

Improvement in light switching speed for (side-chain type liquid crystalline polymer / low molecular weight liquid crystals) composite systems

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Reversible and bistable electro-optical switching characteristics of the induced smectic composite systems composed of side chain type liquid crystalline polymer (nematic LCP) and low molecular weight liquid crystals (nematic LCs) have been investigated. The (nematic LCP / nematic LCs) composite systems and the (LC copolymer : LCcoP / nematic LCs) composite systems were prepared to investigate bistable and reversible light switching characteristics at room temperature. The pseudo LCcoP was used to improve the response speed for bistable light switching by reducing the LCP fraction. Though the pseudo LCcoP with a small fraction of substituted mesogenic side chain did not exhibit any mesophase characteristics at any temperature, the binary composite showed an induced smectic phase over a wide range of both mixing concentration and temperature. The induced smectic composite system showed fairly good reversible and bistable electro-optical switching characteristics with short response time (~ 100 ms) at room temperature.

1. INTRODUCTION

Side chain type liquid crystalline polymers (LCPs) are new types of substances combining the properties of low molecular weight liquid crystals (LCs) such as variable optical anisotropy, induced orientation, high mobility, etc. and those of polymers such as elasticity, easy fabrication as solid films, etc. In particular, the application of LCPs in a glass phase for optical data storages, that is, write-once and erasable thermo-optical recording has been demonstrated since 1983 [1,2].

The binary systems composed of LCP and LCs which had the similar chemical structure to that of the mesogenic side chain in LCP were studied in order to improve the switching speed of LCPs [3-5]. The binary systems in a homogeneous smectic phase showed reversible and bistable electro-optical switching but the response speed was not fast at room temperature [6,7]. It was reported that the binary mixtures of LCs with a strong polar cyano or nitro terminal group and a weak polar one exhibited an induced smectic phase [8,9]. This concept was applied to the binary mixture of nematic LCP with a weak polar end group in the side chain and nematic LC with a strong polar end group in order to reduce the response time for bistable and reversible light switching [10,11]. Another method to prepare the optimum composite systems with bistable memory switching characteristics has been tried by using smectic LC copolymer (smectic LCcoP) with

dimethylsiloxane groups in the main chain. In the case of the introduction of LCcoP into the composite system, a faster electro-optical switching with a bistable memory effect at room temperature might be expected for the smectic (smectic LCcoP / nematic LCs) composite systems, due to an apparent reduction of the LCcoP fraction [12].

In this paper, a novel type of a pseudo LCcoP with a small fraction of substituted mesogenic side chain has been proposed in order to improve the response speed for bistable light switching at room temperature.

2. EXPERIMENTAL SECTION

Figure 1 shows the chemical structures and physical properties of nematic LCP, pseudo LCcoP, and nematic LCs used in this study. These PS3EM ($n=24$) and pseudo PS(3EM/DM)($n=12$) were synthesized by a standard method reported by Finkelmann et al [13]. The chemical structures were confirmed by NMR and FT-IR. The average molecular weights and purities of PS3EM and PS(3EM/DM) were determined by gel permeation chromatography in tetrahydrofuran using the polystyrene standards. The binary composite systems were prepared from acetone solutions of PS3EM or PS(3EM/DM) and E7 by a solvent casting method. The phase transition behavior and the aggregation states of the binary composites were

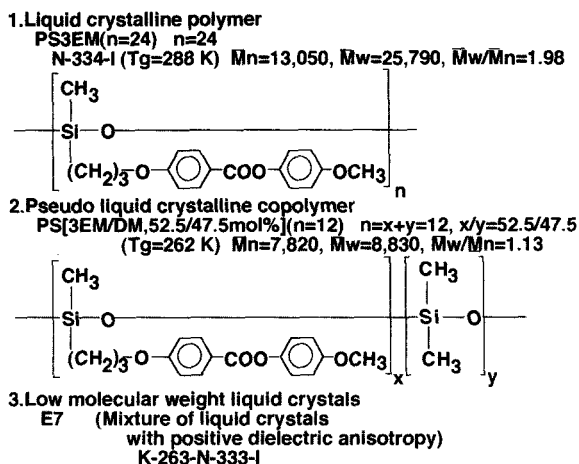


Figure 1. Chemical structures and physical properties of samples.

investigated on the basis of differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (WAXD) studies, in order to determine the phase diagrams of the binary composite systems. For electro-optical studies, the composite film was sandwiched between two indium-tin-oxide (ITO) -coated glass plates which were separated by the PET film spacer of 10 μm thick. The experimental setup used for measuring the electro-optical switching characteristics is illustrated in Figure 2. A He-Ne laser (wavelength of 632.8 nm) was used as an incident light being transmitted normal to the film surface and an external a.c. electric field was applied across the composite film. The transmitted light intensity were measured with a photodiode without any polarizers under the modulation of an a.c. electric field. The intensity of transmitted light with the elapse of time was recorded with a digital storage oscilloscope to evaluate the stability of memory effect for the composite systems.

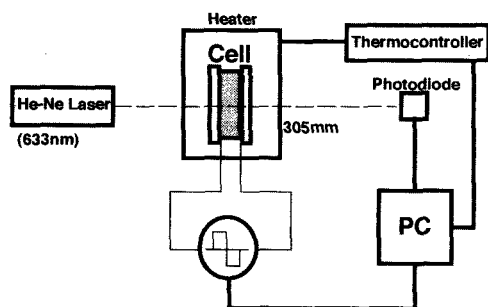


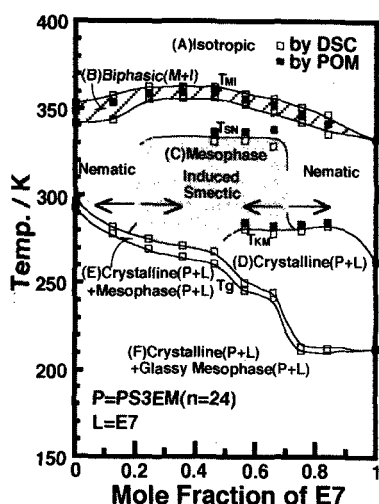
Figure 2. Measuring system for electro-optical properties of the composite system.

3. RESULTS AND DISCUSSION

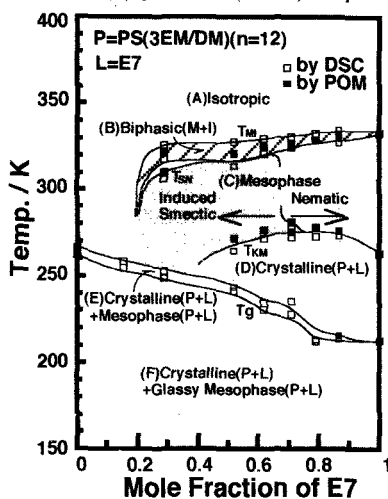
3.1. Mesomorphic characterization of induced smectic composite systems

On the basis of differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and wide angle X-ray diffraction (WAXD) studies, it was confirmed that PS3EM(n=24) showed a nematic state, while PS(3EM/DM,52.5/47.5mol%) (n=12) which was a pseudo LC copolymer (pseudo LCcoP) with 52.5 mol% substituted mesogenic side chain in a main chain was an isotropic state at room temperature.

Figure 3 shows the phase diagrams of the [PS3EM(n=24)/E7] (a) and the [PS(3EM/DM)(n=12)/E7] (b) composite systems. The glass transition temperature, T_g of PS3EM or PS(3EM/DM) decreased with an increase in the E7 fraction due to the plasticizing effect of E7. Since a single endothermic peak assigned to the mesophase-isotropic transition, T_{M/I} was measured, the composite systems might be in a homogeneously mixed mesomorphic phase (molecularly dispersed state). Therefore, it is reasonable to consider that E7 is miscible over a whole concentration range of PS3EM or PS(3EM/DM) in both isotropic (A) and mesomorphic states (C). The assignments for the (A) and (C) regions were also confirmed by POM observations. X-ray diffraction studies were also carried out in the mesophase (C) in order to investigate the aggregation state of the composite. In a 29~81 mol% (35~85 wt%) range of PS3EM and a 33~78 mol% (45~85 wt%) range of PS(3EM/DM), the sharp small angle X-ray scattering corresponding to an induced smectic layer structure was observed. Also, a fan-shape texture being characteristic of a smectic state was observed under POM. These results apparently indicate that the [PS3EM(n=24)/E7] and the [PS(3EM/DM)(n=12)/E7] composite systems showed a homogeneous induced smectic phase in these composite regions. The homogeneous induced smectic phase plays an important role to realize an excellent memory effect which is enabled due to its remarkable high viscosity in comparison with that in a nematic state. Although PS(3EM/DM) did not show any mesophase at any temperature as shown in Figure 3 (b), the [PS(3EM/DM)(n=12)/E7] composite system exhibited a compatible induced smectic phase in a 33~78 mol% of PS(3EM/DM). It is suggested that the pseudo LCcoP has a latent ability to form an induced smectic phase for the binary composite system. The temperature range of an induced smectic state for the [PS(3EM/DM)



(a) [PS3EM(n=24)/E7].



(b) [PS(3EM/DM)(n=12)/E7].

Figure 3. Phase diagrams of [PS3EM(n=24)/E7] (a) and [PS(3EM/DM)(n=12)/E7] (b) composite systems.

(n=12)/E7] composite system was fairly lower than that for the [PS3EM(n=24)/E7] one. Thus, the induced smectic (pseudo LCcOP / nematic LCs) composite system is expected to develop the novel type of LC display with a bistable memory effect with the short response time.

3.2. Electro-optical properties of the induced smectic composite systems

The [PS(3EM/DM)(n=12)/E7] composite systems could be driven over a wide range of mixing concentration (35-75 mol% of pseudo LCcOP) at room temperature as expected from the phase diagram of Figure 3 (b). Figure 4 shows the

frequency dependence of the transmittance for the [PS(3EM/DM)(n=12)/E7] composite systems with the different component fractions under the electric field strength of $E=5.00 \text{ Vrms} \cdot \mu\text{m}^{-1}$ at 301 K. A reversible and bistable light switching was recognized for the [PS(3EM/DM)(n=12)/E7,48/52 mol%(60/40wt%)] and the [PS(3EM/DM)(n=12)/E7,38/62mol%(50/50wt%)] composite systems that showed an induced smectic phase at room temperature as shown in Figure 3 (b). Each composite system changed to a highly transparent state upon the application of a high frequency electric field because of the electric field effect of the side chain part of the composite and turned into a remarkable light scattering state upon the application of a low frequency electric field owing to the electric current effect on electro hydrodynamic motion of main chains. Each transparent and turbid state was stably memorized after the removal of electric fields. The [PS(3EM/DM)(n=12)/E7,48/52mol%(60/40 wt%)] composite system exhibited a somewhat hysteresis in the increasing and decreasing processes of the electric field frequency, but the [PS(3EM/DM)(n=12)/E7,38/62mol%(50/50wt%)] composite system did not show the distinct hysteresis. It seems reasonable to consider that the change of the polar balance between terminal groups induces the variation of viscosity of the composite system and the mechanical strength of the smectic layer. On the other hand, in the case of the [PS(3EM/DM)(n=12)/E7,29/71mol%(40/60 wt%)] composite system, since a homogeneous nematic phase was observed under the experimental conditions studied here, a light scattering state was not observed upon the application of a low frequency electric field (0.1 Hz).

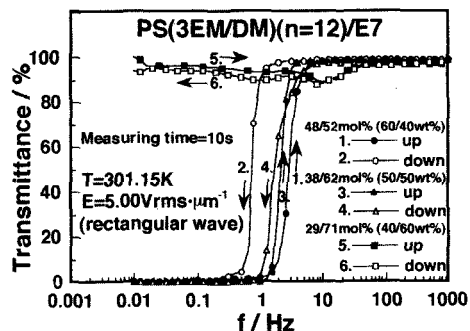


Figure 4. Frequency dependence of transmittance for [PS(3EM/DM)(n=12)/E7] composite system.

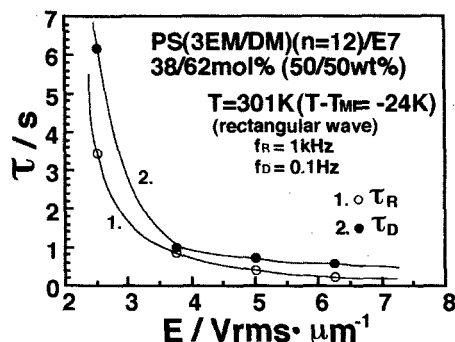


Figure 5. Relationship between response times (τ_R , τ_D) and applied electric field for [PS(3EM/DM)($n=12$)/E7,38/62mol%(50/50wt%)] composite system.

Figure 5 shows the relationship between response times (τ_R , τ_D) and applied electric field for the [PS(3EM/DM)($n=12$)/E7,38/62mol%(50/50wt%)] composite system. The rise response time, τ_R for a random - homeotropic alignment change was evaluated as the time period required from a turbid state to a transparency one corresponding to the 10~90 % transmittance change. Similarly, the decay response time, τ_D for a homeotropic - random alignment change was evaluated as the time period required from a transparency state to a turbid one corresponding to the 90~10 % transmittance change. A reversible and bistable electro-optical switching with quite shorter response times at room temperature was realized for the [PS(3EM/DM)($n=12$)/E7,38/62mol%] composite system as shown in Figure 5. The turbid (light scattering) and the transparent states for the composite system could be stably kept for a long period (more than three years) at room temperature.

On the other hand, the [PS3EM($n=24$)/E7] composite systems did not exhibit a fast bistable electro-optical switching, but the response times ranged above several seconds under an appropriate electric field at room temperature. It is apparently concluded from the results mentioned above that the introduction of pseudo LCcOP into the induced smectic composite systems is strikingly effective to reduce the electro-optical switching times with a stable memory effect at room temperature.

4. CONCLUSIONS

In this study a pseudo LCcOP with a weak polar methoxy terminal group in the side chain was used

in order to improve the bistable light switching speed of the induced smectic binary composite system at room temperature. The pseudo LCcOP with substituted mesogenic side chain of 52.5 mol% did not exhibit any mesophase characteristics. However, the binary composite showed an induced smectic phase over a wide range of both mixing concentration (33~78 mol% of LCcOP) and temperature (250~320 K). A reversible and bistable electro-optical switching with a short response time (~100 ms) at room temperature was realized for the binary composite system in the induced smectic state. Introduction of pseudo LCcOP with a small substituent fraction of mesogenic side chain into the induced smectic binary composite system is extremely effective in order to improve the switching speed of the binary composite system.

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