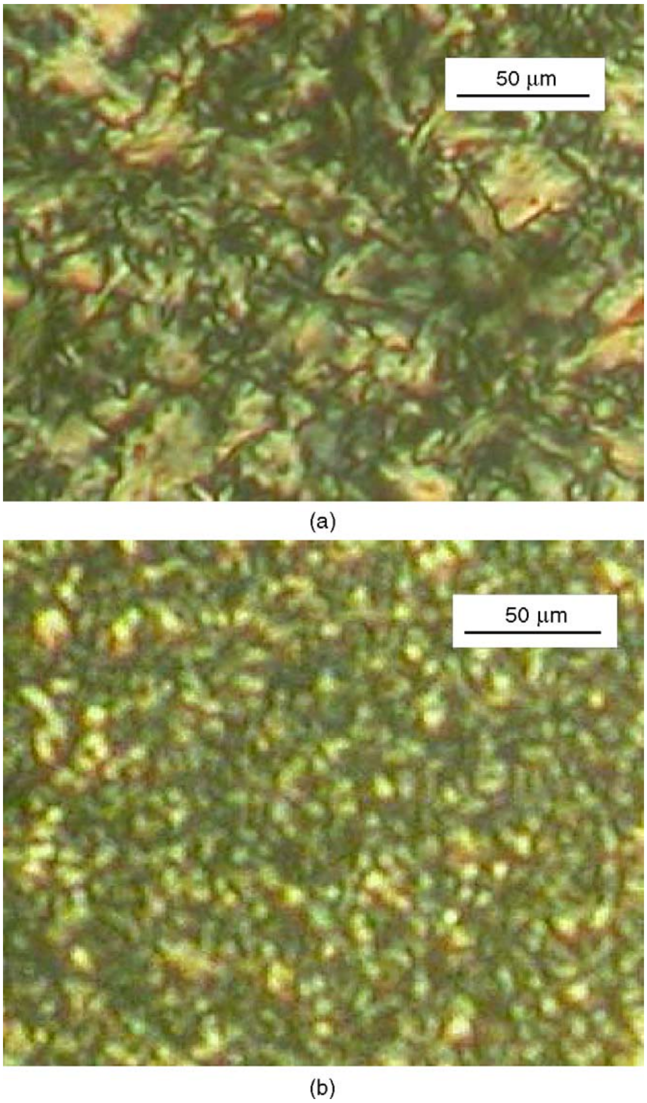


Fig. 10. (a) Polarized optical microscopy of BPDGE/PN (first mixed at 165 °C, then quickly brought to room temperature within 5 min). (b) Polarized optical microscopy of BPDGE/PN (after cured at 120 °C) for 5 h.

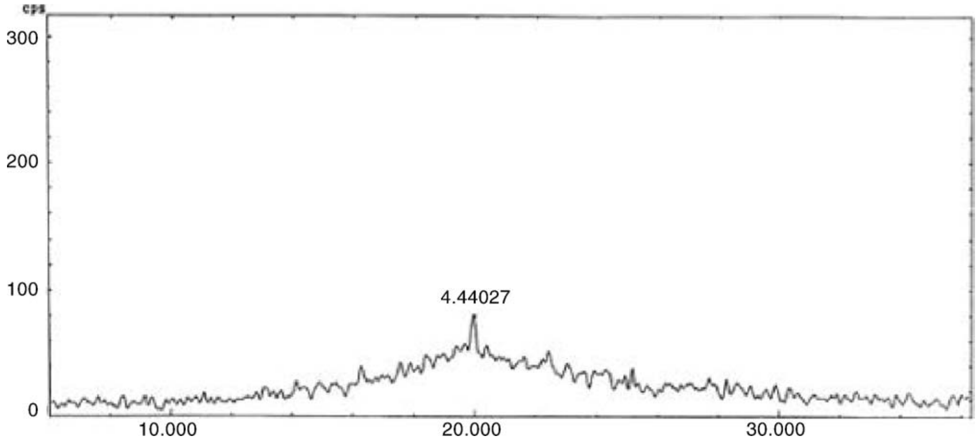


Fig. 11. Wide-angle X-ray diffraction of BPDGE/BP/TPP (120 °C)/5 h.

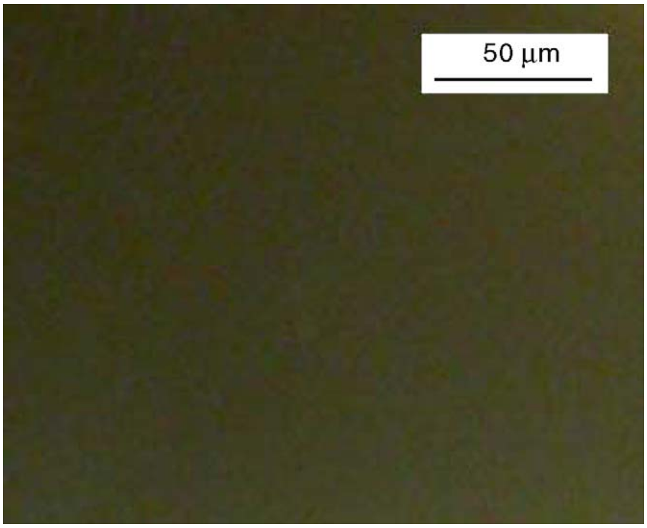


Fig. 12. Polarized optical microscopy of BPDGE/PN/TPP (165 °C/5 min).

3.2. *Optical properties of liquid crystalline epoxy resins*

Ochi and his coworkers reported that BPDGE could not form an oriented structure when cured with phenol novolac in the presence of TPP [17,18]. They assumed that it was due to the stereostructure of active hydrogens in the phenolic curing agents, but did not provide any POM, DSC or WAXD information. However, after proper curing process, DSC, POM and WAXD studies have confirmed the presence of a nematic phase in the cured network of BPDGE and PN in our previous work [19]. The proper process for BPDGE/PN/TPP to form LC domains was given in following way: the BPDGE and PN were first mixed well at 165 °C on a slide, then 1 phr TPP was added in the mixture and stirred quickly for 10 s, the mixtures were quickly brought to room temperature within 5 min. The POM picture of the prepolymer of BPDGE/PN+1 phr TPP was shown in Fig. 10-a. After cured the prepolymer at 120 °C for 5 h, it can be seen from Fig. 10-b, the structural coarsening proceeds by the growth of the droplet-like domains through domain expansion and/or coalescence. The possible reason may be the branching and cross-linking occurring in the curing reduce the mobility of the disclination defects [30]. The nematic phase was further confirmed by WAXD result, which showed a broad peak at $2\theta = 19.98^\circ$ as given in Fig. 11.

However, if the BPDGE/PN/TPP were cured at 165 °C for 5 min, no birefringence was observed by POM, as shown in Fig. 12. It indicated that the curing rate of BPDGE/PN/TPP was very fast, especially at high temperature, when BPDGE and the hardener were melted and mixed at 165 °C (which is the melt point of BPDGE) in the presence of TPP, the blends system entered the stage of branching reaction, and even quickly became gelification. There was no sufficient time for the LC monomers to form LC domains before extensive cross-linking took place. This also meant that only the BPDGE/PN/TPP was cured at a relative low temperature that a moderate curing rate was given for the LC monomers to form LC domains before extensive cross-linking took place.

4. Conclusions

Dynamic DSC was used to explore the BPDGE/PN and TMBPDGE/PN system. The kinetic results showed that the curing process of biphenol epoxy/PN/TPP can be described using an isoconversional method, and the effective activation energy is dependent on the conversion. At the early stage of cure, the reaction is mainly controlled by primary epoxy addition, followed by the autocatalytic process, and finally is in practically diffusion-control. The phase structure of BPDGE/PN/TPP was investigated using POM and WAXD. The results showed that with a moderate curing rate at a relative low temperature, the LC monomers will have sufficient time to form the LC domains before branching reaction takes place, which results in the formation of a nematic LC phase during the curing of BPDGE/PN/TPP. The LC texture coarsens further upon further isothermal curing.

Acknowledgements

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