Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electro-Optical Effect of Varied SCLCP/LC Blend Systems

Ping Xie [a], Limin Sun [a], Daorong Dai [a], Dongsheng Liu [a], Ze Li [a] & Rongben Zhang [a]

[a] Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing, 100080, China

Version of record first published: 24 Sep 2006.

To cite this article: Ping Xie , Limin Sun , Daorong Dai , Dongsheng Liu , Ze Li & Rongben Zhang (1995): Electro-Optical Effect of Varied SCLCP/LC Blend Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 269:1, 75-87

To link to this article: http://dx.doi.org/10.1080/10587259508037322

Mol. Cryst. Liq. Cryst., 1995, Vol. 269, pp. 75–87
Reprints available directly from the publisher
Photocopying permitted by license only

Electro-Optical Effect of Varied SCLCP/LC Blend Systems

PING XIE, LIMIN SUN, DAORONG DAI, DONGSHENG LIU, ZE LI, and RONGBEN ZHANG

Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080 China

(Received May 4, 1994; in final form October 18, 1994)

Varied blend systems containing Imine-based side chain liquid crystalline polysiloxanes or ladderlike polysilsesquioxanes and corresponding low mass liquid crystal (LC) analogues were prepared by blending or crude solution mixing. In later case, in situ crosslinking took place by hydrolysis and further condensation of remained Si-H groups in the macromolecules. Electro-optic measurement results indicate rise time and optical contrast of the blend system are related to the polarity and applied voltage: the blend system containing a weak polar component exhibits lower optical contrast and "recovery" effect, meanwhile, strong polar blend system exhibits "memory" effect; short rise time and lower driving voltage for the PNLC (Polymer Network Liquid Crystal) system containing low content of polymer are similar to that of ordinary low mass LC system. Some peculiar behaviour may be caused by the "anchoring" effect and elastic deformation of the cavity. The blend system containing ladderlike polysilsesquioxane exhibits sharp electro-optic behaviour and distinct thresold voltage.

INTRODUCTION

About twenty years ago, the twisted nematic liquid crystal display (TNLCD) was developed as an electro-optic device. Later, LC compound directly used as monomer for the preparation of polymeric liquid crystals have also become of increasing interest. The side chain liquid crystalline polymers (SCLCP) are similar to the low molar mass LC, the electro-optic phenomena exhibited by these polymers[1] have also been considered in terms of potential device applications. The first electro-optical effect of SCLCP's was reported by Finkelmann and Ringsdorf.[2] In general, polymeric materials have a high viscosity compared with the low molecular nematogen. Finkelmann *et al.*[3] have tried to realize a rapid response using new silicone polymers containing a high polar cyanobiphenyl side group. In order to overcome the slow response speed, Coles *et al.*[4] attempted to examine the response behaviour of new systems in a SCLCP, which dissolves low molecular weight nematic material, short response time below 200 ms can be realized at modest voltages.

Quite recently, new optoelectronic materials based on polymer dispersed liquid crystals (PDLC)[5] showed great potential for application in displays and light shutters. New problems associated with molecular anchoring at a polymer wall were provided for further study.

This report describes the electro-optic properties of varied SCLCP/LC blend systems. The materials tested were comb-like single and double (ladderlike) chain polysiloxanes with Schiff's base (imine) group as mesogen in the side chain and low molecular LC compounds of chemically equivalent structures. One of the monomers is an aromatic nitro compound to achieve high dielectric anisotropy, and the others contain alkoxy-terminated groups.

In the crude solution mixing system, in situ crosslinking occurred due to the hydrolysis and condensation of remained Si-H groups to produce a glass-like, transparent and uniform film.

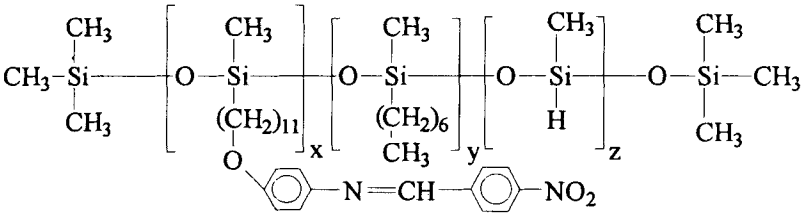
EXPERIMENTAL

Materials

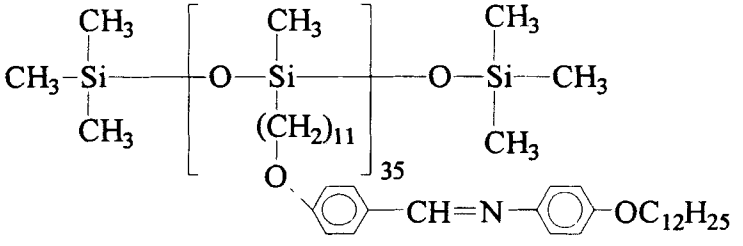
The synthesis of monomers and low mass analogues used in this experiment was referred to in ref.[6–13]. Their structures and principal properties are listed in Table 1.

The SCLCP's were synthesized via hydrosilylation reaction. The monomers containing NO_2-terminated Schiff's base mesogen and longer spacer were grafted to single chain polymethylhydrosiloxane (PMHS) or ladderlike copolysilsesquioxane (CPSQ) by the method described in literature.[14–15] Their structures are shown in the following scheme.

SP-11-NO_2



SP-3-12



Since the monomer with strong polar terminal group NO_2 cannot be added to polysiloxane main chain stoichiometrically, it is not easy to calculate the real molecular composition (i.e. x, y, z,...). Only approximate estimation was made for SP-11-NO_2 based on element analysis: x: 55%, y: 25% (starting materials mole ratio of M-11-NO_2: heptene: Si-H = 0.6: 0.4: 1).

TP-11-NO_2

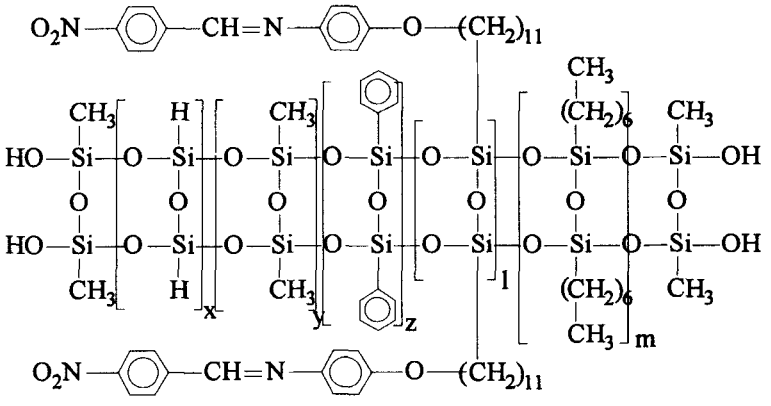


TABLE 1

The structures and characterization of LC monomers and model compounds

Compounds	Abbreviated as	T_m (°C)	T_{cl} (°C)	Textures	Mesomorphism
R'O⟨⟩CH=N⟨⟩R					
R' = C_3H_5, R = $OC_{12}H_{25}$	M-3-12	103	107	mosaic	N
C_4H_9, $OC_{12}H_{25}$	L-4-12	99	109		N
C_3H_5, CH_3	M-3-CH_3	62	no lc		
C_4H_9, CH_3	L-4-CH_3	64	72	mosaic	N
RO⟨⟩N=CH⟨⟩NO_2					
R = C_3H_5	M-3-NO_2	106	no lc		
C_4H_9	L-4-NO_2	72	62	Schlieren	N
$C_{11}H_{21}$	M-11-NO_2	67	82	broken fan, mosaic	S_A, N
$C_{12}H_{25}$	L-12-NO_2	64.5	90.2	broken fan	S_A

PREPARATION OF SCLCP/LC MIXTURE SYSTEMS

Simple solution blending was made by dissolving the purified SCLCP and analogous low mass compound in toluene and then solvent was removed by evaporation. The blend composition is listed in Table 2.

TABLE 2

Composition and transition temperatures of SCLCP/LC blend systems

No	Composition		Weight ratio of SCLCP/LC
	SCLCP	LC	
1	SP-11-NO_2	L-4-12	1: 1
2	SP-3-12	L-4-NO_2	1.5: 1.3
3	SP-11-NO_2	L-4-NO_2	1: 1

In the case of crude solution mixing system, after the hydrosilylation reaction was finished, low mass LC compound was dissolved in the crude reaction solution by mixing. In order to prepare the crosslinkable macromolecules the content of fixed side chains was controlled at lower than the total Si-H content on the macromolecules to allow for hydrolysis and condensation of the remaining Si-H groups, crosslinking and phase separation would take place during the heat-treatment to remove the solvent from the coated film. The composition of the crude solution blends is listed in Table 3.

SEM result proved the presence of the polymer network structure as shown in Figure 1. The crosslinking degree was controlled by content of 1-heptene as blocking reagent for Si-H groups. The sample with higher crosslinking was solidified.

ELECTRO-OPTIC MEASUREMENT

The sample sandwiched between two transparent conducting ITO glass plates was tempered on a hot stage of polarized microscope. The sample thickness about 20 μm

TABLE 3

Composition of LCP/LC crude solution blends

No	Composition SCLCP	LC	Weight ratio of LC/LCP
A2	SP-11-NO_2	L-12-NO_2	5: 1
B1	TP-11-NO_2	L-12-NO_2	1: 1
A4′	SP′-11-NO_2	M-11-NO_2	8: 1
B1′	TP′-11-NO_2	M-11-NO_2	10: 1

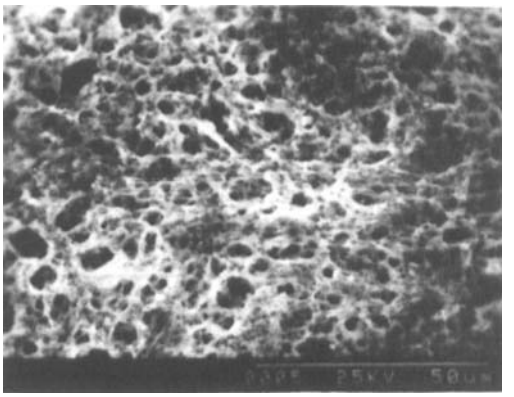


FIGURE 1 SEM photograph of solvent etched surface of B1′ film (LC: polymer = 1: 1).

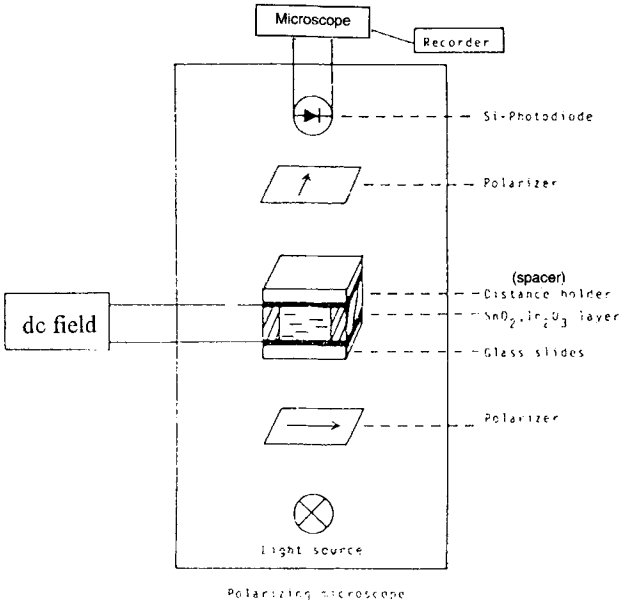


FIGURE 2 Schematic drawing of the measuring arrangement.

was controlled by polycarbonate spacers. The light intensity transmitted through the sample between two crossed polarizers was measured by a photomultiplier and recorded by a X-Y recorder. Recorded light information was attributed to the refractive index change. The whole apparatus is shown in Figure 2.

RESULTS AND DISCUSSION

A. Simple SCLCP/LC blending system

Compared with simple SCLCP with similar structure,[16] the electro-optic response of the blend system was enhanced by addition of low mass LC compound.

Effect of composition and polarity

Blend sample 3, in which both SCLCP and low mass LC compound had strong polar groups, exhibited lower driving voltage and higher optical contrast $(I_0 - I_v)/I_0$ (I_0, the initial transmission; I_v, the transmission after voltage applied) as shown in Figure 3, compared with other blend systems in which one component was of weak polarity (samples 1 and 2 as shown in Figures 4 and 5). After the electric field was turned off, sample 3 exhibited "memory" effect, meanwhile for samples 1 and 2 some relaxation or recovering would take place. This difference may be caused by two factors: (1) Viscosity effect: the addition of the component of weak polarity would decrease viscosity of system; (2) "Anchoring" effect: when the electric field was applied, the strong polar

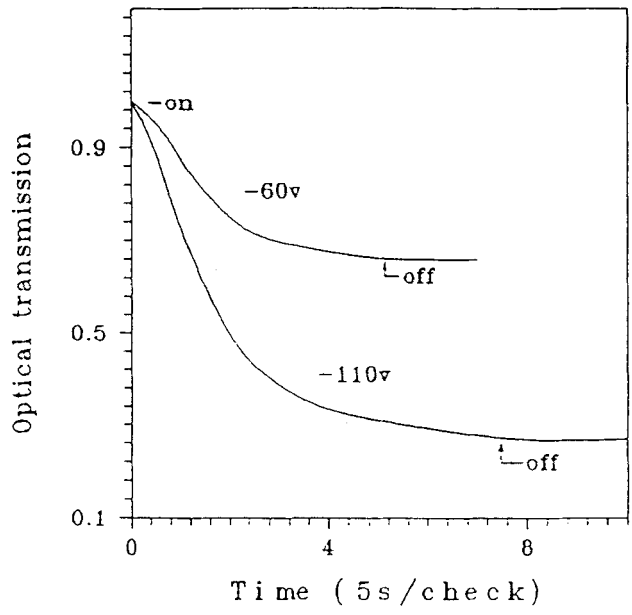


FIGURE 3 Effect of dc field on the optical response of sample 3 at 120 C (simple blend system with strong polarity).

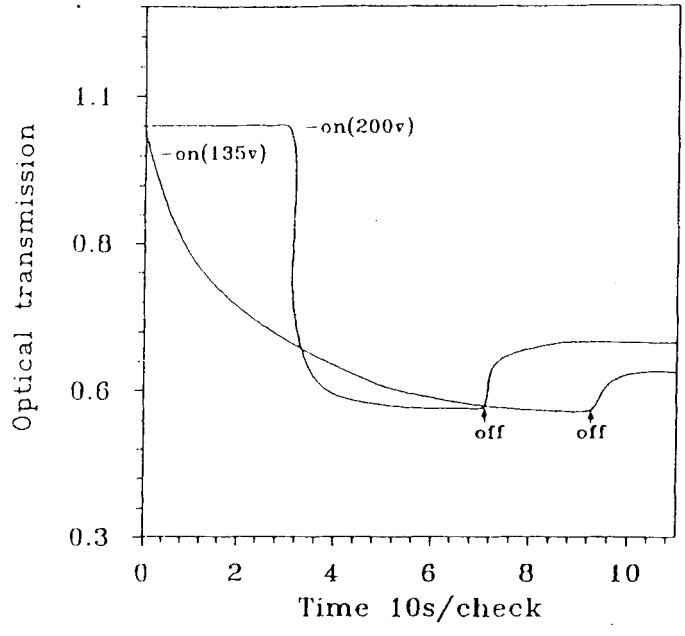


FIGURE 4 Effect of dc field on the optical response of sample 1 at 156 C (simple blend of a strong polar SCLCP and a weak polar low mass LC).

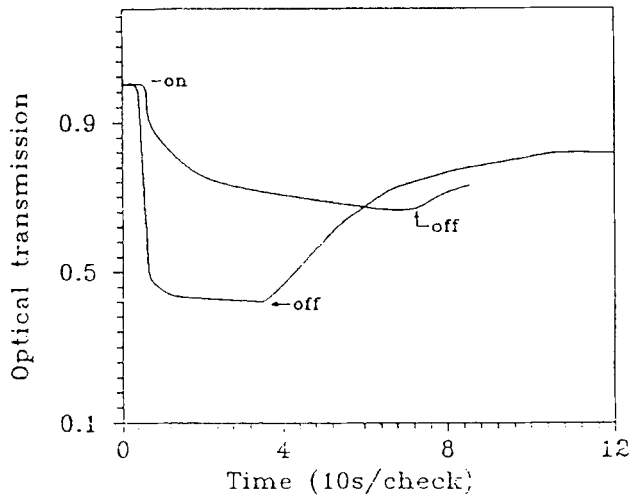


FIGURE 5 Effect of dc field on the optical response of sample 2, above: 140 C, 110 V; below: 151 C, 230 V (simple blend of a strong polar low mass LC and a weak polar SCLCP).

component would turn to homeotropic alignment immediately, but weak polar component only aligned passively in part, so lower optical contrast was displayed. When the electric field was turned off, molecules of weak polarity would exhibit insitu "anchoring effect" and withdraw the aligned molecules from the direction of the field, especially for the blend system in which LCP was of weak polarity (Figure 5). Some data are listed in Table 4.

Effect of DC Voltage and its Application History

As shown in Figures 3–5 and Figures 6 and 7, optical contrast increased with increasing applied voltage, and its application history would affect the final optical contrast,

TABLE 4

Effect of composition and polarity on electro-optic response (simple SCLCP/LC blend systems)

Sample*	Polarity		Appl. voltage	Hot stage	$I_o - I_v/I_o$	t_r (s)
	SCLCP	LC	(v)	T(°C)	%	
1	S	W	135	156	49	50
			200	156	48	6
2	W	S	110	140	33	44
			230	151	58	25
3	S	S	60	120	34	14
			110	120	73	16

* The composition was shown in Table 2.

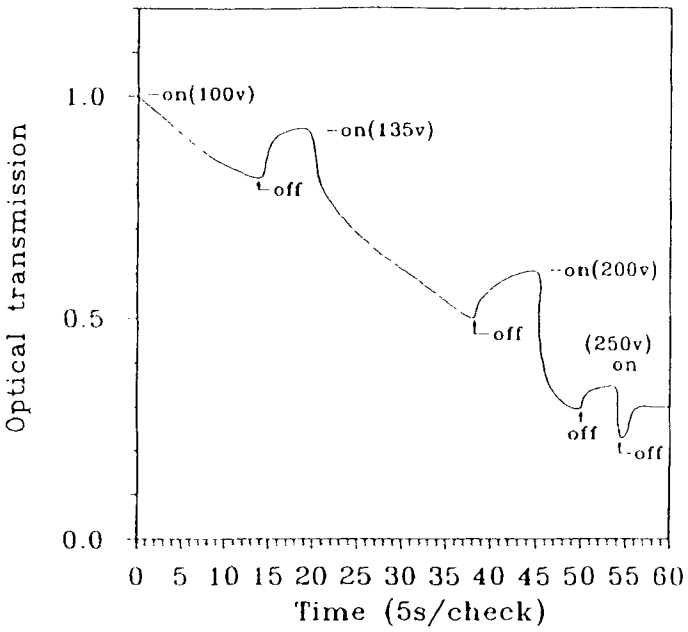


FIGURE 6 Effect of voltage applying history on the optical response of sample 1 at 156 C.

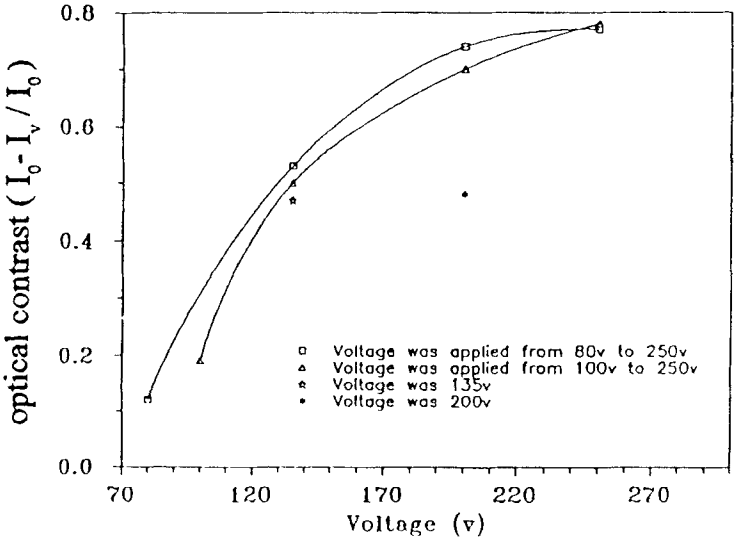


FIGURE 7 Effect of voltage applying history on the optical contrast of sample 1 at 156 C.

i.e. much higher optical contrast has been got through increasing the voltage in step by step (as shown in Figure 6) than immediately increasing to high voltage (Figures 5 and 7). The effect of voltage application history was only observed in the blend systems containing one component of weak polarity. This may be due to passive alignment of

the weak polar molecule which cannot synchroize with rapid orientation of strong polar molecule upon applying a high voltage.

B. Crude solution blend crosslinking system

Crude solution mixing system was composed of crosslinkable liquid crystalline macromolecules containing mesogenic side chains and analogous low mass liquid crystal. When the solvent was removed by heating, crosslinking and phase separation may take place depending on the remaining Si-H bond, blend composition and annealing temperature. A new kind of SCLCP containing ladderlike polysiloxane as backbone was also used in a new blend system to compare with the system containing single chain polymer.

The electro-optic response of the lower crosslinked (remained Si-H was about 5%) blend system was similar to that of the simple blend system (as Figures 8 and 9). Blend sample B1 containing ladderlike polymer exhibited sharper electro-optic behaviour and distinct threshold voltage (Figure 10).

The highly crosslinked (remained Si-H was 10–15%) blend system would be very similar to the PNLC system, in particular when the polymer content is much lower (2%–8%), crosslinked polymer almost did not contribute to the changes in refractive index, only acted as thin supporting wall to form many small cavities to divide the low mass liquid crystal compound into many small droplets. So the electro-optic response of the blend system was similar to that of low mass liquid crystal system, such as lower threshold voltage, short response time and higher optical contrast would be expected. Here the director field was complicated as a result of competition between the following factors: (1) elastic forces, which determined the director field for the liquid crystal in the

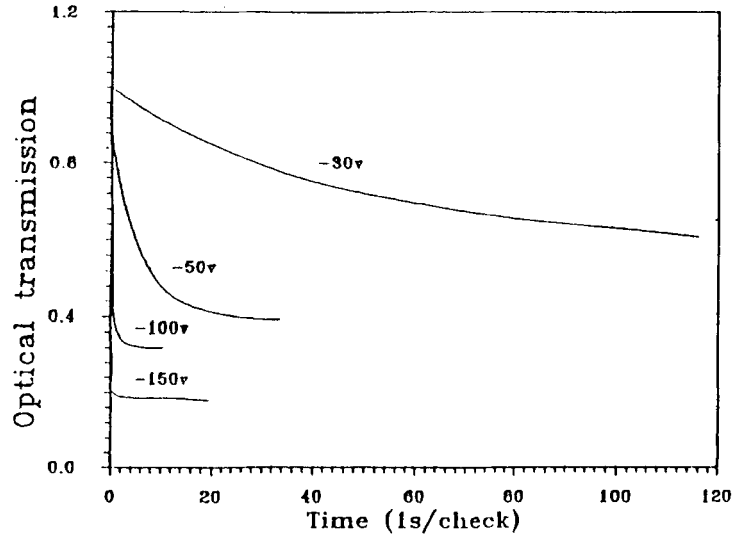


FIGURE 8 Electro-optical response of low-crosslinked blend sample A2 containing single chain polymer.

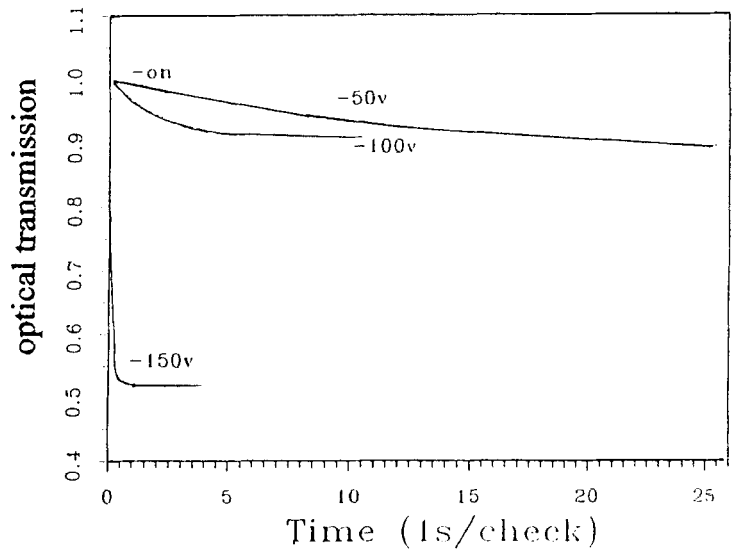


FIGURE 9 Electro-optical response of low-crosslinked blend sample B1 containing ladderlike polymer.

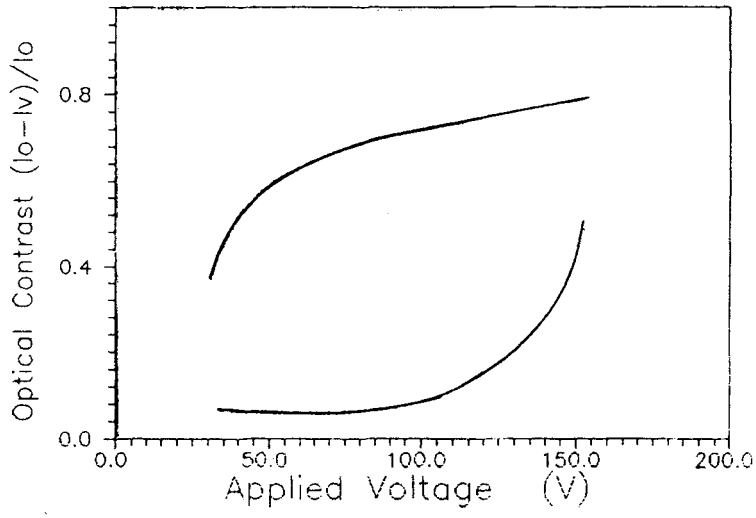


FIGURE 10 Comparison of electro-optic behaviour between two blend samples: A2 containing single chain polymer (above) and B1 containing ladderlike polymer (below).

bulk; (2) surface anchoring, which became dominant if the liquid crystal was confined to a very small cavity; and (3) field effect, which tends to align the director, as well as causes elastic deformation of the cavity. The anchoring state of LC on the thin polymer wall would be affected by side chain or group on the polymer, and the elastic deformation of

the cavity in the field would depend on the rigidity of the polymer and crosslinking degree. Some interesting phenomena was observed although it is not easy to give a satisfactory explanation.

The negative effect was seen for the PNLC system containing about 10% single chain polysiloxane with the side chains containing mesogen and paraffin when the moderate dc field (50 V) was applied (Figure 11). We suppose a model as scheme 2 to explain it. On the off state, the anchoring effect on the polymer wall with longer side chain would induce LC molecules to align perpendicular to the cavity wall, the moderate field would induce the deformation of the cavity to a vertical ellipsoid, some LC molecules anchored on the two side walls would align approximately perpendicular to the field, so optical transmission would oppositely increase depending on the elastic deformation which was relative to the temperature, when the electric field was turned off it was recovered immediately. In comparison with this, for the PNLC system containing ladderlike polymer, the positive effect was observed at lower field 25 V (as Figure 12a) and at higher field 105 V (as Figure 12c). At the lower field, the effect of the elastic deformation of the cavity would be neglected due to the higher rigidity of the main chain, the electro-optic effect was attributed to alignment of the "free" LC molecules within the cavity, when the field was turned off, it was recovered immediately similar to low mass liquid crystal system. However, at the higher electric field, the recovery was delayed depending on the elastic deformation of the cavity induced by high field. Between them, moderate field would induce some deformation, but then the director would turn to align in the field, so the optical transmission would be changed completely as shown in Figure 12b. Besides, the "optical pulse" shown in Figure 12a may be contributed to the movement of the ions present in the cavity.

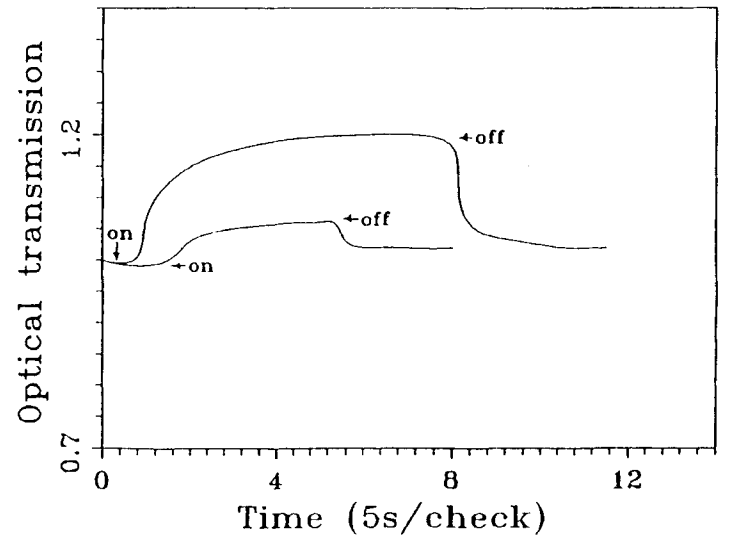
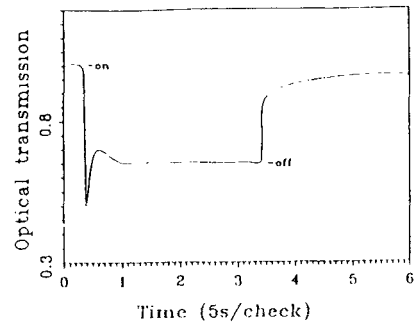
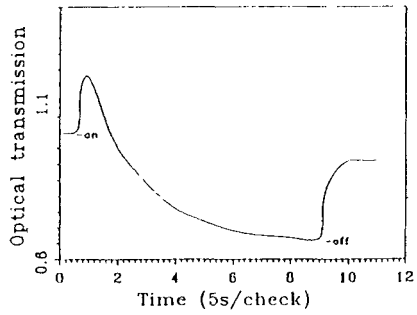


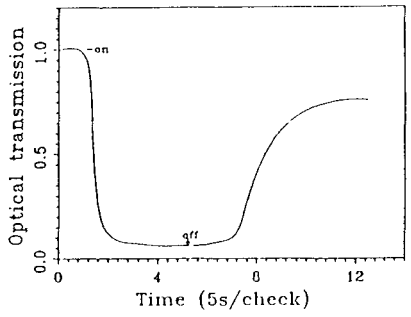
FIGURE 11 Electro-optical response of sample A4′ containing, above: 50 V, 72 C; below: 50 V, 68 C higher crosslinked single chain polymer.



(a) at 25v and 78 °C

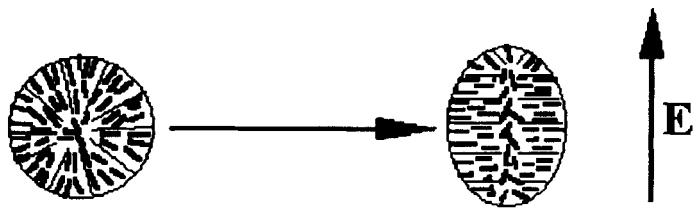


(b) at 65 v and 78 °C



(c) at 105v and 78 °C

FIGURE 12 Electro-optical response of sample B1′containing higher crosslinked ladderlike polymer.



SCHEME 2: Model representation of elastic deformation of the cavity extended in the applied electric field.

CONCLUSION

Electro-optic measurements indicated:

1. As same as normal LC system, response time and optical contrast of the blend systems containing SCLCP and low mass liquid crystal were related to their polarity and applied voltage.
2. The blend system containing a weak polar component exhibited lower optical contrast depending on the voltage application history.
3. When the electric field was turned off, it recovered for the blend system containing a weak polar component, and meanwhile, strong polar blend system exhibited "memory" effect.
4. For the PNLC system containing low content of polymer (either single chain or ladderlike polysiloxanes with mesogenic side chains), which almost did not contribute to the changes in refractive index, only acted as thin supporting wall to form many small cavities to divide the liquid crystal compound into many small droplets, short response time and low driving voltage was similar to that of real low mass LC system. Some peculiar behaviour would be related to the "anchoring" effect of LC molecules on the cavity wall and elastic deformation of the cavity forced by field.
5. The crosslinked LC blend system containing ladderlike macromolecules revealed sharp electro-optic behaviour and distinct threshold voltage.

Acknowledgments

The authors are pleased to acknowledge the financial support from Polymer Physics Lab., Academia Sinica and NSFC, and very kind help from Dr. Z. M. Xiu in preparing the experimental device.

References

1. **H. J.** Coles, *Developments in Crystalline Polymers* (D. C. Bassett Ed.), Elsevier Applied Science **2**, 297 (1988).
2. H. Finkelmann, and H. Ringsdorf, *Makromol. Chem.*, **179**, 273 (1978).
3. H. Finkelmann, H. Rinsdorf, and D. Naegele, *Makromol. Chem.*, **180**, 803 (1979).
4. A. I. Hopwood, and H. J. Coles, *Polymer.*, **26**, 1312 (1985).
5. J. W. Doane, N. A. Vaz, B. -G. Wu, and S. Zumer, *Appl. Phys. Lett.*, **48**(4), 27 (1986).
6. N. Koice, *Mol. Cryst. Liq. Cryst.*, **139**, 47 (1986).
7. D. Demus, *Mol. Cryst. Liq. Cryst.*, **165**, 45 (1988).
8. C. R. Noller, *Org. Synth.*, **II**, 358 (1943).
9. M. Marcos, *Mol. Cryst. Liq. Cryst.*, **91**, 157 (1983).
10. D. J. Dyron, *Mol. Cryst. Liq. Cryst.*, **58**, 179 (1980).
11. P. Keller, *Solid State Physics, Suppl.*, **14**, 19 (1986).
12. Z. Galewski, *Mol. Cryst. Liq. Cryst.*, **151**, 233 (1987).
13. Z. Galewski, *Mol. Cryst. Liq. Cryst.*, **191**, 211 (1990).
14. (a) R.-B. Zhang, Z. S. Xie, Y. Z. Wan, S. Z. Jin, and J. A. Hou, *Chinese J. Polym. Sci.*, **11**(3), 210 (1993); (b) L. M. Sun, P. Xie, and R. B. Zhang*, *International symposium of fine chemistry and functional polymers*, Hangzhou, China, Sept. 11–16 (1992), Preprints p.309.
15. Z. S. Xie, Y. Z. Wan, and R. B. Zhang, *Chinese J. Polym. Sci.*, **10**(4), 361 (1992).
16. P. Xie, L. M. Sun, D. R. Dai, and R. B. Zhang*, *Chinese J. Polym. Sci.*, **11**(4), 380 (1993).