Aggregation states and electro-optical properties of the induced smectic phase by mixing a nematic liquid crystalline polymer and a low molecular weight liquid crystal

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Aggregation states and electro-optical properties of a binary mixture by mixing a nematic side chain type liquid crystalline polymer (LCP) and a nematic low molecular weight liquid crystal (LC) have been studied. The nematic LC with a strong polar terminal group was miscible with the nematic LCP having a weak polar terminal group. The binary mixture showed an induced smectic phase over a wide range of mixing concentrations and temperature. The reversible turbid (light scattering)–transparent change was observed upon application of electric fields with low and high frequencies, respectively. Both transparent and turbid states of the binary mixture could be maintained stably even when the electric field was turned off (bistable and reversible light switching). A novel type of electro-optical effect based on light scattering was obtained for the mixture in the induced smectic state.

(Keywords: liquid crystalline polymer; induced smectic phase; light scattering; bistable and reversible light switching; memory effect)

INTRODUCTION

The orientation of nematic low molecular weight liquid crystals (LCs) is easily controlled by applying electric or magnetic fields. Various types of polymer–LC composite systems have been reported as large area and flexible light-intensity controllable films[1–8]. Thermotropic liquid crystalline polymers (LCPs) with mesogenic side chains have characteristics of both polymers and LCs. The electro-optical properties of LCPs have become of increasing interest over recent years. However, LCPs in a mesophase state are more viscous than LCs. Therefore, the response time of an LCP to an external stimulation, such as an electric or a magnetic field, is much longer than that of a LC. A LCP–LC mixture in which the LC acts as the solvent or diluent has been studied in order to reduce the viscosity of the LCP[9–15]. Reversible and bistable electro-optical effects based on light scattering have been recognized for the smectic phase of a LCP–LC composite system[12–15]. It was reported that binary mixtures of LCs with a strong polar cyano or nitro terminal group and a weak polar group gave an induced smectic phase (ISP)[16–22]. The smectic state of the LCP–LC mixture is expected to be a novel type of 'light valve' exhibiting a memory effect (bistable light switching).

In this paper, the phase transition behaviour and the aggregation state for a binary mixture composed of a side chain type LCP with a weak polar terminal group and a LC with a strong polar group have been studied. Also, a bistable and reversible light switching based on light scattering has been investigated for a binary mixture of a LCP–LC composite system in an ISP.

EXPERIMENTAL

Materials

The chemical structures of the LCP [poly(4-methoxyphenyl 4'-propyloxy benzoate methylsiloxane), PS3EM, $T_g = 288$ K] and LC (4-cyano 4'-pentyloxy biphenyl, 5OCB) are shown in *Figure 1*. The side chain type LCP is poly(methylsiloxane) with a weak polar terminal unit in the mesogenic side group. The molecular weight of the PS3EM is 1.1×10^4. The LC has a strong polar cyano end group. The mesomorphic phase of the LCP and LC is nematic. The LCP–LC mixture was dissolved in acetone and the LCP–LC composite film was prepared by solvent casting.

Characterization

The phase transition behaviours and the aggregation state of the LCP–LC mixture were investigated by d.s.c., polarizing microscopy and X-ray diffraction. The d.s.c. heating/cooling rates were 5 K min^{-1} and the microscopy heating/cooling rates were 1 K min^{-1}. The temperature was regulated to within ± 0.1 K. X-ray diffraction patterns were photographed by a flat plate camera collimated with toroid mirror optics, using Ni-filtered CuKα radiation ($\lambda = 0.1542$ nm). The integrated X-ray diffraction intensities were measured by continuous radial scanning every 0.05° along the Bragg angle (2θ).

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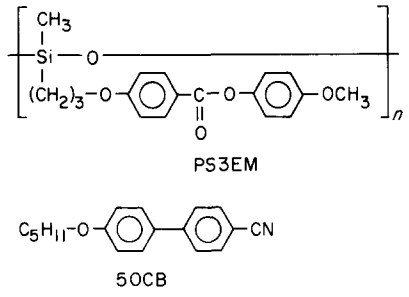

Figure 1 Chemical structures of the LCP (PS3EM) and low molecular weight LC (50CB)

Measurements of electro-optical properties

In order to measure the electro-optical properties, the LCP–LC mixture was sandwiched between two transparent ITO-glass electrodes, which were separated by a poly(ethylene terephthalate) spacer (10 μm thick). The ITO-glass surface had not been treated. The electro-optical properties of the LCP–LC mixture were studied under an a.c. electric field. A change in transmission intensity of the He–Ne laser light through the cell was detected by means of a photodiode and recorded by a digital storage oscilloscope. The distance between the cell and the photodiode was 305 mm.

RESULTS AND DISCUSSION

Phase transition behaviour and aggregation state of the LCP–LC composite system

Figure 2 shows the d.s.c. curves of the PS3EM–50CB composite systems. The d.s.c. heating rate was 5 K min^{-1}. The second heating data were used. The d.s.c. curve of PS3EM showed a deviation from a base line and an endothermic peak which corresponded to the glass transition (T_g = 288 K) and the nematic–isotropic (T_{NI} = 334 K) phase transition, respectively. Two endothermic peaks corresponding to the crystalline–nematic (T_{KN} = 321 K) and the nematic–isotropic (T_{NI} = 341 K) phase transitions were observed for 50CB. The T_g of PS3EM decreased from 288 to 244 K on increasing the molar fraction of 50CB from 0 to 57.5%. The decrease in T_g is due to a plasticizing effect of 50CB to PS3EM. A broadening of the nematic–isotropic phase transition of PS3EM was observed with an increase in the 50CB molar fraction. The endothermic peaks corresponding to the crystalline melting of 50CB were observed in the region above 57.5 mol% 50CB and they mostly disappeared below 50 mol%. The T_{NI} showed a maximum around the 50/50 molar fraction of PS3EM–50CB. The rise of T_{NI} with the molar fraction of 50CB may be attributed to an increase in thermal stability of the mesophase by mixing PS3EM with 50CB. The exothermic peaks on the heating runs for 10/90, 20/80, 30/70 and 40/60 at ~280 K corresponded to recrystallization of the quenched LC molecule during cooling.

As shown in *Figure 3*, the X-ray diffraction patterns of PS3EM and 50CB were broad and obscure, which is characteristic of a nematic phase. Also, the PS3EM–50CB (50/50 mol%) mixture exhibits sharp Debye rings in the lower Bragg angle region. Since the reciprocal of these spacings is roughly 1:2:3, *Figure 3* clearly indicates the existence of a layer structure corresponding to an ISP. A diffuse reflection at a wide Bragg angle region corresponds to an intermolecular distance in the mesogenic phase composed of the side chain group of PS3EM and 50CB molecules. The sharp, low angle X-ray diffraction rings from an ISP were observed for the PS3EM–50CB mixture in the range of 80/20–20/80 (mol%).

The relationship between the smectic layer spacing (d-spacing) and the PS3EM–50CB mixture ratio is shown in *Figure 4*. The maximum molecular lengths for

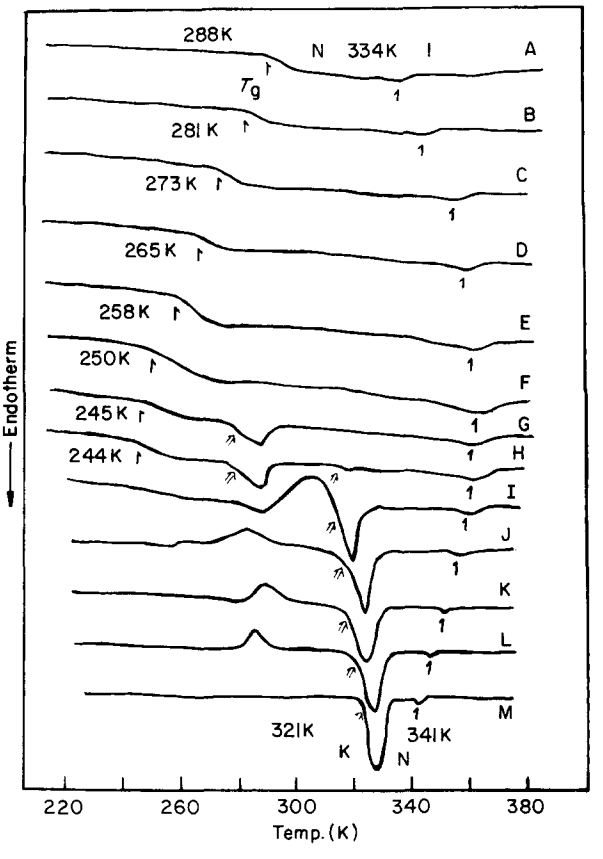

Figure 2 D.s.c. curves of the PS3EM–50CB mixture. PS3EM–50CB: (A) 100/0; (B) 90/10; (C) 80/20; (D) 70/30; (E) 60/40; (F) 50/50; (G) 43.5/56.5; (H) 42.5/57.5; (I) 40/60; (J) 30/70; (K) 20/80; (L) 10/90; (M) 0/100

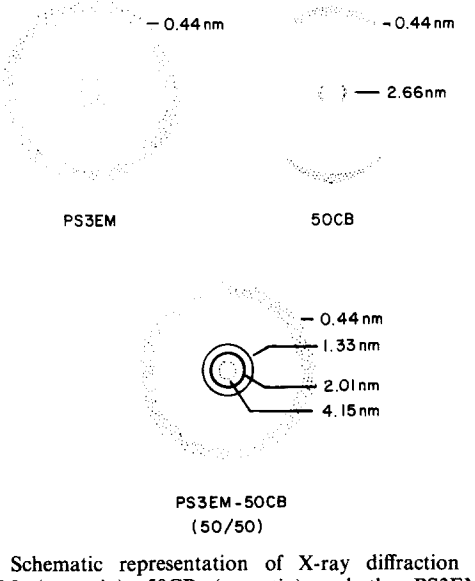

Figure 3 Schematic representation of X-ray diffraction patterns of PS3EM (nematic), 50CB (nematic) and the PS3EM–50CB (50/50 mol%) (induced smectic) mixture at 329 K. The sharpest diffraction of the mixture corresponded to a repeat distance of 2.01 nm

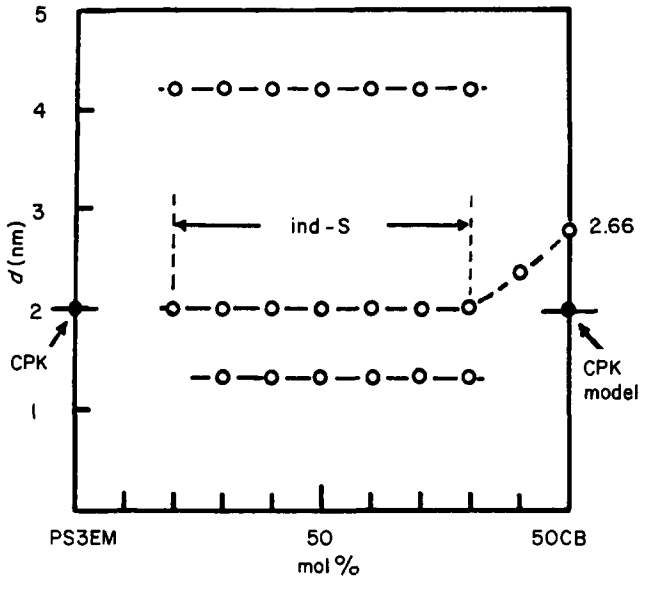

Figure 4 Dependence of layer spacing on the PS3EM–50CB mixture at 329 K

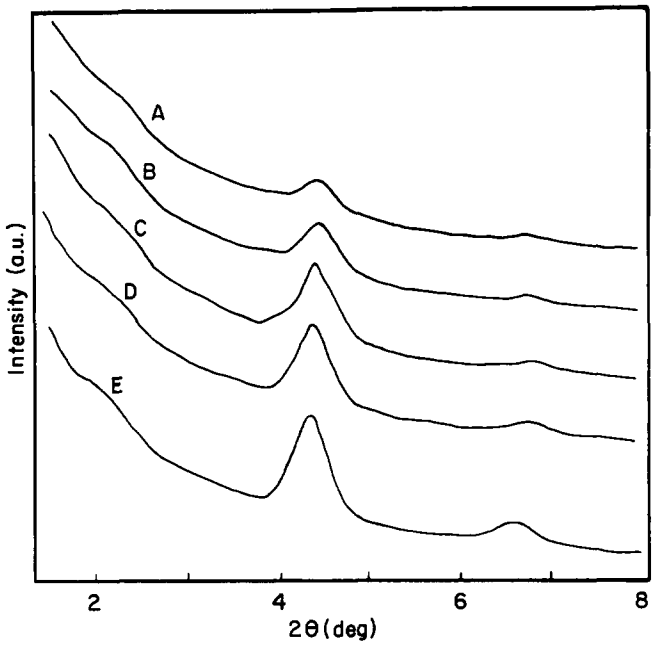

Figure 5 Angular dependence of the X-ray diffraction pattern of the PS3EM–50CB mixture (50/50 mol%) at various temperatures: (A) 345 K; (B) 339 K; (C) 333 K; (D) 328 K; (E) 300 K

50CB and the side chain of PS3EM, calculated under an assumption of the most extended conformation on the basis of the Corey–Pauling–Koltun (CPK) molecular model, were 1.97 and 2.00 nm, respectively. However, the *d*-spacing of 50CB evaluated from the X-ray diffraction pattern was 2.66 nm, which was about 1.35 times the calculated molecular length. The difference indicates that 50CB forms an overlapped head-to-tail molecular association in order to cancel its strong dipole moment polarization. In the range of 80/20–20/80 mol% of the PS3EM–50CB mixture, a sharp and strong X-ray diffraction pattern with a *d*-spacing of 2.01 nm and sharp but weaker patterns of 4.15 and 1.33 nm were observed (*Figure 3*). It is suggested that the single smectic layer with a spacing of 2.01 nm is composed of a mixture of one molecule of 50CB and one side chain of PS3EM, and then, the repeating unit is twice as long as the single smectic layer because the structurally symmetrical smectic layers are formed on the opposite side of the PS3EM main chain. The quantitative investigation of the X-ray diffraction intensity was also carried out by a counter technique. *Figure 5* shows the X-ray intensity curves of the PS3EM–50CB samples which were taken at different temperatures. The three peaks of $2\theta = 2.14$, 4.40 and 6.66° correspond to 4.15, 2.01 and 1.33 nm, respectively. The area ratio of these three peaks, which was calculated after subtracting the background scattering, was 1.2:6.3:1.0. It could be easily recognized that the peak intensities decreased continuously with an increase in temperature and also with an increase in the 50CB molar fraction. However, the area ratio of the three peaks was almost independent of temperature and the mixture ratio.

Figure 6 is the phase diagram of the PS3EM–50CB mixture obtained by d.s.c., polarizing microscopy and X-ray diffraction. The d.s.c. heating/cooling rates were 5 K min^{-1} and the microscopy heating/cooling rates were 1 K min^{-1}. The specimen temperature was controlled to within ±0.1 K. The PS3EM and 50CB were completely miscible over the whole composition range, especially above ~320 K. The binary mixture formed an ISP over a wide mixing range (20–80 mol% 50CB) and temperature range (250–353 K). A narrow biphasic nematic–isotropic region of ~3 K where the nematic and isotropic phases coexisted, and another narrow biphasic region of ~0.8 K where the smectic and nematic phases coexisted were found by microscopic examination. (These regions are shown by oblique lines in *Figure 6*.)

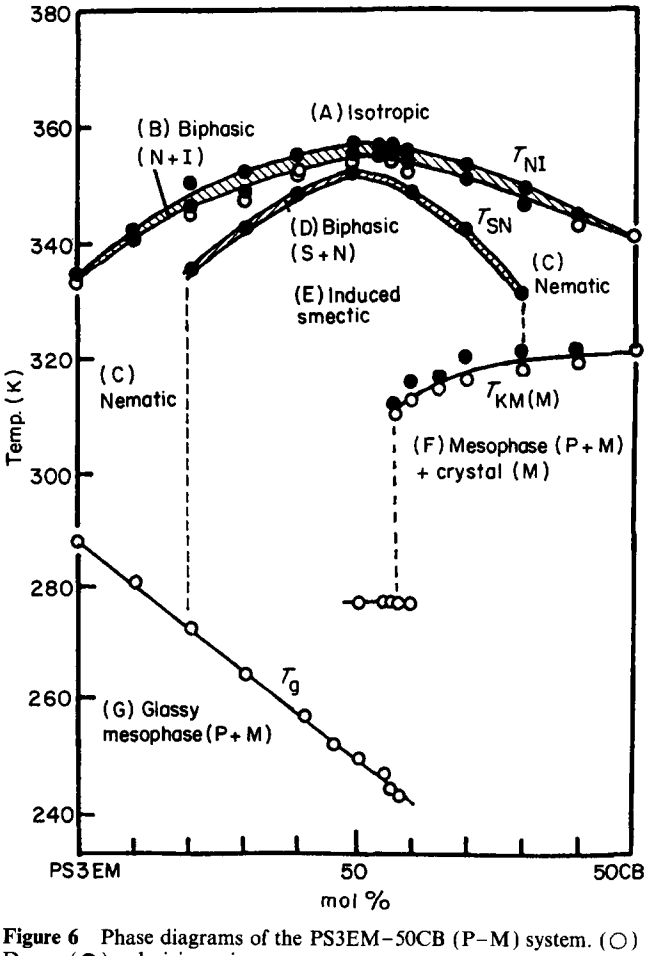

Figure 6 Phase diagrams of the PS3EM–50CB (P–M) system. (○) D.s.c.; (●) polarizing microscopy

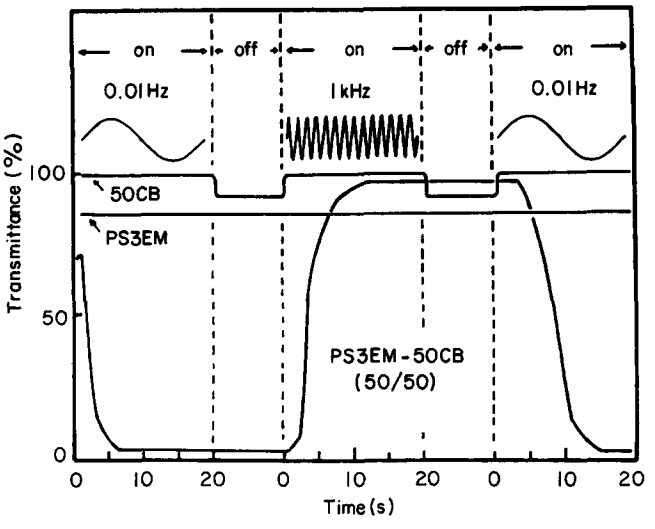

Figure 7 Electro-optical effect of PS3EM (nematic), 50CB (nematic) and the PS3EM–50CB (50/50 mol%) (induced smectic) mixture under low and high frequencies of an a.c. electric field of 14.7 MV m^{-1}. The measured temperature was $T_{NI} = -33$ K and the cell thickness was 16 μm

Electro-optical effect

The electro-optical effect based on light scattering was investigated under various conditions of an a.c. electric field. The transmittance of the He–Ne laser through the cell without any optical polarizers was measured by a photodiode. *Figure 7* shows the electro-optical effects of PS3EM, 50CB and the PS3EM–50CB (50/50 mol%) mixture. The measured temperature was $T_{NI} = -33$ K and the magnitude of the applied a.c. electric field was 14.7 MV m^{-1}. The cell thickness of the mixture sample was 16 μm. There is no remarkable difference in the light transmittance due to thermal history. In the case of PS3EM and 50CB, no distinguishable transmittance change and ~8% change were observed with the a.c. electric field off and on, respectively. Also, the degree of transmittance of 50CB was independent of the frequency of the a.c. electric field. On the other hand, the PS3EM–50CB (50/50 mol%) mixture exhibited a bistable and reversible light switching driven by a.c. electric fields with low and high frequencies. In the case of a low frequency a.c. electric field ($< \sim 0.1$ Hz), a turbulent flow of PS3EM main chains was induced by an ionic current when an a.c. electric field above the threshold value was applied. A turbulent flow of PS3EM main chains collapses laterally large smectic layers into many small smectic domains, resulting in an increase in light scattering due to the effective formation of an optically heterogeneous structure in a similar manner to a smectic LCP–nematic LC mixture[12,13,15]. On the other hand, in the case of a high frequency a.c. electric field (> 10 Hz) light transmittance increased up to 98%, since the homeotropic alignment in the smectic state was formed by the dielectric characteristics of the mixture[12,13,15]. As mentioned above, it is reasonable to consider that the reversible turbid–transparent change upon application of electric fields with low and high frequencies can be reasonably explained by the formation of many small smectic domains induced by ionic current and laterally large homeotropic alignment due to dielectrically positive anisotropy of the mesogenic group, respectively. Also, both the transparent and turbid (light scattering) states could be maintained due to the fairly stable highly viscous smectic phase, even though the electric field was turned off (memory effect). Both the rise and decay response times of the mixture were of the order of several seconds at room temperature.

CONCLUSIONS

A binary mixture of a nematic LCP having a mesogenic side group with a weak polar terminal unit and a nematic LC with a strong polar cyano end group was miscible over a wide range of mixing concentration and temperature. The binary mixture formed an ISP in a similar fashion to a binary mixture of nematic LCs. The addition of the LC component to LCP reduced the T_g of LCP due to a plasticizing effect. The reversible bistable turbid–transparent change was successfully realized for the ISP upon application of a.c. electric fields with low and high frequencies with a response time of several seconds at room temperature. The transparent and turbid states were maintained (memory effect) even though the electric field was turned off.

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