

# Liquid-Crystalline Epoxy Resins

H. Galina, B. Mossety-Leszczak

Department of Industrial and Materials Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

Received 11 March 2006; accepted 28 July 2006

DOI 10.1002/app.26014

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new liquid-crystalline epoxy monomer (LCEM) containing central triaromatic mesogen and aliphatic spacers consisting of eight methylene units terminated with epoxy groups was synthesized and characterized by means of IR and NMR spectrometry, differential scanning calorimetry (DSC), polarized optical microscopy, and wide-angle X-ray scattering. The cure reaction of LCEM with primary aromatic diamines in a stoichiometric ratio and with a tertiary amine catalyst of polymerization and the properties of the cured

products were investigated with a DSC technique. The effects of the curing conditions (polyaddition vs anionic polymerization) and the structures of the amines on the formation of liquid-crystalline networks were studied. The monomer cured with selected amines yielded an anisotropic network. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 224–228, 2007

**Key words:** crosslinking; liquid-crystalline polymers (LCP); monomers; resins; thermosets

## INTRODUCTION

Epoxy resins are important thermosetting polymers used in many applications as adhesives and composite materials. These resins have good thermal and mechanical properties and chemical resistance but are brittle and have poor resistance to crack propagation.<sup>1</sup> One of the ways of modifying these properties is the incorporation of rigid mesogenic groups into the network. Such materials with molecular order can also show anisotropic properties and are called liquid-crystalline epoxy resins (LCERs). LCERs have been synthesized and investigated by many research groups.<sup>2–16</sup> In the preparation of LCERs, it is important to obtain networks with both high density and high supramolecular order. Detailed studies have revealed their unique and unusual properties, such as high thermal and orientational stability, low shrinkage upon curing, fracture resistance, low coefficients of thermal expansion, anisotropic optical properties, and high moduli. The combination of the advantages of liquid crystals and highly crosslinked thermosets gives materials that can be used in advanced technologies as nonlinear optic components, self-reinforcing composite materials, or photoreactive materials in electronics. From some LCERs, nanocomposites filled with carbon nanotubes,<sup>17</sup> polyaniline nanorods,<sup>18</sup> or organoclays<sup>19</sup> have been prepared.

Liquid-crystalline epoxy networks have been obtained mainly through the crosslinking of epoxy monomers containing mesogenic groups. The long triaromatic ester mesogenic group in epoxy monomers makes the mesophase stable because of significant geometrical anisotropy. The synthesis and curing of monomers with these mesogenic groups have been studied by various authors.<sup>10–14,20,21</sup> Our study deals with one such monomer. We describe the synthesis of a new liquid-crystalline epoxy monomer (LCEM) and report the results obtained while curing this monomer with selected aromatic diamines. We also examine the properties of the products after crosslinking. The molecular order was preserved after the crosslinking reaction.

## EXPERIMENTAL

### Materials

All starting materials were commercial reagents [(Sigma-Aldrich, Seelze, Germany), (Fluka, Buchs, Switzerland), and (Merck, Darmstadt, Germany)] and were used without further purification. The synthetic scheme leading to the LCEM is illustrated in Figure 1. Bis(4-hydroxybenzoate) *p*-phenylene was obtained by the esterification of 4-hydroxybenzoic acid with hydroquinone in the presence of a catalytic amount of *p*-toluenesulfonic acid with the procedure described by Kangas et al.<sup>22</sup>

### Synthesis

To 0.1 mol (3.5 g) of bis(4-hydroxybenzoate) *p*-phenylene and 0.02 mol (3.76 g) of 10-undecenoic acid in 80 cm<sup>3</sup> of dry dichloromethane, 0.022 mol (4.54 g) of

This article is dedicated to the memory of Professor Marian Kryszewski.

Correspondence to: B. Mossety-Leszczak (mossety@prz.edu.pl).

*Journal of Applied Polymer Science*, Vol. 105, 224–228 (2007)  
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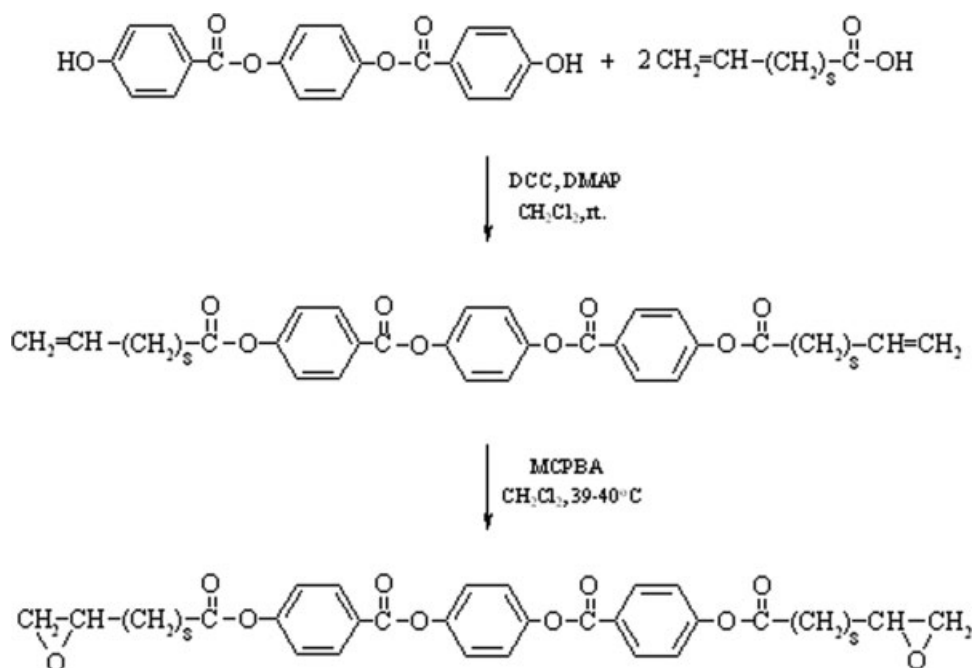


Figure 1 Synthesis of the LCEM.

*N,N*-dicyclohexylcarbodiimide (DCC) and a catalytic amount ( $8 \times 10^{-4}$  mol, 0.0977 g) of 4-dimethylaminopyridine (DMAP) were added. The reaction mixture was stirred for 24 h, and then *N,N*-dicyclohexylurea was filtered off; after the removal of the solvent, the crude product was washed with methanol (yield = 54%). Next, to a solution of 0.01 mol (6.82 g) of the diolefin in 60 cm<sup>3</sup> of dichloromethane, 6.16 g (0.025 mol, 70%) of *m*-chloroperoxybenzoic acid (MCPBA) was added under continuous stirring. The mixture was refluxed for 48 h. After cooling and subsequent filtration, the mixture was washed with 60 cm<sup>3</sup> of aqueous 5% Na<sub>2</sub>SO<sub>3</sub>, 60 cm<sup>3</sup> of aqueous 5% NaHCO<sub>3</sub>, and 45 cm<sup>3</sup> of a saturated NaCl solution. The organic layer was dried over MgSO<sub>4</sub>, and the solvent was evaporated. Recrystallization from ethyl acetate yielded the final product.

Yield: 80%. Epoxy number: 0.277 (calcd 0.280). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ, ppm): 8.2 (4H, d, aromatic), 7.2 (8H, d, aromatic), 2.85 (2H, m, CH of epoxy), 2.6 (4H, m, CH<sub>2</sub> of epoxy), 2.4 (4H, m, CH<sub>2</sub>), 1.4 [28H, m, (CH<sub>2</sub>)<sub>7</sub>]. IR (KBr, ν, cm<sup>-1</sup>): 3071, 1605–1465, 1016, 855 (aromatic), 2925–2851 (CH<sub>2</sub>), 1756, 1735 (C=O), 1267–1072 (C–O), 922 (epoxide).

#### Preparation of the samples for curing

The LCEM synthesized in this work was cured with 4,4'-diaminodiphenylmethane (DDM), 2,4-diaminotoluene (DAT), *p*-phenylenediamine (PDA), and 4-(*N,N*-dimethylamino)pyridine (DMAP). The chemical structures of the curing agents and their melting points are shown in Figure 2.

The mixtures for curing were prepared by the dissolution of stoichiometric amounts of the LCEM and curing agent in dichloromethane at room temperature. The diepoxy monomer was treated as a difunctional one, and amines DDM, DAT, and PDA were treated as tetrafunctional systems. The sample with DMAP was prepared in a similar way through the dissolution of 1 part of this amine per 100 parts of LCEM. After the evaporation of the solvent, the mixtures were dried *in vacuo* and stored at 5–10°C before use.

#### Measurements

The structure of the products was determined by <sup>1</sup>H-NMR and IR spectroscopy with a Bruker (Rheinstetten, Germany) AC 300 spectrometer and a Paragon 1000 FTIR (PerkinElmer, Waltham, MA) spectrometer. Microscopic observations were made with a Zeiss polarizing microscope at a magnification of 80× with crossed polarizers. Differential scanning calorimetry

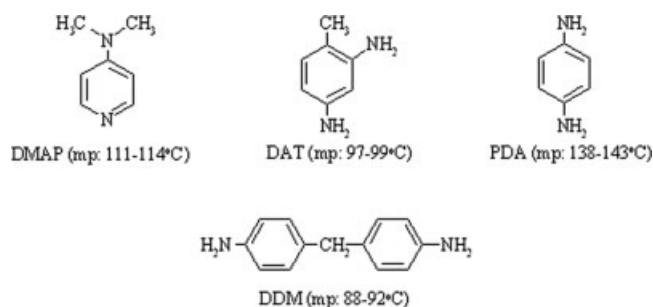


Figure 2 Curing agents.

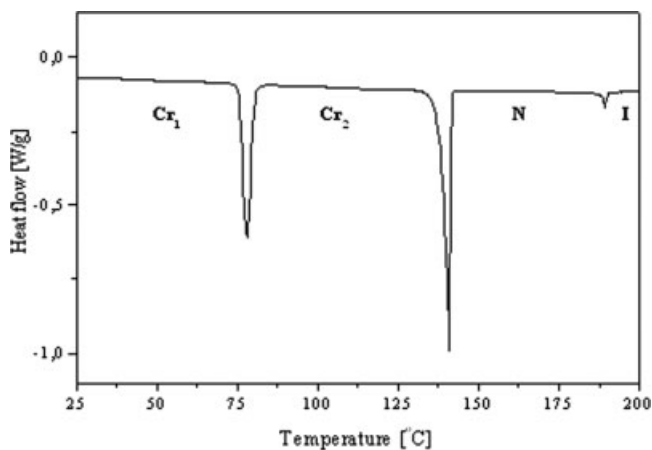


Figure 3 DSC thermogram of LCEM at 2°/min in N<sub>2</sub>.

(DSC) measurements were performed with a Mettler-Toledo DSC822<sup>e</sup> (Greifensee, Switzerland) instrument under a nitrogen atmosphere. Wide-angle X-ray scattering (WAXS) experiments were carried out with a rotating-anode X-ray beam (Rigaku, Tokyo, Japan) with pinhole collimation, a two-dimensional 1024 × 1024 detector (Siemens, Munich, Germany), and a double graphite monochromator for Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). The beam diameter was about 0.5 mm, and the sample-detector distance was 80 mm.

## RESULTS AND DISCUSSION

The LCEM used in our studies was synthesized in a two-stage method. First, esterification of bis(4-hydroxybenzoate) *p*-phenylene with 10-undecenoic acid was carried out, and in the second stage, the resulting olefinic precursor was oxidized with MCPBA. The chemical structure of the product, purified by recrystallization, was confirmed by <sup>1</sup>H-NMR and IR spectroscopy. The mesomorphic properties of the LCEM were examined with DSC, polarized microscopy, and WAXS. The DSC thermogram is shown in Figure 3.

Upon heating, there were three endothermic peaks corresponding to the crystal-crystal transition, crystal-nematic transition, and isotropization. Between 138 and 189°C, the textures observed by polarized microscopy and WAXS patterns were typical for the nematic mesophase. Table I lists the temperatures and enthalpies of the LCEM phase transitions.

TABLE I  
Thermal Transitions of LCEM

Transition	Temperature (°C)	Enthalpy (kJ/mol)
Cr <sub>1</sub> → Cr <sub>2</sub>	78	31.7
Cr <sub>2</sub> → N	138	45.5
N → I	189	1.3

Cr = crystal phase; N = nematic phase; I = isotropic liquid.

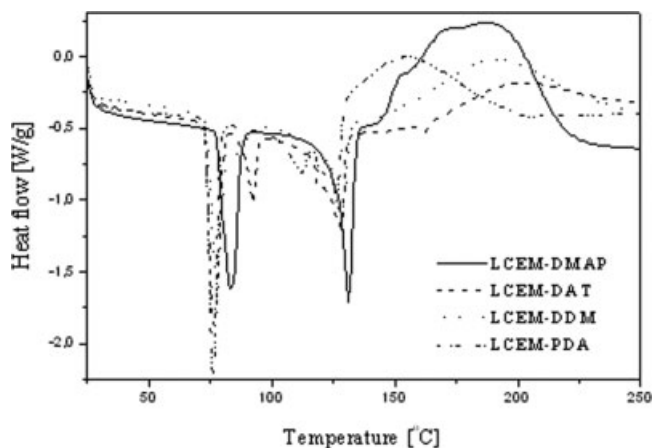


Figure 4 Dynamic DSC curves of LCEM-amine mixtures (10°/min in N<sub>2</sub>).

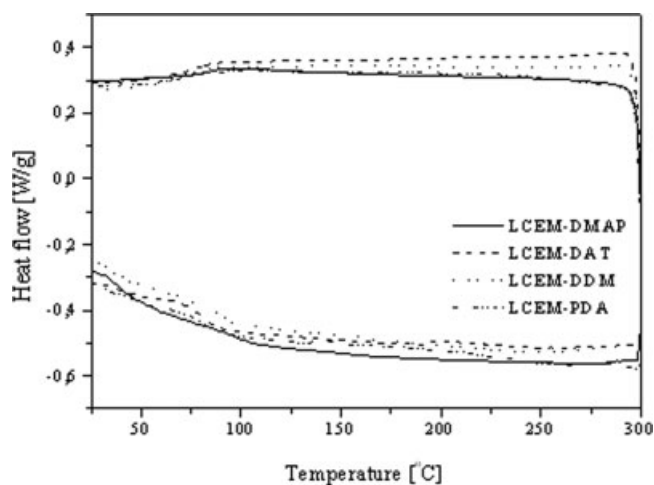
The reactivity of the LCEM was examined in coupling with four aromatic diamines: DAT, DDM, PDA, and DMAP. The primary diamines DAT, DDM, and PDA were added in stoichiometric proportions. Crosslinking with this type of curing agent is a polyaddition reaction. Tertiary amine DMAP, added in a small amount (1% w/w), catalyzed the anionic polymerization through the ring opening of oxirane rings. This method of curing liquid-crystalline epoxides was analyzed by Ribera's group.<sup>23</sup>

The DSC thermograms of the mixtures of the LCEM with selected diamines recorded during heating at 10°/min are shown in Figure 4. The first endothermic peak in all DSC curves is attributed to the polymorphic transition of the LCEM crystals, and the second smaller peak corresponds to the melting of amines DAT, DDM, and PDA. The melting of DMAP in a mixture of LCEM and DMAP was not recorded because the amount of amine was too small. The endothermic peak around 130°C is connected to the melting of the LCEM. The exothermic effect caused by the initiation of the crosslinking reaction appeared at about 130–135°C just after the melting of the epoxy monomer. The total heat of the curing reaction evaluated from the DSC thermograms varied from 47.9 to 86.5 kJ/mol (Table II).

TABLE II  
DSC-Determined Curing Data for Mixtures of LCEM with DMAP, DAT, DDM, and PDA

Curing agent	Maximum temperature (°C)	Total heat of the curing reaction (kJ/mol of epoxy groups)
DMAP	184	86.5
DAT	202	47.9
DDM	191.5	89.8
PDA	154	74.3

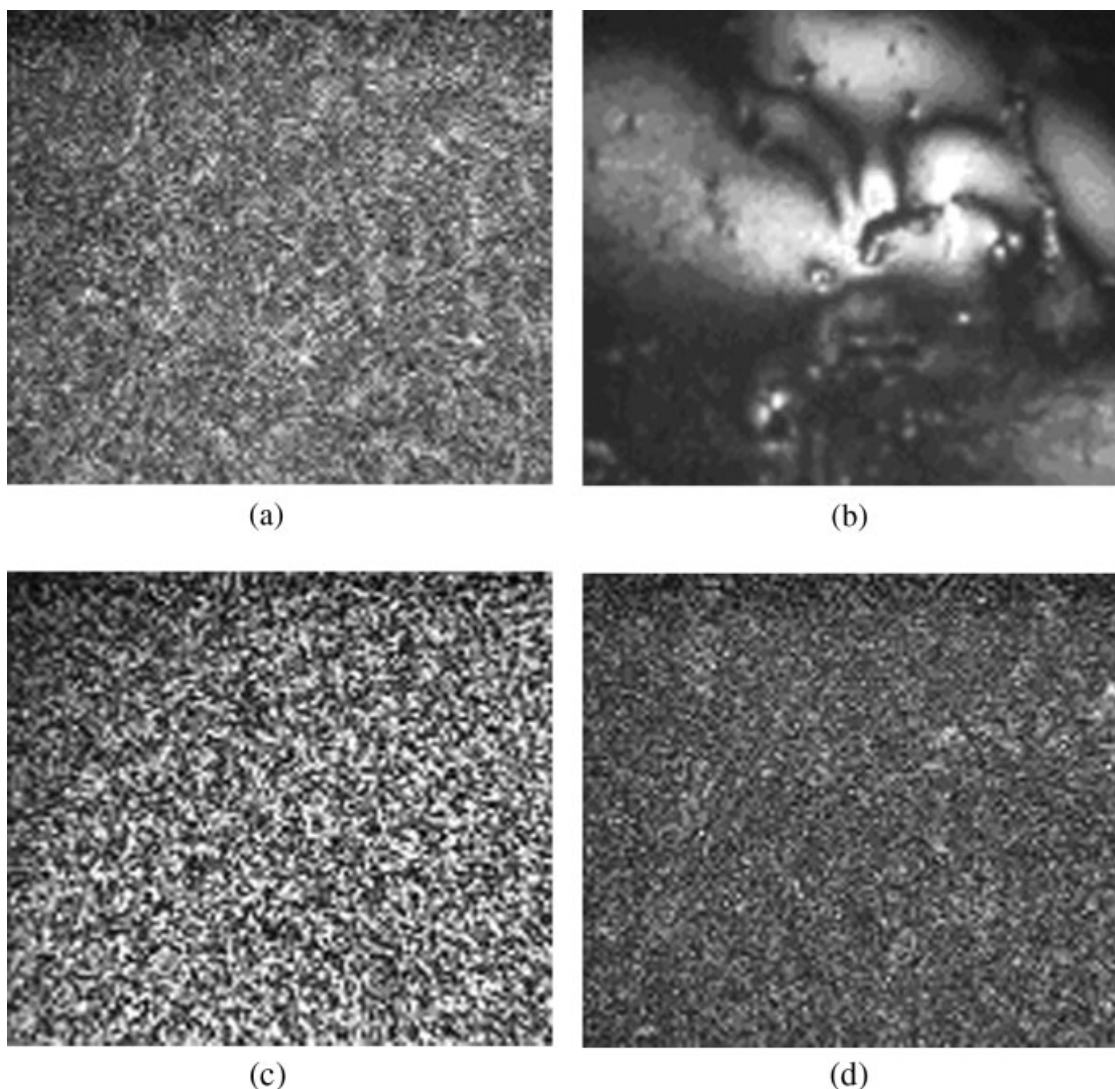




**Figure 5** DSC thermograms of LCEM cured with DMAP, DAT, DDM, and PDA (10°/min in N<sub>2</sub>).

These values, especially for the reaction with primary amines, are smaller than the curing enthalpies of epoxy resins reported in the literature, which are in the range of 100–118 kJ/mol of epoxy group, that is, close to the heat of the epoxy ring opening.<sup>24</sup> In the second heating cycle up to 300°C on the DSC curves, no residual heat of reaction was detected. This suggests that the curing reaction was completed. The curing enthalpies were probably lowered by the melting enthalpies of the monomer and amines. The curing started during the melting of the monomer, and hence part of the epoxy–amine reaction heat was included in the enthalpy of LCEM melting in the curing mixture. The reaction enthalpy of LCEM curing with the tertiary amine (DMAP) was similar to that reported by Ribera et al.<sup>23</sup>

The curing conditions for mixtures of LCEM with DMAP, DAT, DDM, and PDA were established from



**Figure 6** Textures of LCEM cured with (a) DMAP, (b) DAT, (c) DDM, and (d) PDA at 160°C for 4 h and postcured at 180°C for 2 h.

DSC analysis. Samples (0.5 g) of all compositions were cured at 160°C for 4 h and postcured at 180°C for 2 h. Other samples, placed between two glass plates with 20- $\mu\text{m}$  spacers for optical observations, were cured under the same conditions. The extent of the LCEM cure in all mixtures was determined from FTIR spectra. The bands characteristic of epoxy groups at about 920  $\text{cm}^{-1}$  disappeared almost completely in the postcured networks in all samples. This means that curing under these conditions was practically completed. At room temperature, the resulting samples were rigid, opaque, yellow-brown materials insoluble in typical organic solvents such as methanol, ethanol, dimethyl sulfoxide, dimethylformamide, and acetone but underwent swelling in chloroform.

The thermal properties of the cured compositions were analyzed by DSC. The thermograms for the networks are presented in Figure 5.

No significant changes in the thermal properties of the cured samples were recorded in the heating and cooling cycles in a wide range of temperatures (25–300°C). The small inflexion of the DSC curves around 90°C, characteristic of the glass transition, was related to an increase in the molecular mobility of the  $(\text{CH}_2)_8$  aliphatic chains in the network structure.

In this temperature range, the textures of the cured samples were observed with polarizing optical microscopy. The optical micrographs of the networks obtained for the curing of LCEM with DMAP, DAT, DDM, and PDA, recorded at 25°C, are shown in Figure 6. At about 90°C, near the relaxation temperature, no changes were observed. Further heating up to 300°C did not cause any texture change, either.

The samples of all polymer networks prepared from LCEM were anisotropic. The textures observed with polarized optical microscopy were typical for nematic liquid crystals and suggested that the mesomorphic properties of the nematic epoxy monomer were preserved after curing.

Inevitably, the structure of epoxy networks depends on the type of curing method applied. In networks prepared by a polyaddition reaction (with primary amines), the mesogenic component is substantially diluted with the curing agent. On the other hand, when the anionic polymerization of epoxy rings is used in the curing, the amount of the other component (tertiary amines) in the final product is small. In this preliminary study, however, we did not observe any specific differences between the textures or thermal properties of the networks prepared in these two ways. If the differences in the structure do influence the mesomorphic properties of cured epoxies, this could probably be observed with more sophisticated analytical methods, and the curing process should preferably be carried out in a force field (e.g. magnetic field) applied to the whole sample.

## CONCLUSIONS

A new epoxy monomer based on a triaromatic mesogen (LCEM), synthesized and characterized in this work, showed thermotropic, nematic liquid-crystalline properties in the temperature range of 138–189°C. The crosslinking reaction of the LCEM with primary and tertiary aromatic amines led to networks retaining anisotropic nematic mesophases. The anisotropic structure of the networks was stable up to 300°C. The thermosetting monomer prepared in this work could be applied to manufacturing anisotropic materials.

This article is dedicated to the memory of Professor Marian Kryszewski.

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