

Preparation of Anisotropic Films for Liquid Crystal Display Application

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ABSTRACT

The photoinitiated polymerization of 2-chloro-1, 4-phenylene bis[4-[6-(acryloyloxy)hexyloxy]benzoate](1M) and trans-1, 4-bis(4-(2-(2,3-epoxypropyloxy)-ethoxy)-phenyl)-cyclohexyldicarboxylate (3M) were studied. Both monomers exhibit a wide temperature range of nematic phase. The monomers were oriented in their nematic phase at a substrate having been coated with polyimide and unidirectionally rubbed with a nylon cloth. During polymerization, the ordering of the LC molecules was fixed, yielding a uniaxially crosslinked network. The clear LC networks exhibit a birefringence between 0.14 and 0.19, depending on the polymerization temperature. Finally, the nonmesogenic diluents, tetra(ethylene glycol) diacrylate and 1,2-bis(2,3-epoxypropyloxy)ethane were mixed with monomers 1M and 3M, subsequently decreasing the birefringences of the obtained LC networks. The LC networks containing non-mesogenic diluent exhibit not only a smaller birefringence but also a weaker birefringence dispersion in the visible region.

Keywords: LC network, compensation film, wide viewing angle, liquid crystal display.

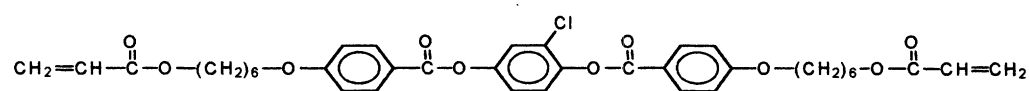
1. INTRODUCTION

Oriented liquid crystal (LC) network are an interesting class of polymeric materials with potential use in a wide variety of applications. One of the important anisotropic properties of the oriented LC thermosets is their optical anisotropy. This kind of optically anisotropic LC thermosets can be used as compensation films for liquid crystal display.¹ The macroscopic orientation of polymeric LCs has been achieved by several methods. Recently Broer²⁻⁵ et al., Hikmet⁶⁻¹² et al. have reported the in-situ photopolymerization of the oriented LC monomers to provide macroscopically ordered LC polymers by the use of photoinitiators. This paper presents data from in-situ photopolymerization of oriented mixtures of mesogenic and nonmesogenic diacrylates as well as diepoxides. The optically anisotropic properties of the oriented LC networks are discussed.

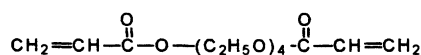
2. EXPERIMENTAL

All four monomers 1M - 4M (Figure 1) were synthesized according to literature methods^{11,12} and

purified by column chromatography. The phase behavior of the monomers and monomeric mixtures was determined by optical polarizing microscopy (Zeiss, Axiophot) and DSC analysis (Seiko, SSC/5200). Oriented networks were obtained by sandwiching the monomer with 6 μm spacers between two glass substrates provided with uniaxially rubbed polyimide films. Polymerization mixture was made by dissolving 99 wt. % of monomer and 1 wt. % of photoinitiator in dichloromethane and subsequent evaporation. Biphenyl iodonium hexafluoro-arsenate and benzophenone were used respectively as photoinitiators for diepoxide and diacrylate monomers. Polymerization of the oriented monomers was carried out with a UV intensity of 9 mW/cm^2 at 350 nm. The wavelength dependent birefringence of the obtained polymer networks was measured by a Otsuka multichannel retardation measuring system RETS-2000 (Osaka, Japan)



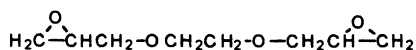
1M	Heating	K 65.7 N 116.5 I	
	Cooling	I 113.1 N 24.9 K	



2M



3M	Heating	K 93.6 N 158.4 I			
	Cooling	I 156.0 N 94.0 S	A 60.6 K	1 52.5 K	2



4M

Figure 1: Chemical structures and phase transitions of monomers 1M-4M.

3. RESULTS AND DISCUSSION

3.1 Mesomorphic properties of monomers 1M - 4M and their mixture.

Figure 1 presents the chemical structures and phase transitions of monomers 1M - 4M. As can be seen from figure 1, monomer 1M exhibits an enantiotropic nematic phase while monomer 3M displays an enantiotropic nematic and a monotropic smectic A phases. Both monomers 2M and 4M are nonmesogenic compounds and are used as diluents. Figure 2 shows the phase diagrams of the mixture of 1M and 2M. Diagram A in Fig. 2 describes the phase behavior of the mixture of 1M and 2M obtained from DSC heating scan. Both of the crystal to nematic phase transition and clearing temperatures decreases with increasing the monomer 2M content. This behavior leads to reduce dramatically the nematic temperature range. Diagram B in Fig. 2 describes the phase behavior of the mixture of 1M and 2M obtained from DSC cooling scan. The mixture reveals a nematic liquid crystal behavior even though it contains 40 mol % of the nonmesogenic diluent. Figure 3 presents the phase diagrams of the mixture of 3M and 4M. The mixture displays very similar.

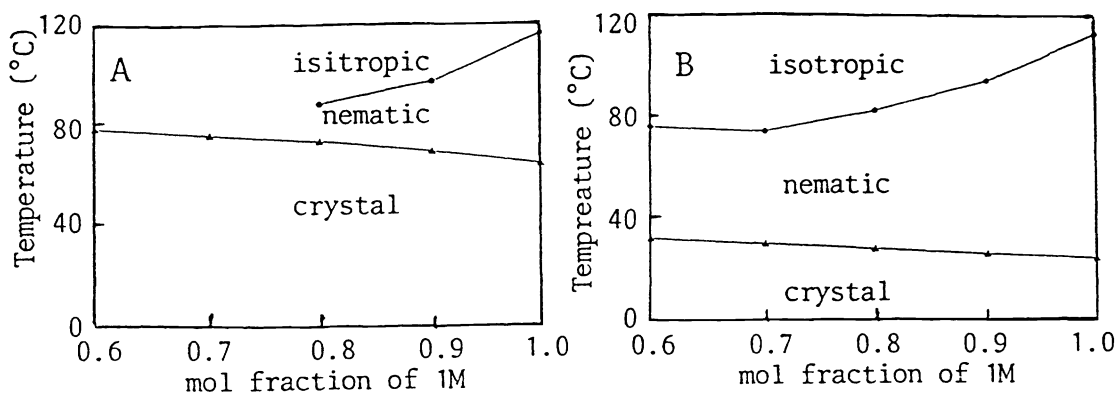


Figure 2: The phase diagram of mixtures of 1M and 2M:

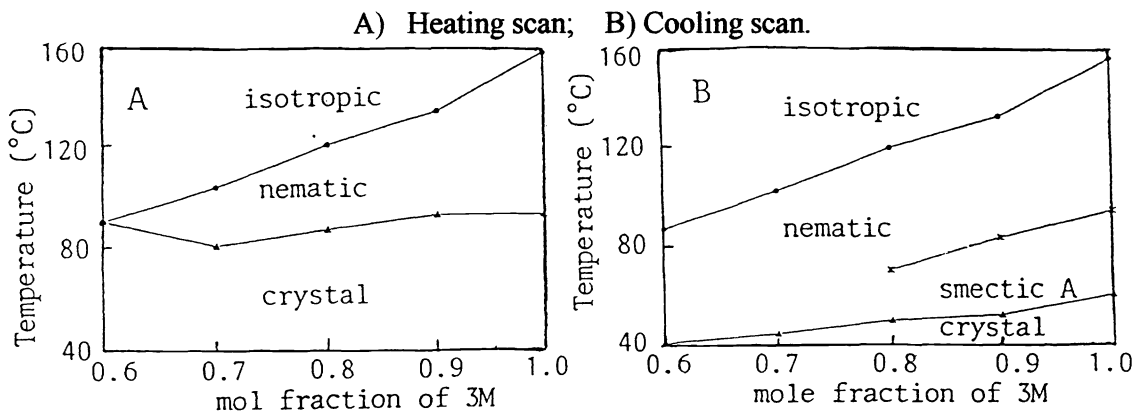


Figure 3: The phase diagrams of mixtures of 3M and 4M:

A) Heating scan; B) Cooling scan.

3.2 Polymerization of the monomers and monomeric mixtures

mesomorphic behavior with that of the mixture of 1M and 2M. Monomers and their mixtures were macroscopically oriented in a glass test cell provided with rubbed polyimide layers. The cell was filled by capillary flow at elevated temperatures ($> 50^{\circ}\text{C}$). The film thickness was about $6\ \mu\text{m}$. Upon irradiation with a UV lamp, the oriented monomers polymerized, yielding transparent polymeric films with perfect macroscopic orientation.

Monomer 1M shows a very wide temperature range of mesophase. It exhibits a nematic phase from 113.1 to 24.9°C on the DSC cooling scan. Figure 4 displays the wavelength dependent birefringence (Δn) of the LC networks (samples A – E) obtained by photopolymerization of monomer 1M at 95 , 80 ,

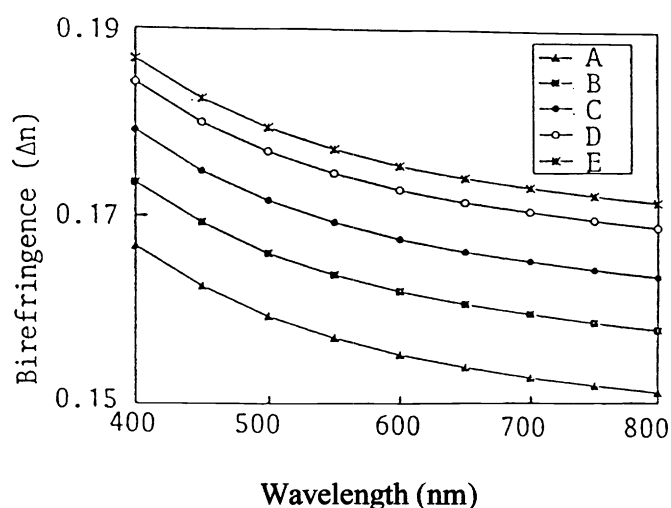


Figure 4: Wavelength dependent birefringence of LC thermosets obtained by polymerized at A) 95°C , B) 80°C , C) 65°C , D) 50°C , E) 35°C .

65 , 50 and 35°C . Film polymerized at a higher temperature and consequently at a lower degree of ordering, has smaller birefringence (Δn) than those polymerized at lower temperatures. In other words the birefringence of the oriented networks becomes smaller as the polymerization temperature increases. Since monomer 1M contains three pheny rings, the birefringence of the obtained LC networks is too high to be used for practical application.¹ A nonmesogenic diluent (2M) was designed so as to reduce the birefringence. Figure 5 presents the wavelength dependent birefringence of the LC networks (Samples F - J) obtained by photopolymerization of the mixtures of 1M and 2M at 50°C . It seems apparent that the birefringence of a LC network decreases dramatically with increasing the nonmeogenic diluent content. Sample J which contains a highest diluent content shows the smallest birefringence. Its birefringence is also weaker wavelength-dependent.

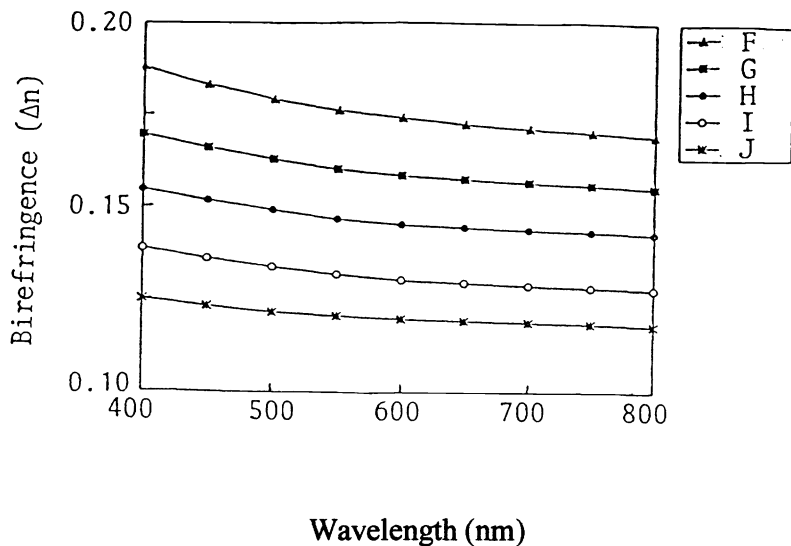


Figure 5: Wavelength dependent birefringence of LC thermosets containing F) 100%, G) 90%, H) 80%, I) 70%, J) 60% of monomer 1M.

Monomer 3M also displays a very wide temperature range of mesophase. It reveals a nematic phase from 156.0 to 94.0°C and a smectic A phase from 94.0 to 60.6°C. Figure 6 presents the wavelength

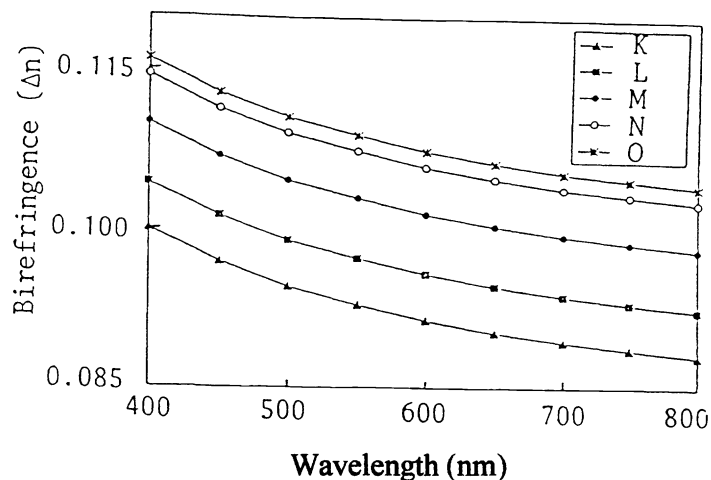


Figure 6: Wavelength dependent birefringence of by polymerized at K) 140°C, L) 125°C, M) 110°C, N) 95°C, O) 80°C.

dependent birefringence of the LC thermosets (samples K - O) obtained by photopolymerization of monomer 3M at 140, 125, 110, 95 and 80°C. Again the birefringence of the oriented networks becomes smaller as the polymerization temperature increases. Since monomer 2M contains only two

phenyl ring in the mesogenic unit, the birefringence of the obtained LC networks is much smaller than that of the LC networks prepared from monomer 1M. Figure 7 shows the wavelength dependent birefringence of the LC networks (samples P - T) obtained by photopolymerization of the mixtures of 3M and 4M at 80°C. The result also demonstrates that addition of the nonmesogenic diluent into the mixture can decrease the birefringence of the obtained LC networks.

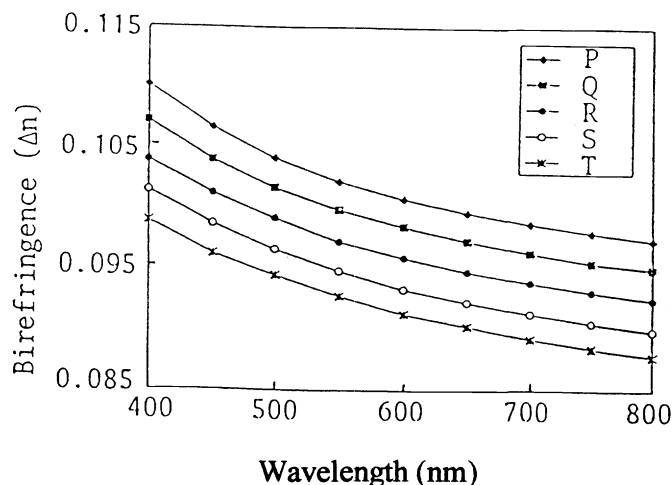


Figure 7: Wavelength dependent birefringence of LC thermostets containing P) 100%, Q) 90%, R) 80%, S) 70%, T) 60% of monomer 3M.

4. CONCLUSIONS

Two liquid crystalline diacrylate and diepoxide with a very wide temperature range of mesophase were synthesized. The photoinitiated crosslinking of both monomers, aligned on a rubbed surface, results in the macroscopically oriented polymeric networks. The obtained LC networks exhibit very large birefringence. The birefringence of the LC networks can be manipulated by controlling the polymerization temperature and the content of the non-mesogenic diluent in a LC mixture. The LC thermostets can be used as compensation films for liquid crystal display.

5. ACKNOWLEDGEMENTS

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