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Synthesis and curing behavior of a novel liquid crystalline epoxy resin

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Abstract This article described the synthesis and mesomorphic behavior transition of a novel liquid crystalline (LC) epoxy resin 4-(2,3-epoxypropoxy)biphenyl,4″-(2,3-epoxypropoxy)phenyl-4′carboxylate (EBEPC), which combined a hydroxyl benzoic aromatic ester and biphenol rigid-rod group. EBEPC showed a clear nematic schlieren texture under curtain conditions. The reaction kinetics of EBEPC cured by 4,4′-diaminodiphenyl-methane (DDM) was studied by using an isoconversional method under isothermal conditions with differential scanning calorimetry (DSC). The isothermal DSC data can be fitted reasonably by an autocatalytic curing model. Smectic phases had been observed in the EBEPC/DDM curing system. The results of DSC showed that the formation of the LC phase had pronounced influence on the curing reaction.

Keywords Curing kinetics · Liquid crystal · Epoxy resins · Phase behaviors

Introduction

Epoxy resin is one of the most important polymeric materials widely used in the polymer industry as coatings, structural adhesives, insulating materials, and polymeric composite materials, etc. [1–3]. The properties of epoxides can be much enhanced if liquid crystalline (LC) structures are incorporated into the epoxy networks [4]. Such combination results in the so-called LC epoxy resins (LCERs). LCERs exhibit excellent properties suitable for versatile practical applications such as high heat resistance, high mechanical properties, low coefficient of thermal expansion, low dielectric constant, and good dimensional stability [5]. During the curing process, LCERs undergo little shrinkage, and they can be used as high performance materials for technological applications such as microelectronics or optical devices, etc. [6]. Over the past decades, many reports have been dedicated to the synthesis of novel LCERs with emphasis on their LC characteristics and specific curing properties [7–9]. The LCERs studied so far can be divided into four basic rigid-rod group types: stilbene, hydroxyl benzoic aromatic ester, azine, and biphenol (BP). Moreover, there are only few investigations on LCERs with mesogenic groups which combine different rigid-rod mesogenic units [10–12].

It is well known that properties of epoxy polymeric materials intensely depend on the curing process, so the studies of cure kinetics for epoxy resins become important, and the kinetics of curing epoxy resins has been widely studied using isothermal or dynamic experiments with differential scanning calorimetry (DSC) [13–16]. Curing of LC epoxy monomers leads to the formation of nematic and smectic networks that are important for the above-mentioned practical applications [8]. The curing behavior and thermal properties of LCERs are dependent on the 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 [17]. So the difference between LC and isotropic epoxies systems, in terms of the curing reactions, has attracted much interest recently.

In this study, we described the synthesis and characterization of a new type of LCER, 4-(2,3-epoxypropoxy)biphenyl,4″-(2,3-epoxypropoxy)phenyl-4′carboxylate

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(EBEPC). The LC behavior of EBEPC was investigated. The curing behaviors and LC phase transition of the EBEPC/DDM system were studied in detail. Finally, we discussed the curing kinetics based on the isoconversional method and Kamal model of the EBEPC/DDM system.

Experimental part

Materials

4,4′-Dihydroxybiphenol was purified by recrystallization from ethanol. *Para*-hydroxybenzoic acid, concentrated sulfuric acid, acetic anhydride, epichlorohydrin (EC), benzyltrimethylammonium chloride (BTMAC), and 4,4′-diaminodiphenyl-methane (DDM) were used in analytical grade without further purification. All the solvents were freshly distilled before use.

Synthesis of 4-(hydroxy)biphenyl,4″-(acetoxy)phenyl-4′carboxylate (**P1**)

4-Acetoxybenzoyl chloride was synthesized according to a method reported in the literature [18]. 4,4′-Dihydroxybiphenol (7.0 g 0.038 mol) and 60 ml THF were added into a reaction flask equipped with a stirrer. 4-Acetoxybenzoyl chloride (7.5 g 0.038 mol) was diluted with anhydrous dichloromethane (100 mL) and poured into the reaction, and then 5-mL pyridine was added as the catalyst. The reaction proceeded in an ice bath for 1 h and was kept stirring at room temperature for 16 h. The mixture was filtered and the filtrate was poured into petroleum ether (150/500, v/v). Finally the resulting white precipitate was separated and recrystallized from a mixture of chloroform and petroleum ether, and the white acicular powders were obtained. Yield: 45.3%; mp: 191.0 °C. IR (KBr): 3 416 (−OH), 3 107 (Ar–H), 1 752 (C=O), 1 598 (–Ar–), 1 448, 1 374 (CH_3), 1 272 cm^{-1} (Ar–O–C). ^{1}H NMR (D-DMSO): $\delta = 2.35$ (3H, CH_3), 6.87, 7.34, 7.41, 7.52, 7.67, 8.20 (12H, aromatic), 9.58 (1H, –OH).

Synthesis of 4-(hydroxy)biphenyl,4″-(hydroxy)phenyl-4′carboxylate (**P2**)

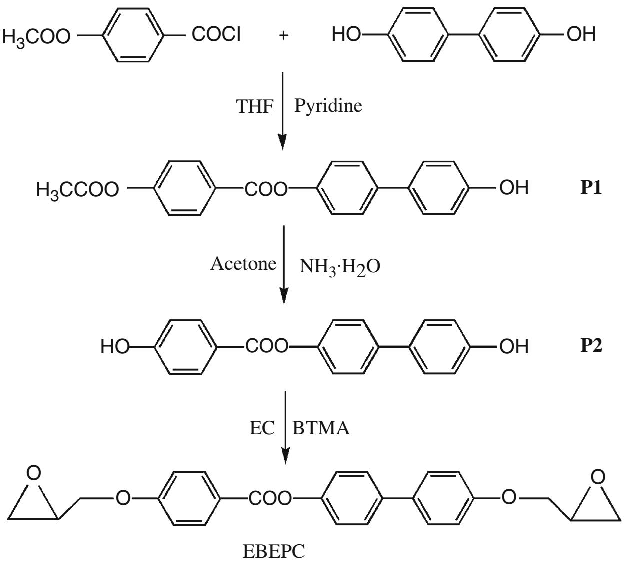
P1 (1.74 g, 0.005 mol) was added into a flask with 100-mL acetone. The flask was cooled in an ice bath, and then 20 wt% AL (10 mL) was added dropwise in 20 min. The mixture was stirred at room temperature for another 15 h and then poured into ice water (100/300, v/v). Brown precipitates were obtained and purified with a mixture of acetone and petroleum ether. Yield: 61.8%; mp: 231.0 °C. IR (KBr): 3 433 (–OH), 3 064 (Ar–H), 1 732 (C=O), 1 605, 1 498 (–Ar–), 1 269 cm^{-1} (Ar–O–C). ^{1}H NMR (D-DMSO): $\delta = 6.87$, 6.96, 7.30, 7.53, 7.65, 8.02 (12H, aromatic), 9.58 (2H, –OH).

Synthesis of 4-(2,3-epoxypropoxy)biphenyl,4″-(2,3-epoxypropoxy)phenyl-4′ carboxylate (LCER or EBEPC) (Scheme 1)

P2 (1.53 g, 0.005 mol), EC (14 g, 0.15 mol), and isopropyl alcohol (16 g) were added into a three-necked reaction flask fitted with a stirrer, condenser, and temperature control equipment. When the flask was heated to 80 °C, the phase transfer agent, BTMAC was added, and then the aqueous solution of NaOH (30 wt%, 8 mL) was dropped out in 15 min. The reaction was continued at 80 °C for 3 h and cooled down to room temperature, then the mixture was put into petroleum ether (50/250, v/v), and the resulting white precipitate was separated and recrystallized from a mixture of chloroform and petroleum ether. Yield: 43.7%; mp: 256.3 °C. IR (KBr): 3 002, 2 929 (Ar–H), 1 727 (C=O), 1 604, 1 496 (–Ar–), 1 262 (Ar–O–C), 1 020 cm^{-1} (C–O–C). ^{1}H NMR ($CDCl_3$): $\delta = 2.78$, 2.92 (4H, epoxy-CH_2), 3.38, 4.0 (4H, glycidyl-CH_2), 4.25, 4.35 (2H, epoxy-CH), 6.98, 7.02, 7.22, 7.50, 7.57, 8.15 (12H, aromatic). $(C_{25}H_{22}O_6)_n$ $(418.44)_n$: Calcd. C 71.76, H 5.30; Found: C 71.35, H 5.35.

Curing process of EBEPC

A stoichiometric ratio of EBEPC and the curing agent DDM were dissolved in proper amounts of acetone. Then, the solvent was allowed to evaporate at room temperature. For the isothermal and dynamic curing studies, the



Scheme 1 The synthetic scheme of EBEPC

homogeneous samples were loaded into the DSC and heated at varied temperatures and heating rates.

Measurements

IR spectra were recorded on a Bio-Rad FTS-6000 Fourier transform infrared (FTIR) spectrometer. ^{1}H NMR spectra were obtained with a UNITY Plus-400 (400 MHz) spectrometer with $CDCl_3$ or dimethyl suloxide-d6 as the solvent and tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) were carried out on an Elementar Vario EL C and H analyzer. Thermal kinetic studies were carried out on a NETZSCH DSC 200 F3 thermal analyzer with N_2 as a purge gas by isothermal and non-isothermal scanning. The textures of the LC phase were observed with an OLYMPUS BX51 polarized light microscope equipped with a Linkam THMSE600 hot stage.

Results and discussion

Structural characterization of EBEPC

EBEPC was structurally characterized with spectroscopic techniques. Figure 1 shows the ^{1}H NMR spectrum of EBEPC, and the chemical shifts of all protons corresponding to the structure have been assigned clearly. The protons in the aromatic ring were found at 6.98–8.15 ppm. The protons of aliphatic groups were found at 2.78–4.35 ppm, respectively.

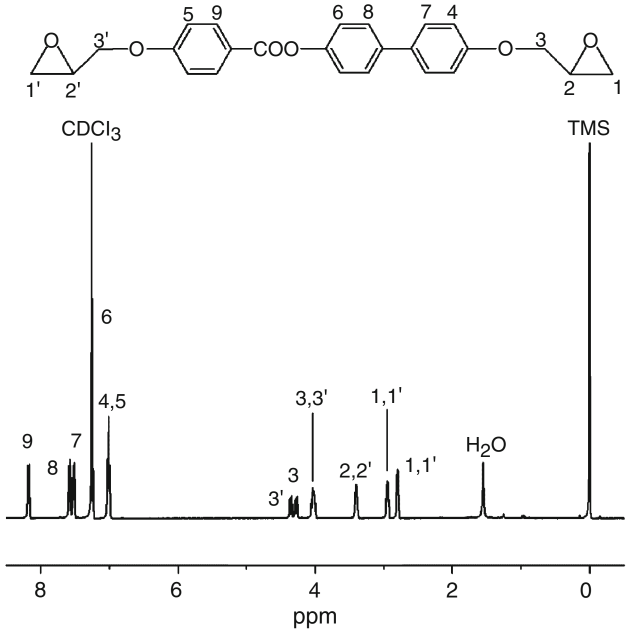


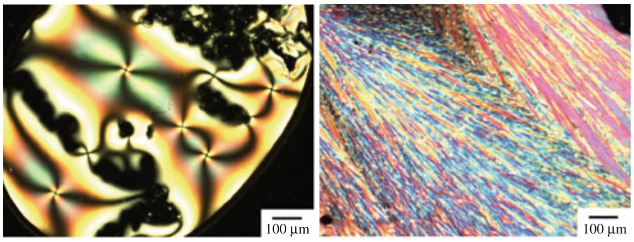
Fig. 1 ^{1}H NMR spectra of EBEPC

LC behaviors of EBEPC

The optical micrograph of EBEPC is shown in Fig. 2. The sample on the glass slide was heated with a scanning rate of 10 °C min^{-1}. Only an isotropic phase was observed 260 °C, A nematic schlieren LC phase could be observed clearly while cooling to 190 °C with a cooling rate of 0.5 °C min^{-1} (Fig. 2a). When cooling down to 140 °C, the system entered into a crystalline phase (Fig. 2b).

Curing behaviors of the EBEPC/DDM system

The curing DSC curve for EBEPC/DDM system at different isothermal temperatures is shown in Fig. 3. The H_{tot} is calculated from the total area under the dynamic scan of curing curve at 10 K min^{-1}, and the corresponding value for EBEPC/DDM system is 299.5 J g^{-1}. The curing rate of the system grows dramatically with the increase of the reaction temperature. In addition, the autocatalytic kinetic behavior is shown from the non-zero initial reaction rate. To investigate the kinetics of the curing reaction, the



(a) (b)

Fig. 2 Polarized optical micrographs of EBEPC: **a** nematic phase at 190 °C and **b** crystalline phase at 140 °C

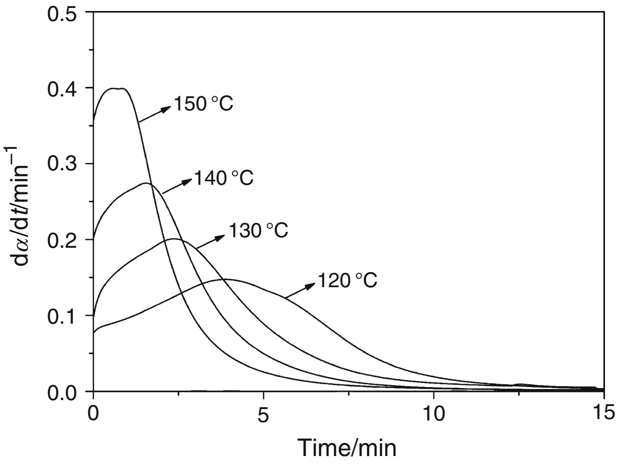


Fig. 3 Isothermal DSC curve for EBEPC/DDM system at different reaction temperatures

relationship between conversion α and the curing time at different curing temperatures are obtained and is shown in Fig. 4.

Kinetics analysis

All kinetics studies start with the basic equation as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(-\frac{E_\alpha}{RT}\right)f(\alpha) \tag{1}$$

where T is the temperature, α is the reaction conversion, A is the pre-exponential factor, R is the gas constant, and $f(\alpha)$ is a model function that depends on the reaction mechanism.

Assuming the heat flow is proportional to the change in the extent of curing reaction:

$$\frac{d\alpha}{dt} = \frac{1}{H_{\mathrm{tot}}}\frac{dH}{dt} \tag{2}$$

where dH/dt represents the rate of heat generated during curing reaction. H_{tot} is the overall heat of reaction.

Under the isothermal condition, we can rearrange Eq. 1 as follows using integral method [19]:

$$-\ln t_{\alpha,i} = \ln\left[\frac{A_\alpha}{g(\alpha)}\right] - \frac{E_\alpha}{RT_i} \tag{3}$$

where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$ is the integral form of the reaction model; and $t_{\alpha,i}$ is the time required to reach a specified conversion α at temperature T_i. So from Eq. 3, E_α can be evaluated from the slope of the plot of $-\ln t_{\alpha,i}$ against T_i^{-1}.

The plots of $-\ln t_{\alpha,i}$ versus $1000/T$ of the EBEPC/DDM system is shown in Fig. 5. The activation energy E_a of EBEPC/DDM system at varied conversions is shown in Fig. 6. It is clear that E_a is not a constant and its dependence on the conversion has the characteristics of the autocatalytic reaction which often occurs in this system. At the initial curing stage, there was a high E_a value at low conversion (64.8 kJ mol^{-1}, $\alpha = 0.1$), which is due to the fact the phenol hydroxyls addition is predominant at this stage. At the final curing stage, the activation energy deceased deeply, indicating the curing reaction started to shift from the mechanism controlled by the chemical kinetics to that controlled by diffusion. This later process is due to the phenomena of gelification, vitrification, and high viscosity existed in the reaction medium [20]. However, there was some difference between the current system and the conventional bisphenol A epoxy/amine system [21] at the final curing stage ($\alpha > 0.6$) where the activation energy started to decrease deeply. This difference may be due to

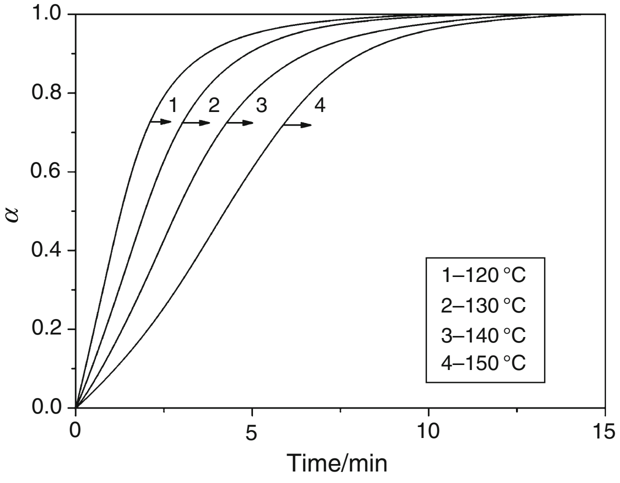


Fig. 4 Conversion as a function of the reaction time at different reaction temperatures for EBEPC/DDM system

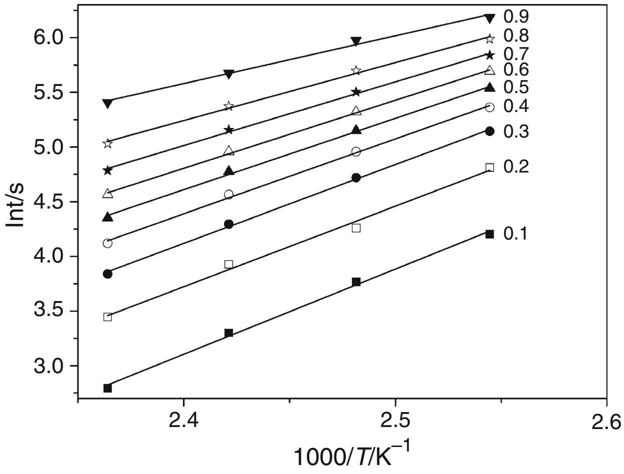


Fig. 5 Isoconversional plots of EBEPC/DDM system from different reaction temperatures

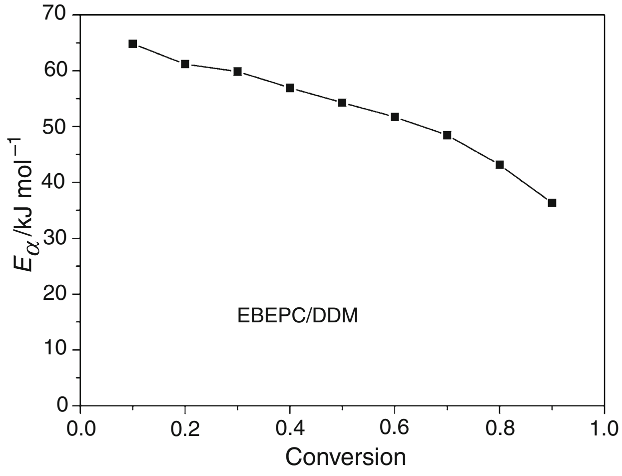
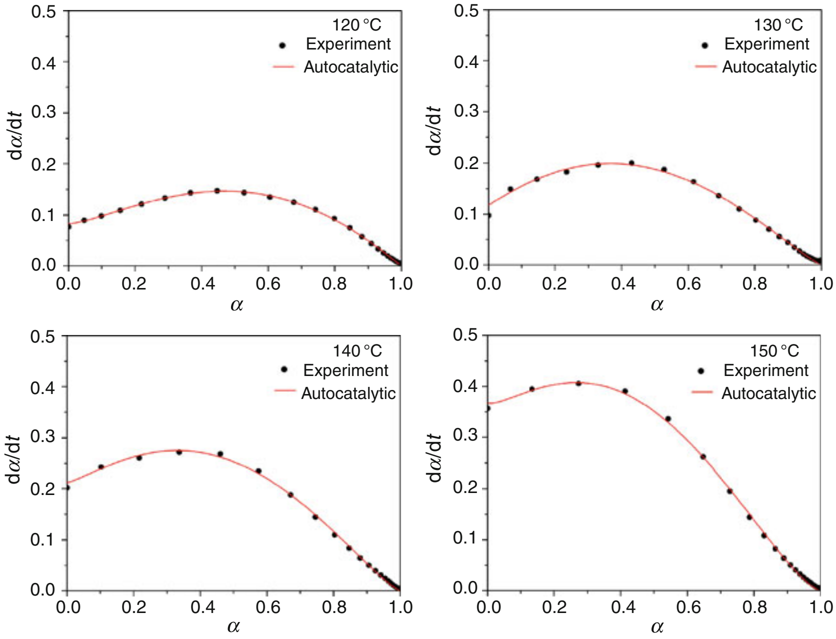


Fig. 6 The relationship between activation energy and the fractional conversion

Fig. 7 Comparison of experimental data with autocatalytic model for EBEPC/DDM system from different reaction temperatures



the formation of the LC phase in the EBEPC/DDM system. In previous works, it had been shown that the LC phase facilitates the reduction of the viscosity [22].

We can also use an autocatalytic model proposed by Kamal [23], which gives a description of curing up to the vitrification point as follows:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{4}$$

Where k_1 is the externally catalyzed rate constant, and k_2 is the autocatalyzed rate constant with Arrhenius temperature dependency. And the constant k_1 can be obtained using the initial reaction rate at $t = 0$ from the intercept of the isothermal curve.

The fitting curves from the experimental data to the autocatalytic kinetic model are shown in Fig. 7. The kinetic parameters confirmed are listed in Tables 1 and 2. The activation energy E_{a1} and E_{a2} were calculated from k_1 and k_2 at different temperatures using Arrhenius relationship, respectively. Regardless of the temperature, the maximum reaction rates located around the conversion of 0.2–0.4, and there was a good fit with the above model for the experimental data from the start of reaction up to 95% conversion. The deviation at the final stage is due to the fact that the diffusion effect dominates at this stage. This result is consistent with the variety of the effective activation energies.

Table 1 Kinetics parameters of EBEPC/DDM curing reaction of different temperatures

Temperature/°C	k_1/min^{-1}	k_2/min^{-1}	m	n	$m + n$
120	0.083	0.546	1.31	1.05	2.36
130	0.118	0.648	1.05	1.20	2.25
140	0.212	0.9	1.17	1.27	2.44
150	0.368	1.398	1.24	1.45	2.69

Morphologies of the cured blends of EBEPC/DDM

The polarized optical morphology of the EBEPC/DDM system in the curing process is shown in Fig. 8. The sample was heated to 160 °C with a scanning rate of 10 °C min^{-1}. When the mixture started to melt, a birefringence pattern (Fig. 8a) could be observed. The LC phase was a smectic one. When the sample was cured at 160 °C for an hour, the fan smectic LC phase (Fig. 8b) could be observed clearly during the curing process. After this process, the sample was cooled down to room temperature with a scanning rate of 1 °C min^{-1}, the LC phase now showed a twisted texture (Fig. 8c).

Table 2 Kinetics parameters of EBEPC/DDM curing reaction

k_1/min^{-1}	k_2/min^{-1}	m_{avg}	n_{avg}	E_{a1}/kJ mol^{-1}	E_{a2}/kJ mol^{-1}
$1.43 \times 10^8 \exp(-8.39/RT)$ $r = 0.9786$	$2.91 \times 10^5 \exp(-5.21/RT)$ $r = 0.9341$	1.19	1.24	69.7	43.3

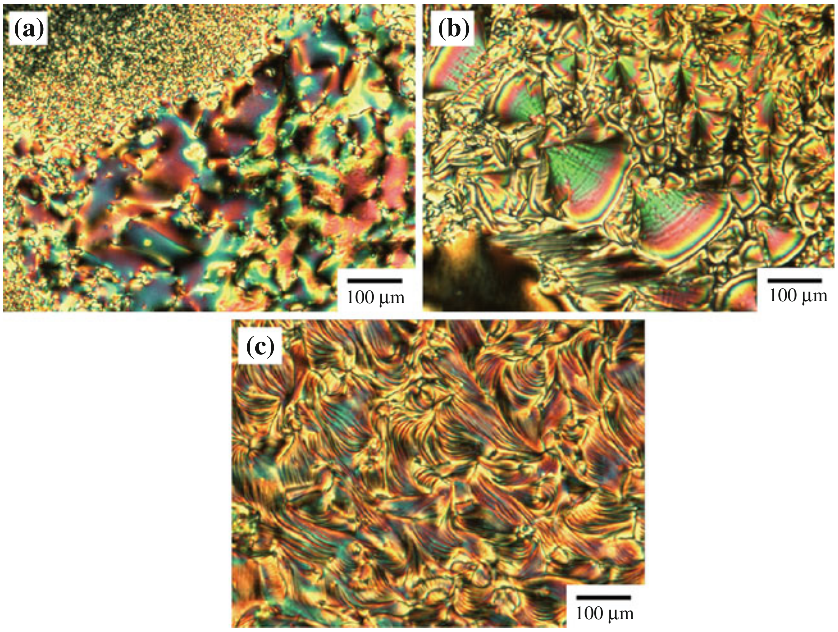


Fig. 8 Polarized optical micrographs of EBEPC/DDM system: **a** 160 °C for 1 min, **b** 160 °C for 60 min, and **c** room temperature

Conclusions

A novel LC epoxy resin, EBEPC, was synthesized and characterized. POM studies revealed that EBEPC had a nematic schlieren texture. Curing kinetics of EBEPC/DDM system was studied using an isoconversional method and Kamal model. The results showed that the effective activation energy was dependent on the conversion, and the effect of diffusion on the curing reaction for EBEPC/DDM system was found at 95% conversion and the formation of LC phase had much influence on the curing reaction. The curing EBEPC/DDM system displayed a smectic texture which became twisted at room temperature.

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