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ORIGINAL PAPER

A new and efficient synthetic method of a liquid crystalline epoxy resin with biphenol and aromatic ester group

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Abstract This article describes a high efficient and economical method to synthesize a liquid crystalline epoxy resin (LCER) containing biphenol and aromatic ester group, 3,3′,5,5′-tetramethylbiphenyl-4,4′-diyl bis(4-(oxiran-2-ylmethoxy) benzoate) (**4**). First, 3,3′,5,5′-tetramethylbiphenyl-4,4′-diyl bis(4-hydroxybenzoate) (**3**) was prepared by direct esterification of 3,3′,5,5′-tetramethylbiphenyl-4,4′-diol (**2**) with *p*-hydroxybenzoic acid (**1**) in the presence of a certain amount of *p*-toluene sulfonic acid (*p*-TSA) as catalyst. And then (**4**) was synthesized by the reaction of (**3**) with epichlorohydrin. The chemical structure, melting range, and liquid crystalline phase transition behavior of (**4**) were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, mass spectroscopy, differential scanning calorimetry (DSC), and polarized optical microscopy (POM).

Keywords Liquid crystalline epoxy resin · Synthesis · Esterification · Cure behavior

Introduction

Liquid crystalline epoxy resins (LCERs) containing rigid-rod mesogenic groups in their backbone have been extensively studied during the past years [1–5]. They are characterized by several unique electrical, mechanical, and optical properties for advanced applications such as microelectrical packing, matrix for composites, and non-linear optics. Many investigations have been reported on the synthesis, curing behavior, phase behavior, and thermal properties of various LCERs, including

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several basic rigid-rod group types such as stilbene [6, 7], hydroxylbenzoic aromatic ester [8–11], azine [12], naphthalene [13], and biphenol [14–17].

The excellent properties of LCERs stem from the preservation of molecular organization in the mesophase of liquid crystalline (LC) precursors and monomers by means of cross-linking reaction. The structure of aromatic mesogenic group and the length of the flexible spacer which decouples the reactive end-functional group from the rigid-rod mesogenic group can offer improvement of rather poor properties in transverse direction to the chain orientation [18, 19]. So, long mesogenic unit and short flexible spacer are generally required to design and obtain novel LCE with high thermal properties.

In order to obtain LCE with high thermal properties, Cai et al. [20, 21] synthesized a novel rigid-rod epoxy monomer containing the long mesogenic unit of biphenyl and aromatic ester group, 3,3′,5,5′-tetramethylbiphenyl-4,4′-diyl bis(4-(oxiran-2-ylmethoxy)benzoate) (**4**) recently. (**4**) has a higher decomposition temperature than flexible epoxies and higher thermal resistance than other rigid-rod epoxies. However, in order to protect the hydroyl group of *p*-hydroxybenzoic acid, a complicated method with five synthetic steps was used to obtain the aim product, (**4**).

In this work, a new and high efficient way was successfully carried out to synthesize (**4**). The chemical structure, melting range, and liquid crystalline phase transition behavior of (**4**) were studied by FT-IR, ^{1}H-NMR, ^{13}C-NMR, mass spectrocopy, differential scanning calorimetry (DSC), and polarized optical microscopy (POM), respectively. The epoxy resin was further cured with 4,4′-diaminodiphenylmethane (DDM) to obtain the epoxy network. The curing behavior of the (**4**)/DDM was studied by DSC.

Experimental

Materials

Sulfolane, *p*-hydroxybenzoic acid (**1**), epichlorohydrin (EC), *p*-toluene sulfonic acid (*p*-TSA), and DDM were obtained from commercially available resources. 3,3′,5,5′-Tetramethylbiphenyl-4,4′-diol (**2**) was a gift from Ao Kai Chemical Engineering Co., Lanzhou city, Gansu province. All solvents were used directly as received.

Instrumentation

Infrared spectra were carried out by a Nicolet 380 Fourier transform infrared (FT-IR) spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a Bruker Avance-400 spectrometer with $CDCl_3$ or DMSO-d_6 as a solvent and tetramethylsilane (TMS) as the internal standard. Elementary analysis was recorded on an Elemetar Vario EL III. ESI–MS or APCI-MS spectra were recorded with a Bruker Esquire HCT plus mass spectrometer. Calorimetric studies were carried out on a Netzsch DSC 204 F1 Phoenix with N_2 as a purge gas by isothermal and nonisothermal scanning. The textures of the mesophase were observed with a polarized optical microscope (Nikon Eclipse E600 POM) equipped with a heating stage.

Synthesis of 3,3′,5,5′-tetramethylbiphenyl-4,4′-diyl bis(4-hydroxybenzoate) (**3**)

A three-necked flask (150 mL) equipped with a stirrer and a thermometer was purged with N_2, into which 3,3′,5,5′-tetramethylbiphenyl-4,4′-diol (**2**) (0.05 mol, 12.1 g), *p*-hydroxybenzoic acid (**1**) (0.2 mol, 27.6 g), sulfolane (50 mL), and *p*-TSA (5 mmol, 0.9 g) were added. The mixture was stirred at 180 °C for 4 h. The crude product was washed with cool water, ethanol to give 19.3 g of (**3**) as white powder. Yield: 80.1%. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 10.57 (s, 2H, OH), 8.04 (d, $J = 8.4$ Hz, 4H, Ar), 7.45 (s, 4H, Ar), 6.95 (d, $J = 8.8$ Hz, 4H, Ar), 2.16 (s, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO, δ, ppm): 163.66, 162.59, 147.64, 137.01, 132.23, 130.44, 126.72, 118.96, 115.61, 16.06. FT-IR (KBr, v, cm^{-1}): 3394 cm^{-1} (O–H), 2924 (C–H), 1694 (C=O), 1608, 1588 and 1512 (C=C), 1276 cm^{-1} (O–H). MS (ESI) calcd for $C_{30}H_{26}O_6$ 482.2, found 481.5. Anal. Calc. for $C_{30}H_{26}O_6$: C, 74.67; H, 5.43. Found: C, 74.45; H, 5.46.

Synthesis of 3,3′,5,5′-tetramethylbiphenyl-4,4′-diyl bis(4-(oxiran-2-ylmethoxy)benzoate) (**4**)

A mixture of (**3**) (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, white precipitate was recrystallized several times with CH_2Cl_2/CH_3OH to give 4.59 g of (**4**) as white powder. Yield: 73.5%. ^{1}H-NMR (400 MHz, $CDCl_3$, 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, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 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. FT-IR (KBr, v, 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). MS (APCI) calcd for $C_{36}H_{34}O_8$ 594.2, found 595.7. Anal. Calc. for $C_{36}H_{34}O_8$: C, 72.71; H, 5.76. Found: C, 72.50; H, 5.79.

Preparation of the polymer

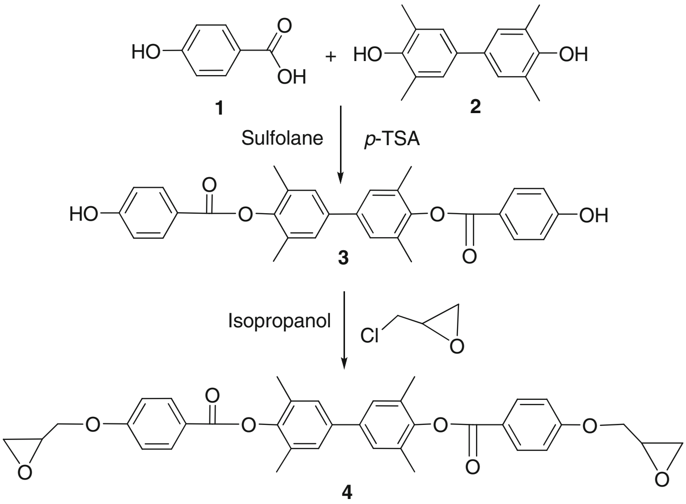
Thermal curing of (**4**) with a curing agent DDM was carried out by means of dynamic differential scanning calorimetry (DSC). First, (**4**) and DDM were pestled in an agate mortar, respectively, and then were mixed together in a molar ratio of 1:1. The experiments were conducted at heating rates of 5, 10, 15, and 20 °C/min. The isothermal DSC experiments were carried out in a certain temperature range 140–190 °C.

Results and discussion

Optimization of the synthesis of (**4**)

Based on previous literatures [22, 23], one of high efficient and economical ways was designed to synthesize (**4**). The synthesis of (**4**) was carried out only in two steps (Scheme 1). First, (**3**) was prepared by direct esterification of (**2**) with (**1**) in the presence of a certain amount of *p*-TSA as catalyst. And then (**4**) was synthesized by the reaction of (**3**) with epichlorohydrin.

(**3**) could be obtained from several common primary materials, including (**1**), (**2**), and EC, by a single-step esterification of (**1**) and (**2**) in a high yield 80.1%. The yield was much higher than the yield (54%) of the 4-step synthesis in the reference [21]. The self-condensation reaction of (**1**) was the major side reaction in this process. The electron-withdrawing carboxyl group at the *para*-position of (**1**) could decrease the electron density and nucleophilicity of the hydroxyl group. Therefore, the self-condensation of (**1**) was relatively difficult. In contrast, the electron-donating methyl and *p*-hydroxylphenyl groups at the *ortho*- and *para*-position of (**2**) could increase the electron density and nucleophilicity of the hydroxyl group. However, high temperature was required in the esterification of (**1**) and (**2**), due to the steric hindrance effect of methyl groups. Therefore, high boiling point solvent sulfolane was used in this reaction. Under the reaction condition of 180 °C for 4 h, the yield of self-condensation reaction of (**1**) was very low, but (**3**) could be obtained in high yield. So, the hydroxyl protection of (**1**) was not required in the new synthesis. On the contrary, the synthesis procedure reported in the literature [21] suggested that the hydroxyl group of (**1**) required special care during the synthesis of the (**3**) and acetic anhydride was used as an acetylating agent and ammonia liquor was used as a deacetylating agent.



Scheme 1 Synthetic route of (**4**)

The epoxy monomer (**4**) was synthesized according to the published literature [21] but with no phase transfer agent such as benzyltrimethylammonium chloride. NaOH solution acted as catalyst and acid binding agent, but excess NaOH could also hydrolyze (**4**) partially. The intermediate of phenate ion (ArO^-) in the reaction could transfer to oil phase easily due to the large lipophilic groups in ArO^-. Therefore, the reaction could process without phase transfer agent and (**4**) could be obtained in high yield (73.5%) by adding NaOH aqueous solution (30 wt%) dropwise. In contrast, the yield of (**4**) in the literature [21] is 55%.

Characterization of (**4**)

The FT-IR spectrum of (**3**) (Fig. 1) show the O–H stretching peak at 3394 cm^{-1} associated with the structure of (**3**). After a reaction with EC, the peak at 3394 cm^{-1} disappeared completely, and several new peaks at 1258, 1167, 917, and 841 cm^{-1} appeared (Fig. 1) because of the formation of oxirane in (**4**). Furthermore, a new peak at 1510 cm^{-1} was due to the formation of CH_2 group.

The chemical structures of (**3**) and (**4**) were also confirmed by ^{1}H-NMR spectra (Fig. 2). The peak at 10.57 ppm was attached to the –OH in (**3**). Nine species of protons could be found in (**4**) according to the different chemical shifts. The protons of the benzene ring were in the low field 7.02, 8.20, and 7.28 ppm, respectively. The protons of aliphatic groups were in the high field 4.34, 4.02, 3.39, 2.93, 2.78, and 2.22 ppm, respectively.

The LC behavior of the epoxy monomer was studied with DSC and POM. Figure 3 shows the DSC scans of (**4**) with a constant heating and cooling rate of 10 °C/min in the temperature range between 100 and 280 °C. It exhibits two endothermal peaks upon the heating: one at lower temperature 251.8 °C due to the

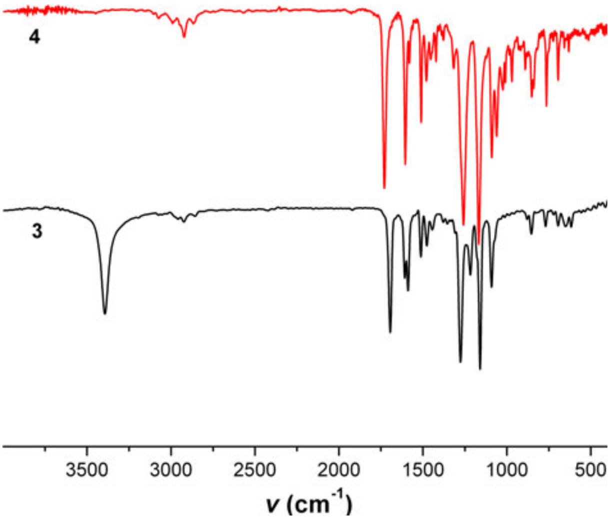


Fig. 1 FT-IR of (**3**) and (**4**)

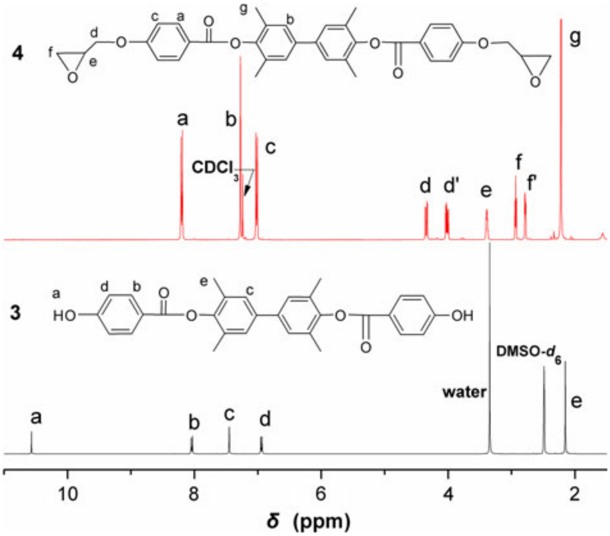


Fig. 2 ^{1}H-NMR of (**3**) (in DMSO-d_6) and (**4**) (in $CDCl_3$)

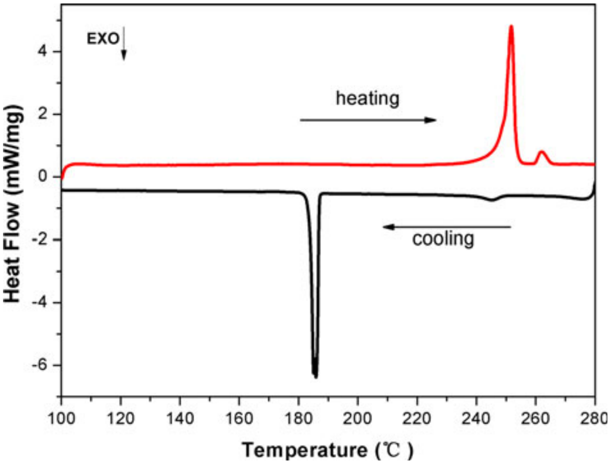


Fig. 3 DSC curves of (**4**) with a rate of 10 °C/min

melting; and the other at higher temperature 262.3 °C attributes to isotropization. The LC phase transition behavior of (**4**) was evident in the cooling curve. With the reduction of the temperature, a blunt peak was observed at the range from 252 to 241 °C indicating the phase transformation of (**4**) from the isotropic phase to LC phase. With the reduction of temperature, the sample began to crystallize at 186.2 °C and a sharp peak appeared. This LC behavior of the epoxy monomer

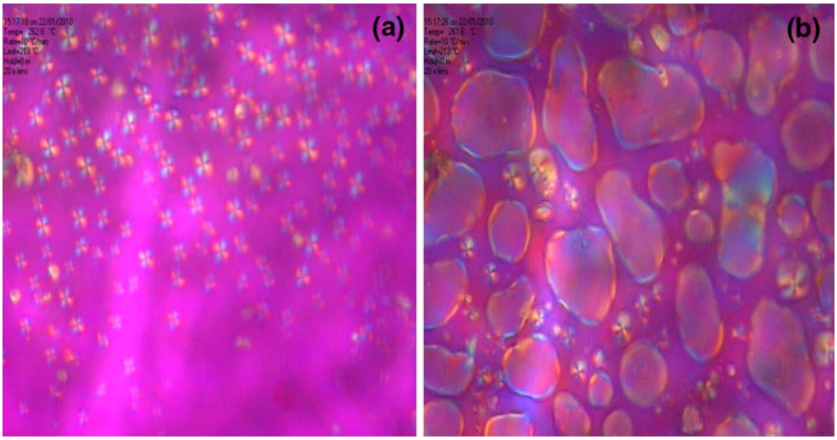


Fig. 4 POM photos of (**4**) (×200) at different temperatures. **a** 262.8 °C; **b** 261.6 °C

revealed by the DSC showed deviation from the reference [21] in which polymesomorphous structure was observed upon cooling. For the deviation, we assume that heating history had a sound influence on LC behavior of the epoxy monomer. Actually we are trying to study the effect of heating history on LC behavior of the LCE monomer by DSC and it will be reported later.

A POM study of (**4**) was carried out to identify the type of LC phase. A pressed sample between two glass slides was kept in a heating stage and it was heated at a rate of 10 °C/min. The sample exhibited birefringence during cooling process under the cross polarized optical microscopy (Fig. 4). The thermal transition temperature from isotropic phase to LC phase observed under POM was a little higher than that observed in DSC, but it remains reasonable due to instrumental error caused by different apparatus and different operators.

Curing of (**4**) with curing agent DDM

The curing behavior of the (**4**)/DDM system was measured with isothermal and nonisothermal DSC. The dynamic DSC thermograms of the (**4**)/DDM as a function of heating rate are presented in Fig. 5. The peak temperature (T_p) and the initial cure temperature (T_i) increased (Table 1) with increasing heating rate. The heat of cure (ΔH) was determined from the area under the cure thermogram.

The isothermal DSC experiments were carried out in the temperature range of 140–190 °C. Below the range, the curing rate was too low to monitor the cure reaction, whereas a small amount of thermal degradation occurred above the range. Figure 6 shows the isothermal curing processes of homogeneous mixtures under different temperatures. The rate of curing reaction was visibly dependent on the curing temperature. The curing rate under 190 °C was much higher than that under 140 °C when other conditions were same.

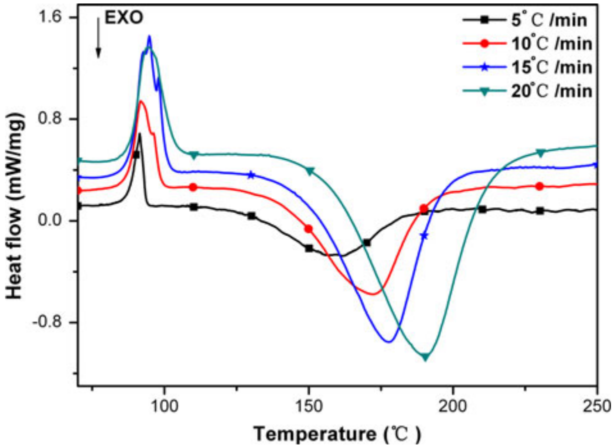


Fig. 5 Dynamic DSC curves of (**4**)/DDM systems at different heating rate

Table 1 T_p and ΔH of (**4**)/DDM system at different heating rate

Heating rate (°C/min)	T_i^a (°C)	T_p^b (°C)	T_f^c (°C)	$-\Delta H^d$ (J/g)
5	125.7	161.9	180.7	152.3
10	142.1	172.3	189.3	165.0
15	148.6	177.9	194.6	157.9
20	156.6	190.3	210.7	168.3

[a] Initial curing temperature

[b] Peak curing temperature

[c] Finish curing temperature

[d] The Heat of cure

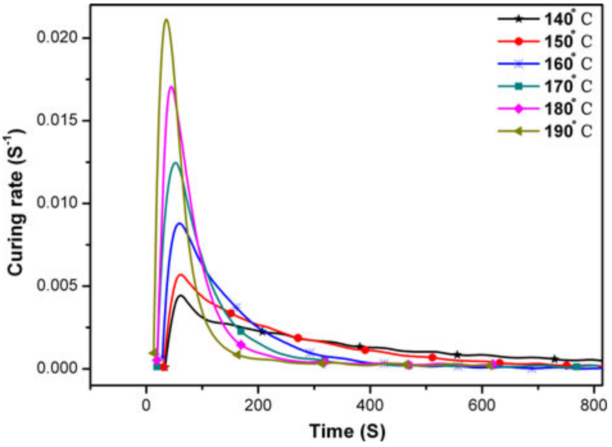


Fig. 6 Isothermal DSC curves of (**4**)/DDM systems under different temperatures

Conclusions

The liquid crystalline epoxy resin (**4**) with biphenol and aromatic ester group was synthesized successfully only in two steps. First, (**3**) was prepared by direct esterification of (**2**) with (**1**) in the presence of a certain amount of *p*-TSA as catalyst in a high yield 80.1%. The hydroxyl protection of *p*-hydroxybenzoic acid was not required in the new synthesis. Then the epoxy monomer (**4**) was synthesized by the reaction of (**3**) with epichlorohydrin without adding phase transfer agent such as benzyltrimethylammonium chloride. All the materials in the new synthesis could be obtained from common commercially available resources. This new and efficient way is advantageous over the 5-step synthesis that was previously reported. Furthermore, epoxy network containing (**4**) was obtained by curing with curing agent DDM.

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