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Relationship between the structure of the bridging group and curing of liquid crystalline epoxy resins

Jun Yeob Lee[a], Jyongsik Jang[a,*], Soon Man Hong[b], Seung Sang Hwang[b], Kwang Ung Kim[b]

[a]*Department of Chemical Technology, College of Engineering, Seoul National University, Shinlimdong 56-1, Seoul, South Korea*
[b]*Polymer Processing Laboratory, Korea Institute of Science and Technology (KIST), PO Box 131, Cheongryang, Seoul, South Korea*

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Abstract

The influence of the bridging group between the mesogenic group and the oxirane ring on the curing behavior and the liquid crystalline phase of liquid crystalline epoxy (LCE) resins was investigated. Two LCE resins containing ether and ester bridging groups were synthesized for this purpose. The ether linkage stabilized the liquid crystalline phase of the LCE and the LCE network more than the ester linkage. The retardation effect of curing was observed in LCE with the ester linkage. The LCE with the ether bridge showed higher mechanical and thermal properties than that with the ester bridge. The liquid crystalline phase of the LCE monomer remained after the crosslinking reaction and it was stable up to 300°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline epoxy resin; Nematic phase; Bridging group

1. Introduction

In recent years, liquid crystalline epoxy (LCE) resins have gained considerable interest due to their excellent properties. High mechanical properties, orientation by external effects and dimensional stability are unique properties of LCE resins.

Three types of LCE resins, ester LCE [1–6], methylstilbene LCE [7–13] and biphenol LCE [14–16], have been intensively studied by many researchers. The photoinitiated polymerization of aromatic ester-based LCE was reported by Jahromi et al. [1] and Broer et al. [2]. They observed birefringence and polymerization rate of LCE during curing. The effects of a flexible spacer and a magnetic field were also investigated [1,3]. Carfagna and co-workers [7–9] and Barclay et al. [10,11] synthesized methylstilbene-based LCE. They prepared an anisotropic LCE network through curing under the influence of a magnetic field. The liquid crystalline phase of the LCE network was affected by the molecular weight of LCE. The smectic phase was obtained on curing low-molecular-weight LCE, while the nematic phase appeared in the case of high-molecular-weight LCE [10]. Biphenol-based LCE synthesized by Su [14] showed a high glass transition temperature of 231°C and a low coefficient of thermal expansion. Mallon and Adams [15] examined the liquid crystalline phase of biphenol-based LCE cured with an aromatic amine and found that the increase in crosslink density resulted in the smectic phase. Among these LCE resins, aromatic ester-based LCE is promising as an advanced material because it is easy to synthesize and has a high heat resistance and excellent mechanical properties.

In this study, two LCE resins based on aromatic ester mesogenic groups were synthesized to investigate the effect of the bridging group on the curing behavior and the liquid crystalline phase of LCE. Ether and ester linkages were introduced as bridging groups connecting the mesogenic group with the oxirane ring. Thermal analysis was performed using a differential scanning calorimeter and the liquid crystalline phase of the cured LCE network was examined at various curing temperatures. The thermomechanical properties of the LCE network were also investigated.

2. Experimental

2.1. Synthesis of LCE resins

The synthetic scheme and chemical structure of LCE are presented in Fig. 1. Allyl alcohol, terephthaloylchloride,

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* Corresponding author. Tel.: +82-2-880-7069; Fax: +82-2-888-1604; E-mail: jsjang@plaza.snu.ac.kr

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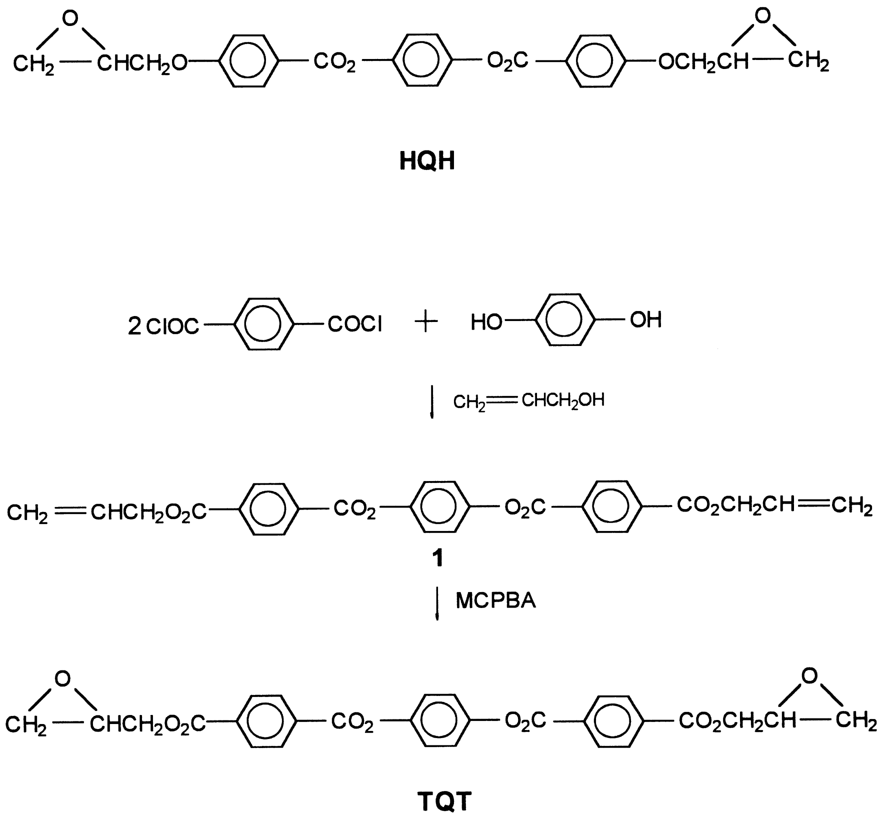

Fig. 1. Synthetic scheme and chemical structure of the liquid crystalline epoxy resin.

3-bromopropene, ethyl-4-hydroxybenzoate and hydroquinone were supplied by Aldrich and used without further purification.

2.1.1. *p-Phenylene-di[4-(2,3-epoxypropyloxy)benzoate] (HQH)*

The synthesis of HQH was reported in a previous paper [6].

$T_{KN} = 181°C$; $T_{NI} = 229°C$.

^{1}H NMR ($CDCl_3$), δ (ppm): 2.82 (2H, dd, CH_2 of epoxy); 2.94 (2H, dd, CH_2 of epoxy); 3.43 (2H, m, CH of epoxy); 4.12 (2H, dd, CH_2 of glycidyl); 4.35 (2H, dd, CH_2 of glydicyl); 7.03 (4H, d, aromatic); 7.34 (4H, s, aromatic); 8.12 (4H, d, aromatic).

2.1.2. *p-Phenylene-di[(2,3-propenyloxy)terephthalate] (**1**)*

A solution of terephthaloylchloride (24.3 g, 0.12 mol) in 500 ml chloroform was prepared and 100 ml tetrahydrofuran solution containing hydroquinone (5.5 g, 0.05 mol) and pyridine (9.0 g, 0.12 mol) was added dropwise over a period of 2 h in an ice bath. The solution was stirred vigorously at 50°C for an additional 6 h and a mixture of allyl alcohol (7.0 g, 0.12 mol) and pyridine (9.0 g, 0.12 mol) was added to the solution dropwise over a period of 2 h. The solution was refluxed for 6 h and cooled slowly to room temperature. The white solid in the solution was filtered and washed with 100 ml of hot chloroform three times. The filtrate was evaporated at room temperature. The solid product was rinsed with 1000 ml of 5% Na_2CO_3 solution and methanol successively. It was dried in a vacuum oven at room temperature for 24 h. A white solid was obtained (17.0 g, yield 70%).

2.1.3. *p-Phenylene-di[(2,3-epoxypropyloxy)terephthalate] (TQT)*

A mixture of **1** (14.6 g, 0.03 mol), 75% 3-chloroperoxybenzoic acid (18.4 g, 0.08 mol) and dichloromethane (200 ml) was refluxed for 4 days. After filtration of the solid, the dichloromethane solution was washed successively with 5% Na_2SO_3 aqueous solution (200 ml), 5% Na_2CO_3 aqueous solution (200 ml) and concentrated NaCl solution (200 ml). The dichloromethane solution was dried over $MgSO_4$ and dichloromethane was evaporated. The pure product was obtained after recrystallization from ethyl acetate (6.2 g, yield 40%).

$T_{KN} = 182°C$; $T_{NI} = 209°C$.

^{1}H NMR ($CDCl_3$), δ (ppm): 2.85 (2H, dd, CH_2 of epoxy); 2.96 (2H, dd, CH_2 of epoxy); 3.39 (2H, m, CH of epoxy); 4.19 (2H, dd, CH_2 of glycidyl); 4.73 (2H, dd, CH_2 of glydicyl); 7.30 (4H, s, aromatic); 8.23 (8H, dd, aromatic).

2.2. *Curing of LCE resin*

Diaminodiphenyl ester (DDE) was used as curing agent for the curing of LCE. DDE was synthesized by reduction of 4-nitrophenyl-4′-nitrobenzoate and recrystallized from an ethanol/water mixed solvent. LCE and DDE were mixed in dichloromethane/acetone cosolvent at room temperature. After evaporation of the solvent the mixture was dried in a vacuum oven and stored at − 10°C before use. The mole ratio of DDE to LCE was 0.45. The mixture was cured at 180°C for 2 h and postcured at 230°C for 2 h.

2.3. Physical measurements

Transition temperatures of LCE resins were determined by differential scanning calorimetry (DSC) using a DuPont 2100 differential scanning calorimeter and a polarized optical microscope at a heating rate of 10°C $\min^{-1}$. Nuclear magnetic resonance (NMR) spectra of LCE resins were obtained using a Varian 200 MHz NMR spectrometer and tetramethylsilane was used as internal standard. The liquid crystalline phase of the LCE resins and LCE networks was observed with a Nikon optical microscope equipped with a Mettler FP82 hot stage and FT80 central processor at a magnification of 200 ×. Dynamic and isothermal curing was performed by DSC to observe the curing behavior of the LCE mixtures. Dynamic curing was performed at a heating rate of 20°C $\min^{-1}$ and the isothermal curing temperatures were 180, 200, 220 and 240°C.

A dynamic mechanical thermal analyzer (Rheometris MK III) was used to measure the elastic modulus (E') and the coefficient of thermal expansion (CTE) of the cured LCE network. Data were collected in tensile mode at a frequency of 1 Hz and the heating rate was 5°C $\min^{-1}$. CTE was measured in static mode at a constant load of 0.1 N.

3. Results and discussion

The two LCE resins, HQH and TQT, synthesized in this experiment exhibited a stable nematic liquid crystalline phase from 181 to 229°C and from 182 to 209°C respectively. The clearing point of HQH with the ether bridge was higher than that of TQT with the ester bridge. The temperature range of the mesophase for HQH possessing the ether bond between the mesogenic group and the oxirane ring was larger than that for TQT with the ester linkage. This relationship is in agreement with the data reported for a low-molecular-weight liquid crystal by Dewar and Goldberg [17] and for a liquid crystalline polymer by Jedlinski et al. [18]. It is well known from extensive research that the stability of the mesophase is mainly affected by the polarity of the mesogenic group and the aspect ratio of the mesogenic molecule. The mesophase of LCE is stabilized through polar interaction between adjacent chains. The long molecule makes the mesophase of the liquid crystal stable because of the increase in the geometrical anisotropy. The ether linkage stabilizes the mesophase of the LCE through mutual conjugation between the ether unit and the central carbonyl unit. On the other hand, the electron-withdrawing ester linkage destabilizes the mesophase as it makes the central carbonyl group less polar and reduces the resonance interaction. The ester-type terminal group is more bulky than ether one and should tend to reduce the anisotropy of the molecule, lowering the transition temperature of LCE. This is easily understood from the geometry of TQT and HQH (Fig. 2). HQH is more linear and has a longer mesogenic group than TQT. The mesogenic length of HQH is 18.3 Å and that of TQT is 17.7 Å. The difference of the stereo structures of the two resins originates from the bulkiness of the terminal group. HQH has a coplanar and linear geometry through mutual conjugation of the mesogenic group. In contrast to HQH, the terephthalate group in TQT is twisted out of the molecular plane due to the steric hindrance of the oxygen in the carbonyl group with the hydrogen in the ortho position of the phenyl ring of the terephthalate group. Thus, the ester terminal group induces steric interaction between the carbonyl oxygen and the hydrogen in the phenyl ring, resulting in a decrease in the mesogenic length.

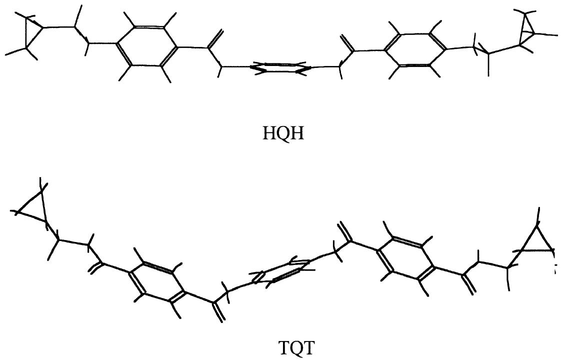

Fig. 2. 3D chemical structures of liquid crystalline epoxy resins.

The curing behavior of TQT and HQH was observed using DSC to investigate the effect of the bridging group on the curing of LCE. Fig. 3 shows dynamic DSC

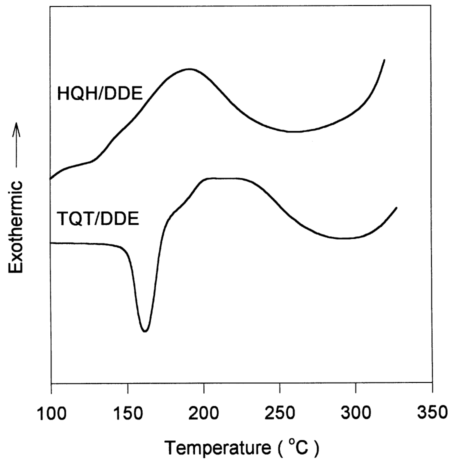

Fig. 3. Dynamic DSC thermograms of HQH/DDE and TQT/DDE.

thermograms of HQH and TQT mixed with DDE. LCE mixtures were heated at 20°C min^{-1} in a nitrogen atmosphere. HQH/DDE showed a broad exothermic peak corresponding to the curing reaction between HQH and DDE. No endothermic peak was displayed in dynamic DSC thermograms, indicating that crosslinking between HQH and DDE occurs prior to melting of HQH and DDE. That is, the curing reaction of HQH/DDE starts in the solid state below 150°C. Therefore, the curing reaction of HQH/DDE proceeds slowly in the early stage of curing. The slope increases steeply above 150°C as the crosslinking reaction of HQH/DDE occurs in the liquid state. From polarizing optical microscopy observations, it was found that the melting of the monomers and partially crosslinked prepolymers occurred at around 150°C. However, the endothermic peak could not be clearly observed as the curing reaction and the melting of HQH/DDE took place simultaneously. TQT/DDE displayed different dynamic curing behavior. An endothermic peak and an exothermic peak with a shoulder were shown in TQT/DDE. The endothermic peak is attributed to co-melting of TQT and DDE and the exothermic peak is assigned to a crosslinking reaction of TQT with DDE. The presence of the melting peak indicates that the curing of TQT/DDE occurs after complete melting. The difference in the dynamic curing behavior can be explained by the chemical reactivity and compatibility of LCE. The high chemical reactivity and low compatibility of HQH with DDE results in the solid state curing initially, while the low chemical reactivity and high compatibility of TQT with DDE leads to the curing reaction after the melting of the monomers. The peak temperature of the exotherm is higher in TQT/DDE than in HQH/DDE, implying that the reactivity of HQH toward DDE is superior to that of TQT with DDE. This will clearly be manifested in isothermal DSC data.

Isothermal DSC thermograms of HQH/DDE and TQT/DDE at 180°C are shown in Fig. 4. A sharp exothermic peak appeared in the isothermal DSC thermograms. Curing of both mixtures was fast enough to be accomplished within 20 min. The initial slope of curing was steeper and the maximum curing rate was higher in HQH/DDE than in TQT/DDE. There are several reasons for the fast curing of HQH/DDE. The electron-withdrawing aromatic ester group may accelerate the nucleophilic substitution reaction between the oxirane ring and the aromatic amine [19] and the curing in the liquid crystalline phase may also be facilitated due to the easy flow of the molecule in the nematic mesophase. The high reactivity of DDE is also another reason. The slow curing of TQT/DDE compared with HQH/DDE should be considered in terms of the crosslinking reaction mechanism of the epoxy resin. With respect to chemical reactivity, TQT should exhibit a higher curing rate than HQH because the electron-withdrawing carbonyl group is adjacent to the reactive oxirane ring if other conditions are equal. However, the opposite result was obtained in this case. This means that another mechanism which does not affect the cure of HQH/DDE is involved in the crosslinking reaction of TQT with DDE. Assuming that other conditions such as the liquid crystalline phase and viscosity during curing are similar, the large difference between TQT and HQH is in the linkage between the mesogenic group and the oxirane ring. TQT has the ester linkage and HQH the ether. The ester unit is polar and contains non-bonded electrons in the oxygen. The non-bonded electron in the carbonyl group acts as a hydrogen bond acceptor, therefore, strong hydrogen bonding is formed between the carbonyl group and the hydroxyl group produced during curing. The hydrogen bonding of the hydroxyl group with the carbonyl group deactivates the catalytic action of the hydroxyl group on curing of the oxirane ring with DDE, resulting in the retardation of the curing of TQT. The ether bond cannot have much influence on the curing as it is a weak hydrogen bond acceptor. This retarding effect of the ester unit outweighs the increase in chemical reactivity, leading to a decrease in the curing rate.

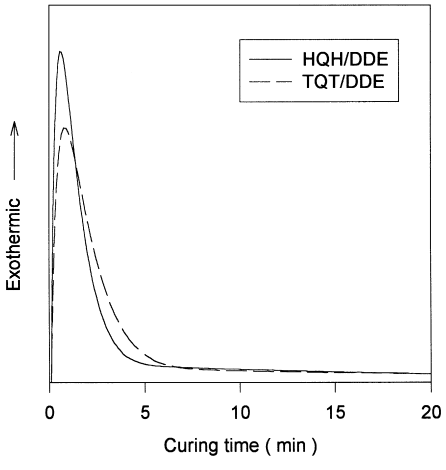

Fig. 4. Isothermal DSC thermograms of HQH/DDE and TQT/DDE.

The maximum curing rates of LCE mixtures calculated from isothermal DSC thermograms are summarized in Table 1. As can be expected from the isothermal DSC thermogram, HQH/DDE showed higher curing rates than TQT/DDE at all curing temperatures. This clearly confirms that the ether linkage facilitates the curing of the LCE resin more than the ester linkage.

HQH/DDE and TQT/DDE were cured at 180°C for 2 h and postcured at 230°C for 2 h. The degree of cure of the two mixtures after curing was similar from Fourier transform infrared (FTIR) measurements. The epoxide deformation peak almost disappeared in the postcured

Table 1
Maximum curing rates (°C min^{-1}) of HQH/DDE and TQT/DDE at various curing temperatures

	Isothermal curing temperature (°C)			
	180	200	220	240
HQH/DDE	0.15	0.18	0.20	0.21
TQT/DDE	0.12	0.15	0.17	0.20

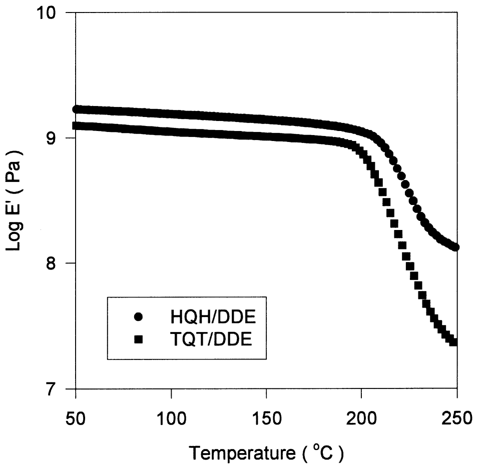

Fig. 5. DMTA thermograms of cured HQH/DDE and TQT/DDE networks.

LCE network, indicating that curing of LCE was nearly complete in this curing condition. Dynamic mechanical analysis (DMA) results of HQH/DDE and TQT/DDE networks are shown in Fig. 5. The HQH network showed a higher elastic modulus than the TQT network over the complete temperature range. In particular, the rubbery modulus of the HQH network was higher than that of the TQT network. The structural difference between HQH and TQT is the major reason for this behavior. The bulky terminal group and the bent mesogenic group of TQT prevents close packing of the TQT network and diminishes the rigidity of the main chain. The loose packing of the TQT network weakens strong interchain interactions like hydrogen bonding, resulting in high mobility of the main chain above the glass transition temperature. The lower glass transition temperature of the TQT network in comparison with that of HQH is also caused by the high chain mobility of the TQT network. The structural inhomogeneity of the TQT network should also be considered. It is known that in the case of an epoxy resin with an ester bridge the oxirane ring can react with ester groups via chain scission of the oxirane ring, followed by insertion of the ring into the C–O bond of the ester [20]. This self-polymerization reaction may reduce the crosslink density and decrease the elastic modulus and the glass transition temperature of the TQT network.

The coefficient of thermal expansion (CTE) of LCE networks was also measured with DMA in the tensile mode both in the glassy region and the rubbery region (Table 2). The CTE of the HQH network was much lower than that of the TQT network. The rigid nature of the HQH network restricts the thermal motion of the chains between the crosslink, leading to a low CTE value, especially in the rubbery region. The CTE of the TQT network was lower than that of the other epoxy resins although it was higher in comparison with the HQH network. The presence of the liquid crystalline phase which has an ordered structure reduces the interchain distance and inhibits the thermal motion of the TQT network.

Table 2
Coefficients of thermal expansion ($10^{-6}\,°C^{-1}$) of HQH/DDE and TQT/DDE

	Glassy region	Rubbery region
HQH/DDE	47	49
TQT/DDE	55	64

The liquid crystalline phase of HQH/DDE and TQT/DDE was observed at various curing temperatures with a polarizing optical microscope. HQH and TQT showed a nematic liquid crystalline phase before curing from 181 to 229°C and from 182 to 209°C respectively. Their nematic texture remained after curing. Polarized optical microscopy (POM) pictures of HQH/DDE and TQT/DDE are shown in Fig. 6. A typical thread-like nematic texture was exhibited in both mixtures. No small angle peak corresponding to long layer spacing was observed in an X-ray diffraction experiment. Their mesophase should be nematic in terms of POM and X-ray diffraction. HQH/DDE displayed the nematic phase when it was cured in the temperature range 171–270°C. Biphase, nematic phase and isotropic phase appeared up to 300°C. That is, an increase in curing temperature causes a reduction of the nematic region and an expansion of the isotropic part. It is known that a linear prepolymer generally grows in the initial stage of curing and then crosslinking locks the LCE network. The mesophase stability of LCE is determined in the early stage of curing as it depends strongly on the linearity of the prepolymer. Crosslinking only fixes and stabilizes the liquid crystalline phase developed by the linear prepolymer. As the curing temperature increases, the branched structure is readily formed initially, destabilizing the liquid crystalline phase of the LCE network. The mesophase of the LCE network was maintained within the temperature range of the

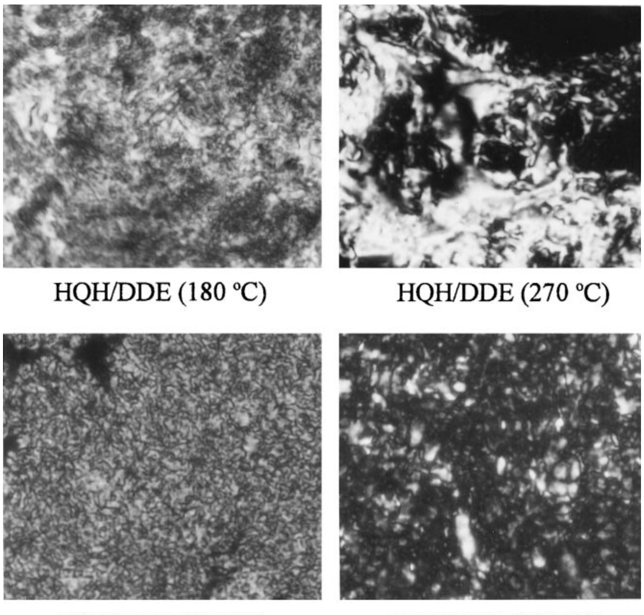
HQH/DDE (180 °C)
HQH/DDE (270 °C)
TQT/DDE (180 °C)
TQT/DDE (230 °C)

Fig. 6. Optical microscopy pictures of HQH/DDE and TQT/DDE.

POM measurement. TQT/DDE also displayed the nematic liquid crystalline phase on curing below 240°C, the biphase up to 255°C and the isotropic phase above 255°C. The mesophase temperature range of TQT/DDE was smaller than that of HQH/DDE as the mesophase of TQT is unstable compared with that of HQH. The development of the mesophase in the isotropic temperature range of LCE is due to the fact that DDE helps the formation of the liquid crystalline phase as it has a linear structure. Linear prepolymer of TQT and HQH cured with DDE exhibits a more stable mesophase than TQT and the HQH monomer itself.

4. Conclusions

The influence of the bridging group on the curing behavior of aromatic ester-based liquid crystalline epoxy (LCE) resins was investigated. The mesophase stability of LCE with an ether linkage (HQH) was superior to that of LCE with an ester linkage (TQT) and the ester linkage retarded the curing reaction of LCE with an aromatic amine. Curing of HQH started the in solid state in dynamic curing, while that of TQT began after melting of LCE and the curing agent. The thermal stability and elastic modulus were higher in the HQH network than in the TQT network and the HQH network showed a higher glass transition temperature in comparison with the TQT network. TQT with the ester linkage destabilized the liquid crystalline phase of the cured network compared with HQH. An increase in the curing temperature resulted in the expansion of the isotropic phase. The nematic liquid crystalline phase of the cured LCE network was stable at temperatures up to 300°C.

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