Synthesis, Characterization, and Mechanical Properties of a Novel Terphenyl Liquid Crystalline Epoxy Resin

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ABSTRACT: A novel terphenyl liquid crystalline (LC) epoxy resin was synthesized and characterized by ^{1}H-NMR, Fourier transform infrared spectroscopy, differential scanning calorimetry (DSC), and polarizing optical microscopy. Depending on the curing temperature, the synthesized resin formed both smectic and nematic LC phases. A time-temperature-transformation diagram was constructed to optimize the curing process, which helped in the preparation of LC and isotropic system. The terphenyl epoxy resin obtained exhibited higher acid resistance than a comparable Schiff-base epoxy resin, and also displayed excellent fracture toughness. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41296.

INTRODUCTION

Epoxy resins are widely used in industrial products such as adhesives, coatings, paints, and electrical insulation materials. Recently, the demand for functional, high-performance resins has increased, especially for use in electronics.

Liquid crystalline (LC) epoxy resins have a LC phase-temperature region because of the interaction of the mesogenic groups located along the backbone of the resin. The effect of the backbone chain orientation on their unique and excellent properties, such as high glass transition temperature (T_g), fracture toughness, bonding property,[1–9] and thermal conductivity,[10–13] has been studied in detail, and a variety of novel LC epoxy resins, epoxy monomers, and curings have been investigated.[13–22]

The relationship between the ordered structure and the physical properties of LC epoxy curings has also been studied. The mesogenic groups of the LC epoxy resins used in these studies contained a Schiff base. Although these resins may be stabilized by π–π conjugation interactions, hydrolysis of the Schiff base can lead to decomposition.

In this study, a novel terphenyl LC epoxy resin (DGETP-Me), which exhibits high chemical resistance to acid, was synthesized and evaluated for chemical stability and fracture toughness. A time-temperature-transformation (TTT) diagram was constructed from polarized optical microscope measurements, and bulk curings were prepared. The resistance of the curings against HCl (aq.) was compared to the resistance of the

diglycidyl ether of terephthalylidene-bis-(4-amino-3-methylphenol) (DGETAM), which contains a Schiff base structure similar to that of the curings. Fracture toughness was then evaluated.

EXPERIMENTAL

Synthesis of DGETP-Me Monomer

DGETP-Me was prepared by the reaction of 4,4′-dihydroxy-3-methylterphenyl (20.00 g, 0.072 mol) with 1-chloro-2,3-epoxypropane (80.0 g, 0.87 mol), using tetra-n-butylammonium chloride as the catalyst, in dimethyl sulfoxide (DMSO) (240 mL) at 80°C for 4.5 h (Scheme 1). A 50 wt % aqueous sodium hydroxide solution (6.96 g, 0.174 mol) was then added to form the glycidyl ether of dihydroxy-terphenyl. The obtained solution was cooled at 25°C and filtered. The precipitate was recrystallized with chloroform, and white crystals were obtained. The synthesized resin was characterized by Fourier transform infrared spectroscopy (FTIR) (Figure 1) and ^{1}H-NMR (Figure 2). The yield of DGETP-Me monomer was 67%.

IR(KBr): 3025–2850 cm^{-1} (CH_2), 1600, 1500 cm^{-1} (aromatic ring), 1080, 1030 cm^{-1} (ether), 915 cm^{-1} (epoxy group). ^{1}H-NMR(CDCl$_3$): 2.31 ppm (s, 3H, aromatic CH$_3$); 2.80–2.92 ppm (m, 4H, epoxy CH$_2$); 3.38 ppm (t, 2H, epoxy CH); 4.00–4.21 ppm (d, 4H, CH$_2$); 6.87 ppm (d, 1H, aromatic); 6.98 ppm (d, 2H, aromatic); 7.37 (d, 2H, aromatic); 7.55 ppm (d, 6H, CH).

The molecular weight distribution of the synthesized DGETP-Me monomer was evaluated by gel permeation chromatography (GPC; Figure 3). A sharp peak at 9.3 mL elution volume with an area ratio of 92% contained the main component, and
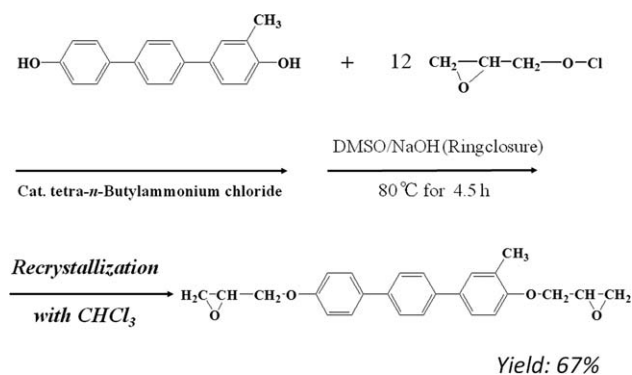
Scheme 1. Synthesis pathway of DGETP-Me.

**Figure 1.** IR spectra of the synthesized DGETP-Me.

another peak, stemming from a side reaction, was present at 8.4 mL elution volume. The epoxy equivalent, calculated by titration using the HCl (aq)-pyridine method, was 215 eq/g (theoretical value: 194 eq/g).

### Synthesis of the Diglycidyl Ether of Terephthalylidene-bis-(4-amino-3-methylphenol)

DGETAM was synthesized by the condensation of terephtalalde-hyde and 4-amino-3-methylphenol and then epoxidation with chloromethyloxirane.[6] The synthesized epoxy resin adopted a nematic phase in the temperature range 169–212°C: C 169, N 212, I.
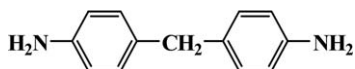
Curing Materials

The epoxy monomers used were the diglycidyl ether of 3-methyl-terphenyl (DGETP-Me; $M_w = 388$)
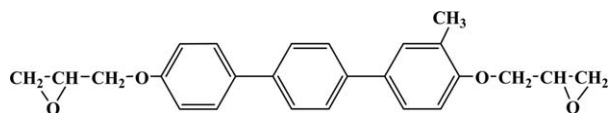
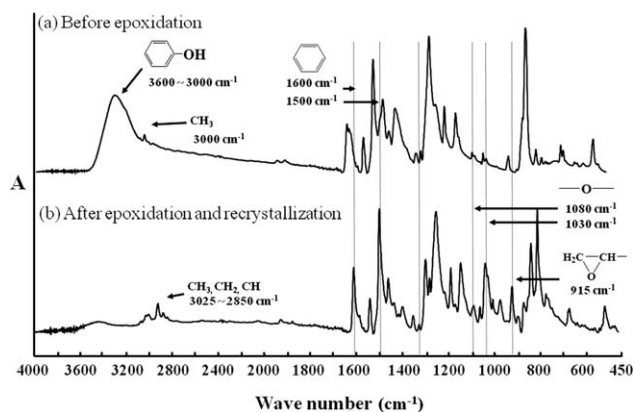and terephthalylidene-bis-(4-amino-3-methylphenol). (DGE-TAM; $M_w = 456$).
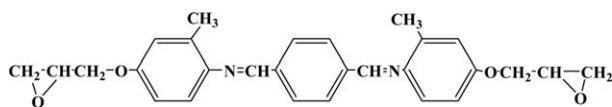
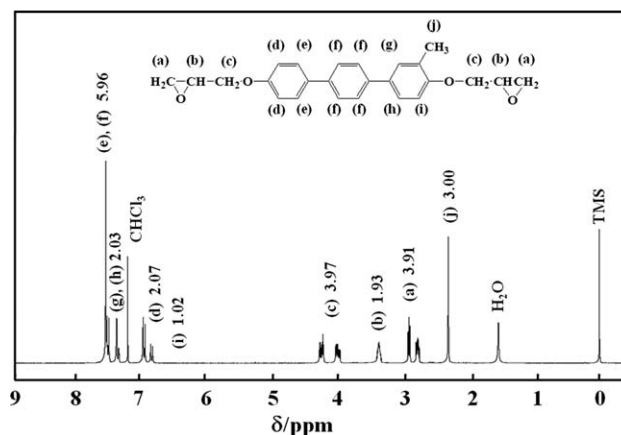The curing agent was 4,4′-diaminodiphenylmethane (DDM; m.p. 91°C, $M_w = 198$, Tokyo Chemical Industry Co., Ltd.).

Curing of the Epoxy Resin (DGETP-Me)

Initially, epoxy monomer (2.00 g, 0.0052 mol) was melted at 220°C in an aluminum sample container ($32 \times 12 \times 10$ mm^3). Then, a stoichiometric amount of curing agent (0.52 g, 0.0026 mol) was added at 240, 170, or 160°C stirred for 1 min, and then cured in an oven for 10 min. All cured systems showed almost same T_g: 230°C.
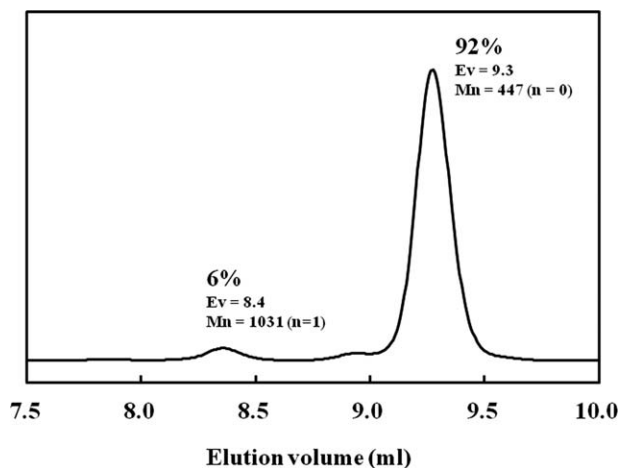

Figure 2. ^{1}H-NMR spectrum of the synthesized DGETP-Me.

Curing of the Epoxy Resin (DGETAM)

A stoichiometric amount of curing agent (0.24 g, 0.0012 mol) and the epoxy monomer (1.10 g, 0.0024 mol) were combined in an aluminum sample container ($32 \times 18 \times 10$ mm^3) and cured for 30 min at 165°C, or 20 min at 190°C. Both cured systems showed almost same T_g: 210°C.

Figure 3. GPC analysis of the synthesized DGETP-Me.
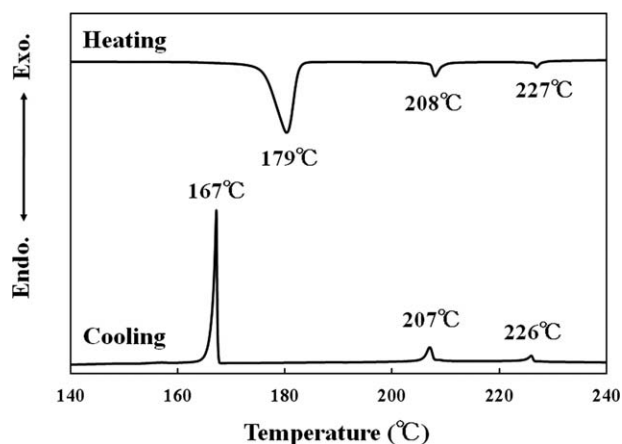
Figure 4. DSC curve of the DGETP-Me during the heating and cooling process.

Figure 6. Time-temperature-transformation diagram of the DGETP-Me/DDM systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Measurement

Characterization. The synthesized epoxy monomers and cured resins were incorporated into KBr pellets and analyzed by FTIR spectroscopy (SPECTRUM 100, Perkin–Elmer, Inc.).

Glass transition temperatures were determined using a differential scanning calorimeter (DSC7020, Seiko Instruments, Inc.) at a heating rate of 5°C/min.

The LC textures of the epoxy monomer and cured resins were analyzed with crossed polarized light from a polarized optical microscope (POM; BH-2, Olympus Co.). The thickness of the polished curings was ∼40 μm.
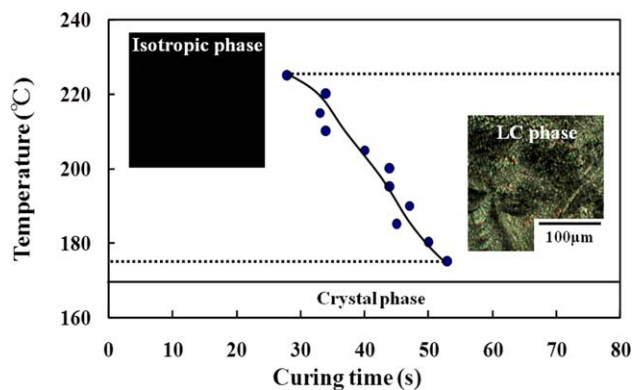
Anisotropy of the network chains in the LC domains was evaluated using a wide angle X-ray diffractometer (XRD; NANO-Viewer MicroMax-007HF, Rigaku Co.) equipped with an imaging plate (R-AXIS IV, Rigaku Co.). Layer spacings were calculated using Bragg's formula ($n\lambda = 2d\ \sin\theta$), and diffraction patterns were obtained with Cu-Kα ($\lambda = 0.154$ nm) irradiation generated at 40 kV and 30 mA. The thickness of the sample was 2.2 mm.

Stability and Fracture Toughness. Acid resistance was evaluated by immersing specimens in $0.5M$ HCl (aq) (pH = 0.3) for 28 days at room temperature. The immersed specimens were removed from the acid daily, rinsed with distilled water, air dried, and weighed.

RESULTS AND DISCUSSION

Characterization and Liquid Crystallinity of DGETP-Me Monomer

The DSC curves of the DGETP-Me during the heating process and cooling process are shown in Figure 4. The DGETP-Me

monomer exhibits three endothermic DSC peaks at 178, 208, and 227°C during the heating process. The large peak area for the feature at 178°C suggests that this is the melting temperature. Moreover, the three exothermic peaks were observed at 167, 207, and 226°C during the cooling process.

To elucidate the phase transition behavior, polarized optical micrographs of the DGETP-Me monomer were obtained (Figure 5). At room temperature, the monomer is crystalline, but at temperatures above 179°C, a birefringence pattern emerged and the focal conic texture associated with a smectic A type LC phase was observed. At 208°C, the monomer transitions to a schlieren texture, consistent with the formation of a nematic LC phase (Figure 5). Smectic A and nematic LC phases in this temperature range emerge because of the self-organization of the mesogenic-containing monomers DGETP-Me. At temperatures greater than 227 C, visibility decreased, indicating an isotropic phase; at high temperature, strong thermal molecular motions disrupt the π–π stacking interaction of the mesogenic groups, leading to the isotropic structure. This analysis showed that, depending on the temperature, the DGETP-Me monomer can exist in one of four forms and can exhibit two types of LC phases over a wide temperature range. Even in the cooling process, the LC pattern of the DGETP-Me monomer was almost the same as that during the heating process.

The time-temperature-transformation (TTT) diagram constructed for the DGETP-Me/DDM system is shown in Figure 6. At 170°C, the epoxy monomer and curing agent mixture retains its crystallinity. At 175–225°C, the system adopts an isotropic phase during the initial curing stage, and gradually develops
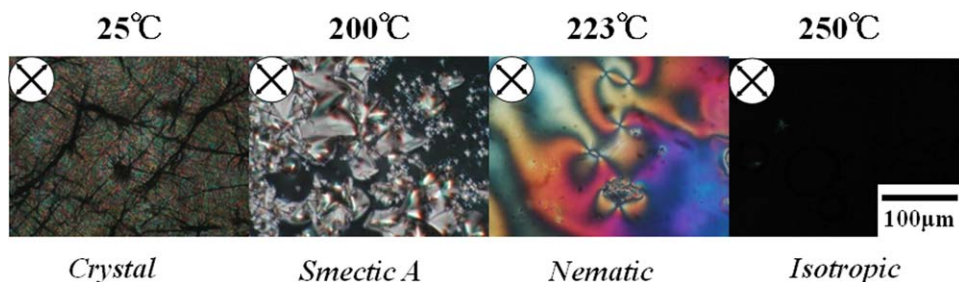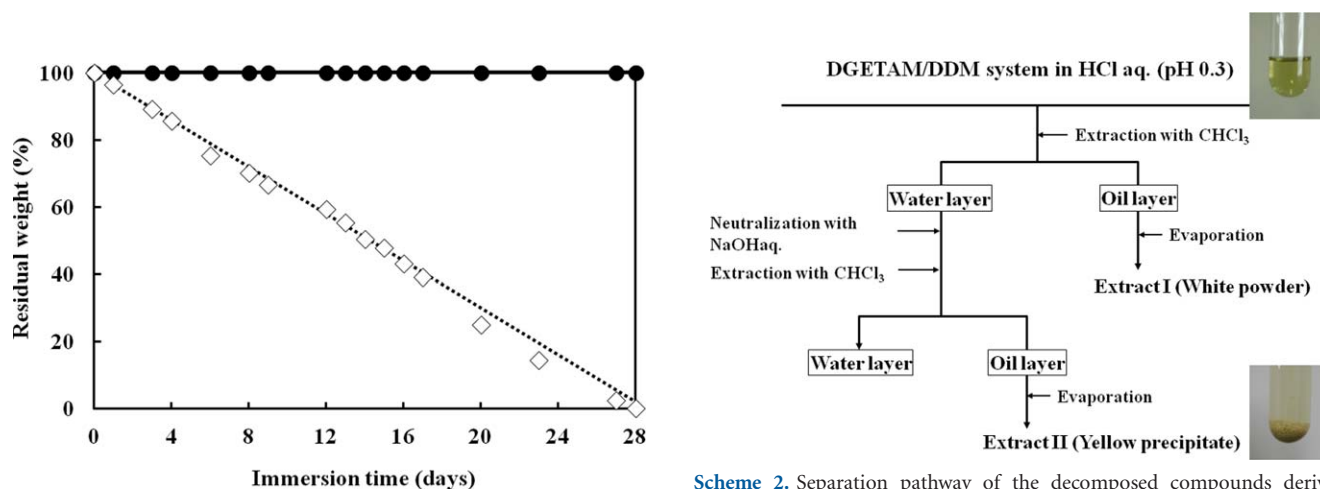

Figure 5. Polarized optical micrographs of the DGETP-Me. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
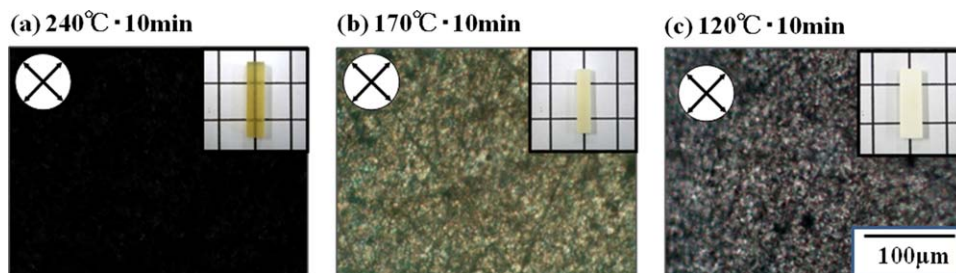
Figure 7. Polarized optical micrographs of the DGETP-Me/DDM systems. (a) 220 °C 10 min, (b) 190 °C 10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
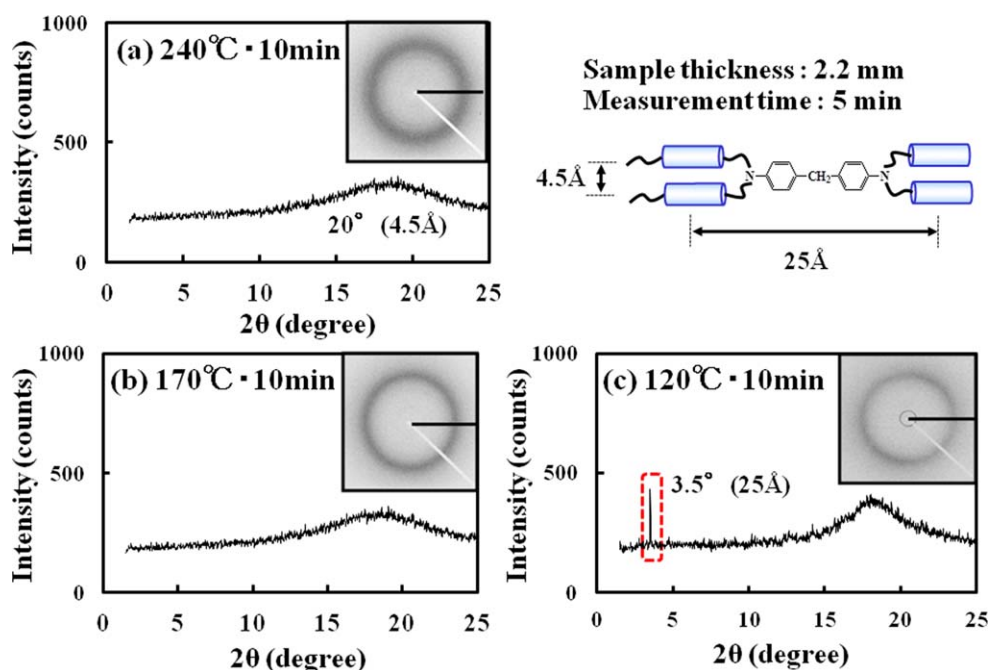
Figure 8. XRD patterns of the DGETP-Me/DDM systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Acid resistance of the (●) DGETP-Me/DDM (LC phase) and (◇) DGETAM/DDM (LC phase) systems.

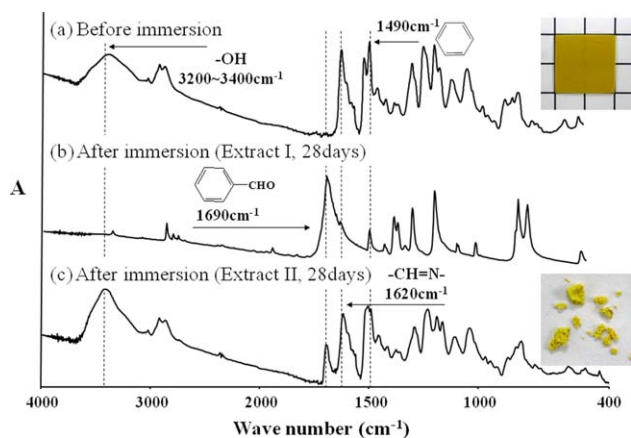**Scheme 2.** Separation pathway of the decomposed compounds derived from DGETAM/DDM system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10. IR spectra of the DGETAM/DDM (LC phase) system immersed in 0.5*M* HCl aq. (pH = 0.3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(between 30 and 50 s) into a LC phase with a characteristic birefringence pattern; a locked LC phase structure formed at these curing temperatures. At temperatures greater than 225°C, the systems were isotropic from the entire curing process. This analysis showed that LC and isotropic systems could be prepared by varying the curing temperature.

Preparation of Bulk DGETP-Me/DDM Systems with Variable Phase Structures and Acid Resistance

The physical properties of bulk isotropic and LC cured systems, prepared using the TTT diagram specifications, were evaluated. It is important to note that the structures of the bulk curings are strongly dependent upon the heat of reaction. As a result, the actual curing temperature was determined by considering

the temperature increase caused by the exothermic curing reaction.

Polarized optical micrographs of the polished, diglycidyl ether of 3-methyl-terphenyl/4,4′-diaminodiphenylmethane (DGETP-Me/DDM) systems cured at 240, 170, and 120°C are shown in Figure 7. The system cured at 240°C was transparent and was observed as a dark field under the cross-nicols, meaning that the network is composed of isotropic chains. Alternatively, the systems cured at 170 and 120°C were opaque and had birefringence patterns consistent with a LC phase.

Figure 8 shows the XRD patterns of the systems cured at 240, 170, and 120°C. The systems cured at 240 and 170°C exhibited broad halos at ∼20° (4.5 Å) indicative of amorphous structures; the system cured at 170°C was previously shown to exhibit a birefringence LC pattern, and likely consists of many nematic LC domains. For the system cured at 120°C, a high intensity peak at 3.5° (25 Å) was observed, which signifies a smectic LC phase. This peak is representative of a layered smectic structure, and the distance calculated using Bragg's law is the length of the layered phase. Based on this data, two types of networks could be prepared depending on the curing temperature chosen.

The resistance of DGETP-Me to acid was compared to that of the DGETAM using HCl aq. immersion tests (see Experimental section for details). The residual weight of the nematic DGETAM/DDM system decreased drastically as a function of immersion time and reached 0 wt % after 28 days, whereas the nematic DGETP-Me/DDM system maintained its original weight over the course of the experiment (Figure 9).

The appearance and IR spectrum of the DGETP-Me/DDM system, before and after immersion in HCl aq., were also
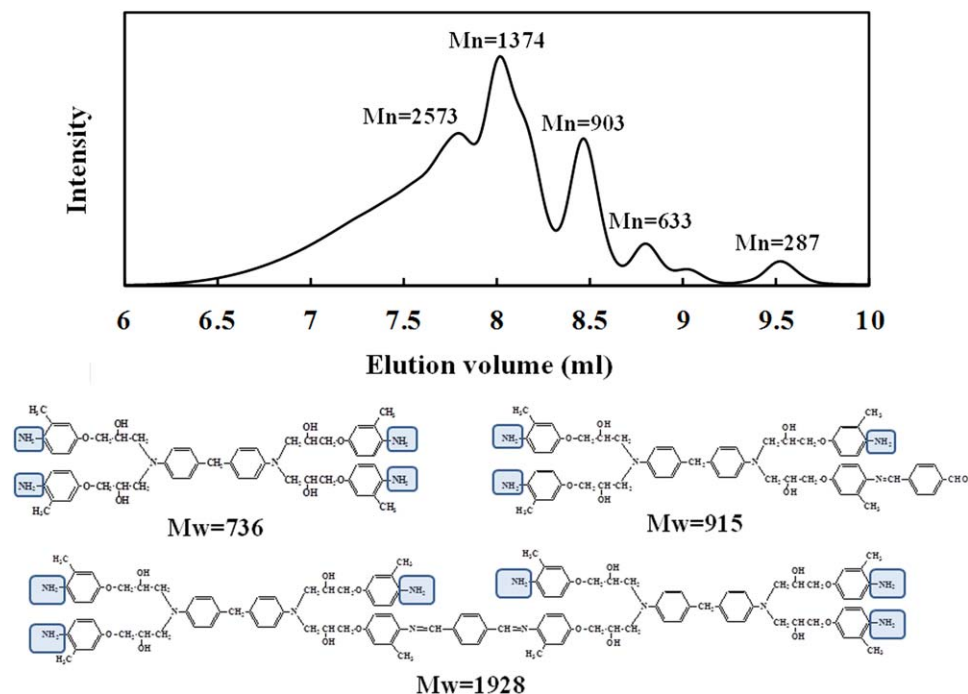
Figure 11. GPC chart of extract II and an example of predicted structures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
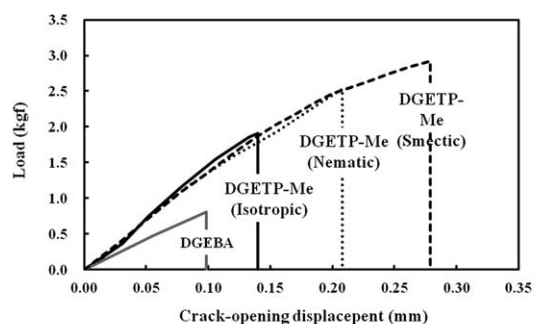
Curing systems	Phase structure		J_{Ic} (kJ/m^2)
DGEBA/DDM			0.38 ± 0.02
DGETP-Me/DDM	Isotropic	(240℃, 10min)	0.61 ± 0.02
	Nematic	(170℃, 10min)	1.15 ± 0.03
	Smectic	(120℃, 10min)	1.60 ± 0.02

Figure 12. Fracture toughness of the DGETP-Me/DDM systems.

evaluated. The sample became green after immersion in aqueous HCl, due to the absorption of water by DDM. IR measurements showed that the peaks associated with hydroxyl stretching, at 3200–3400 cm^{-1}, increased after the sample was exposed to HCl aq., but the peaks in the range 400–1700 cm^{-1} did not change, indicating that the DGETP-Me/DDM system is resistant to degradation by acid.

The DGETAM/DDM system decomposed, and the degradation products dissolved in HCl aq. (pH = 0.3). The procedure to reprecipitate the dissolved components is shown in Scheme 2. White (I) and yellow (II) powder extracts were isolated from the separation process. The IR spectra and appearances of the DGETAM/DDM system before and after immersion in HCl (aq) are shown in Figure 10. Before immersion, the C=N stretching vibration at 1620 cm^{-1} was clearly observed (Figure 10).

However, after immersion, extract I (soluble in CHCl$_3$) showed a drastic decrease in the intensity of the peak at 1620 cm^{-1}, whereas a new peak, corresponding to the aldehyde group, appeared at 1690 cm^{-1}. Based on this result, we assume that this component is p-hydroxybenzaldehyde. The IR spectrum for extract II, which was dissolved in oil after neutralization with NaOH, exhibited peaks at 1620, 1690, and between 3200 and 3400 cm^{-1}, assigned as C=N, aldehyde, and hydroxyl functional groups, respectively. Thus, it is assumed that extract II contains the amine groups formed by the hydrolyzed C=N bond; this extract was soluble in water, likely as a salt, during the CHCl$_3$ extraction.

GPC was performed on extract II to help characterize the degradation products (Figure 11). The GPC data indicates that extract II contains a variety of products over a wide molecular-weight range. Based on this result, it appears that this extract consists of various polyamines containing the partially or fully hydrolyzed DGETAM/DDM. These results suggest that DGETAM, which contains a C=N moiety in the backbone, is easily hydrolyzed in HCl. Therefore, synthesized DGETP-Me exhibits superior chemical resistance when compared to DGETAM.

Fracture Toughness Analysis

Fracture toughness (J_{IC}) of DGETP-Me/DDM with different LC phase structures was evaluated from the relationship between the crack opening displacement versus load and is shown in Figure 12. The load of the systems showed considerable increases with a corresponding increase in the orientation of the LC structures. The isotropic system had a higher J_{IC} value (0.61 kJ/m^2) than the DGEBA system (0.38 kJ/m^2), meaning that even the isotropic LC epoxy resin system had high fracture toughness (Figure 12). Moreover, the nematic and smectic systems showed considerably higher J_{IC} values (1.15 and 1.60 kJ/m^2) than the isotropic system. In summary, high-fracture toughness was achieved by introducing highly ordered polydomain structure into the LC epoxy resin system.

CONCLUSIONS

A terphenyl LC epoxy resin, DGETP-Me, was synthesized and the relationship between its phase structure and curing temperature was determined. It was found that the DGETP-Me LC system showed markedly higher resistance to HCl than the Schiff-base mesogenic epoxy DGETAM LC, and remained intact even after 28 days; the DGETAM system decomposed rapidly due to the hydrolysis of the Schiff-base mesogenic group.[4–6] Moreover, DGETP-Me exhibited excellent fracture toughness.

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