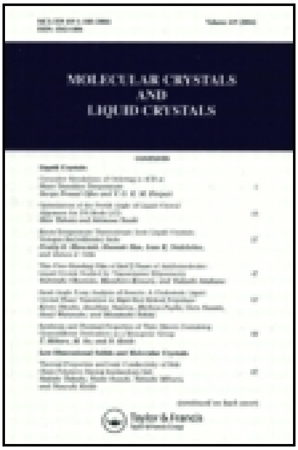

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Bistable Memory Switching of (Liquid Crystalline Copolymer/ Low Molecular Weight Liquid Crystal) Composite Systems

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Bistable Memory Switching of (Liquid Crystalline Copolymer/ Low Molecular Weight Liquid Crystal) Composite Systems

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Bistable electro-optical switching characteristics have been investigated for composite systems in a smectic phase induced by mixing a side chain type nematic liquid crystalline polymer (nematic LCP) or its copolymer with weak polar methoxy terminal groups in the side chains and low molecular weight nematic liquid crystals (nematic LCs) with strong polar cyano end groups. The liquid crystalline copolymer (LCcoP) with weak polar methoxy terminal groups in the side chains attaching to a polysiloxane main chain was used in order to improve the response speed of the bistable light switching for the binary composite system. Although the LCcoP with 52.5 mol% substituted mesogenic side chains did not exhibit any mesophase characteristics at any temperature, this LCcoP induced a smectic state by mixing nematic LCs. A reversible and bistable electro-optical switching with a short response time (~100 ms) was realized for the induced smectic binary composite system upon the application of an appropriate electric field at room temperature.

Keywords: bistable electro-optical switching; induced smectic phase; binary composite system

INTRODUCTION

Side chain type liquid crystalline polymers (LCPs) are a class of materials that combine the properties of low molecular weight liquid crystals (LCs). and polymers [1,2]. The specific anisotropic properties of LCPs are quite similar to those of LCs. An exception is remarkably higher viscosity of LCPs, resulting in slower response with respect to external electric or magnetic fields and mechanical deformation.

In order to improve the switching speed of LCPs, the binary systems composed of side chain type LCP and LC which has the similar chemical structure to the mesogenic side chain in LCP were studied[3-5]. The (LCP / LC) composite systems showed faster switching speed than LCP itself because of a reduction of the viscosity. Furthermore, the binary composite system in a homogeneous smectic phase exhibited reversible and bistable electro-optical switching characteristics upon the application of a.c. electric fields with two different frequencies. The smectic binary composite systems exhibited a highly transparent state upon the application of an a.c. electric field with a high frequency (~kHz) and turned into a remarkable light scattering state upon the application of that with a low frequency (~Hz) or DC[5-7]. Each transparent and turbid state was memorized for a long time after the removal of electric fields due to the mechanical strength of smectic layers in the composite systems. The turbid and transparent states may occur from a balance between an electric current effect based on electrohydrodynamic motion of the LCP main chains and an electric field effect based on the dielectric anisotropy of the LC molecules and the side chain part of the LCP. However, this binary composite system could not be driven at room temperature and also, the response time was around several seconds upon E=9 Vrms•μm^{-1} at 367 K[6,7].

Various methods to prepare the optimum smectic binary composite system with faster bistable switching speed and stable memory characteristics at room temperature have been tried by using different LCPs or liquid crystalline copolymers (LCcoPs)[8]. It is well known that the binary mixtures composed of nematic LCs with a strong polar cyano or nitro terminal group and a weak polar one induce a smectic phase[9-12]. This concept was applied to the binary mixture of the nematic LCP with weak polar end groups in the side chains and the nematic LC with a strong polar end group in order to reduce the response time for bistable and reversible light switching [13,14]. Another method to prepare the optimum composite system with the rapid bistable switching speed has been demonstrated by using smectic LCcoP with dimethylsiloxane groups in the main chain [15]. Since the LCcoP with 52.5 mol% substituted mesogenic side chains did not exhibit any mesophase characteristics at any temperature, this LCcoP was named as pseudo LCcoP in our present study.

In this study, a novel type of pseudo LCcoP with a small fraction of substituted mesogenic side chains with weak polar terminal groups has been applied to prepare an induced smectic composite system for the purpose of a remarkable improvement on the response speed for bistable light switching at room temperature.

EXPERIMENTAL

Figure 1 shows the chemical structures and physical properties of nematic LCP, pseudo LCcoP, siloxane copolymer, and nematic LCs used in this

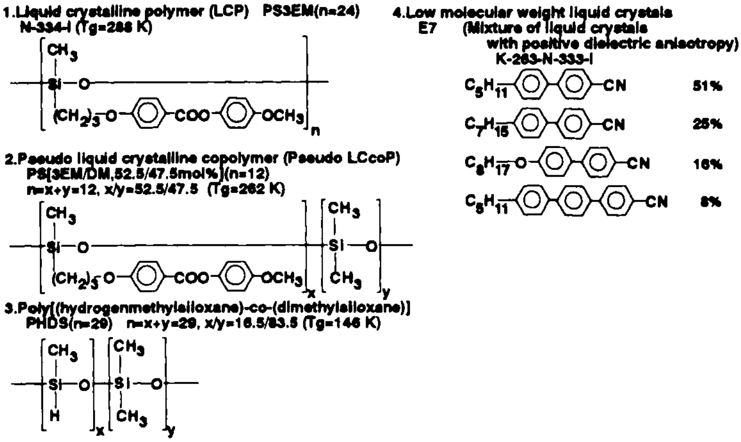


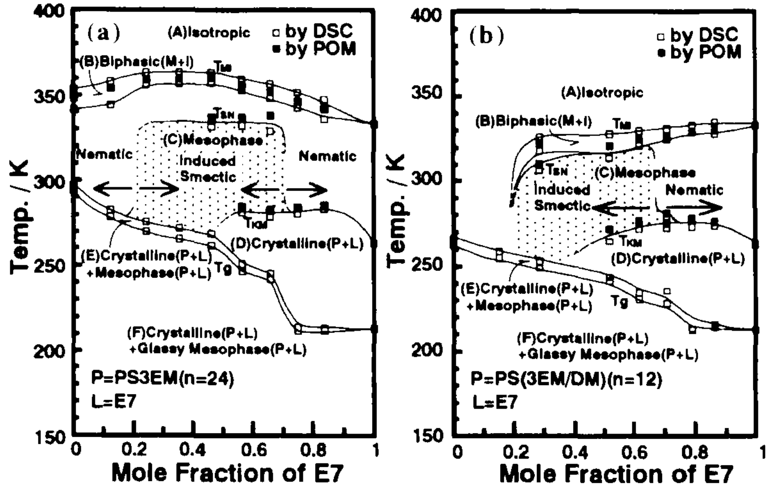
FIGURE 1 Chemical structures and physical properties of liquid crystalline materials.

study. The LCP and the pseudo LCcoP were poly(4-methoxyphenyl 4'-methyloxybenzoatemethylsiloxane) (PS3EM(n=24)) and poly[(4-methoxyphenyl 4'-methyloxybenzoatemethylsiloxane)-co-(dimethylsiloxane)] (PS(3EM/DM)(n=12)). These materials were synthesized by a standard method reported by Finkelmann et al[16]. The binary composite systems were prepared from an acetone solution of (LCP / LCs) and (LCcoP / LCs) by a solvent casting method. The phase transition behavior and the aggregation states of the binary composites were 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. 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. A He-Ne laser providing 2 mW at 632.8 nm (beam diameter of 0.63 mm) 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 rise response time, τ_R for the light switching from a light scattering state to a transparent one (a random-homeotropic alignment change) was evaluated as the time period required of a 10-90 % transmittance change. Similarly, the decay response time, τ_D for the light switching from a transparent state to a light scattering one (a homeotropic-random alignment change) was also evaluated as the time period required of a 90-10 % transmittance change.

RESULTS AND DISCUSSION

Thermal Properties and Phase Transition Behavior of the Composite Systems

Figures 2 (a) and (b) show the phase diagrams of the [PS3EM(n=24)/E7] and the [PS(3EM/DM)(n=12)/E7] composite systems, respectively. These phase diagrams were obtained on the basis of DSC and X-ray studies and also, POM observations. The phase diagrams were mainly divided into the six regions, that is, (A) Isotropic state, (B) Biphasic (Mesophase + Isotropic) state, (C) Mesophase (induced smectic or nematic) state, (D) Crystalline (LCP or pseudo LCcoP + LCs) state, (E) Crystalline (LCP or pseudo LCcoP + LCs) + Mesophase (LCP or pseudo LCcoP + LCs) state, and (F) Crystalline (LCP or pseudo LCcoP + LCs) +Glassy Mesophase (LCP or pseudo LCcoP + LCs) state.



(a) (b)

FIGURE 2 Phase diagrams of the [PS3EM(n=24)/E7] (a) and the [PS(3EM/DM)(n=12)/E7] (b) composite systems.

In the case of the [PS3EM(n=24)/E7] composite system, a homogeneous mesophase was formed over the whole mixing concentration of LCP. On the other hand, in the case of the [PS(3EM/DM)(n=12)/E7] composite system, a homogeneous mesophase was formed over a mixing range above 22 mol% of E7 fraction. The [PS3EM(n=24)/E7] and the [PS(3EM/DM)(n=12)/E7] composite systems formed the homogeneous induced smectic phase in the 19-71 mol% range of E7 and in the 22-67 mol% range of E7, respectively. In the series of these induced smectic binary composite systems composed of nematic LCP or pseudo LCcoP with weak polar methoxy terminal groups and nematic LCs with strong polar cyano terminal group, a definite fraction range of approximately 30-80 mol% of LCP or pseudo LCcoP is necessary to form an induced smectic phase, in analogy with the binary mixtures of nematic LCs. The homogeneous induced smectic phase played an important role to realize an excellent memory effect due to its remarkable high viscosity in comparison with that in a nematic state[13,14]. Although PS(3EM/DM)(n=12) did not show any mesophases states in a temperature range studied here, the [PS(3EM/DM)(n=12)/E7] composite system formed a homogeneous induced smectic phase in the 22-67 mol% range of E7. This indicates that though the pseudo LCcoP is amorphous, this has possibility to form an induced smectic phase when E7 is mixed to the amorphous LCcoP as the second component. The temperature range of an induced smectic state for the [PS(3EM/DM)(n=12)/E7] composite system was fairly lower than that for the [PS3EM(n=24)/E7] one.

Electro-optical Properties of the Induced Smectic Composite Systems

Figure 3 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 Vrms•μm^{-1} at 301 K. The reversible and bistable light switching was recognized for the [PS(3EM/DM)(n=12)/E7,48/52mol%] and the [PS(3EM/DM)(n=12)/E7,38/62mol%] composite systems in an induced smectic state at room temperature. Each composite system exhibited a highly transparent state upon the application of a high frequency a.c. electric field (1 kHz) due to the electric field effect based on the dielectric anisotropy of LCs molecules and the side chain part of the pseudo LCcoP and also, a remarkable light scattering state upon the application of a low frequency a.c. electric field (0.1 Hz) owing to the electric current effect based on the electrohydrodynamic motion of the LCcoP main chains. The transparent and turbid states were maintained stably, even though a.c. electric fields were turned off. The [PS(3EM/DM)(n=12)/E7,48/52mol%] composite system exhibited a somewhat hysteresis in the increasing and decreasing processes of the electric field frequency, maybe due to the higher aggregation stability generated by the homeotropic alignment in smectic domains. On the other hand, in the case of the nematic [PS(3EM/DM)(n=12)/E7,29/71mol%] composite system, a light scattering state was not observed, even though upon application of a low frequency a.c. electric field (0.1 Hz). The composite system also showed a low contrast and did not show a memory effect due to a homogeneous nematic state. These results apparently indicate that since the mixing fractions of pseudo LCcoP and LCs for the binary composite system directly corresponds to the change in the polar balance between terminal groups of the binary components, the viscosity of the binary composite system and also, the mechanical strength of the smectic layer depend strongly on the components fraction.

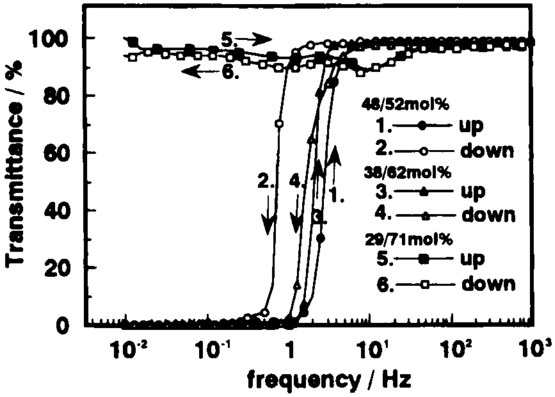


FIGURE 3 Frequency dependence of the transmittance for the [PS(3EM/DM)(n=12)/E7] composite systems at 301 K. The applied electric field was 5.00 MVm^{-1}.

Figure 4 shows the frequency dependence of the transmittance for the [PS(3EM/DM)(n=12)/E7,38/62mol%] composite system under the electric field strengths, E=3.79 Vrms•μm^{-1} and E=5.00 Vrms•μm^{-1} at 301 K. In the case of E=3.79 Vrms•μm^{-1}, the binary composite system exhibited a somewhat hysteresis in the increasing and decreasing processes of the electric field frequency, maybe due to the aggregation stability generated by the homeotropic alignment in smectic domains. On the other hand, under the electric field strength, E=5.00 Vrms•μm^{-1}, the binary composite system did not show an apparent hysteresis. It is worth noting that though the binary composite system showed a highly transparent state in the frequency range from 10 Hz to 100 kHz, the binary composite system also changed to a light scattering state in the higher frequency region than several hundreds kHz as shown in Figure 4, in a similar fashion to the low frequency region. Since the dielectric anisotropy of both LCs molecules and the side chain part of the pseudo LCcoP was reversed from positive to negative value in the higher frequency region than several hundreds kHz in analogy with low molecular weight nematic LCs[17,18], it is reasonable that a light scattering state was recognized in this a.c. frequency region due to a transient change of LC molecular alignment. When the reversible light switching is repeated many times under application of a.c. electric fields with low (DC or ~0.1 Hz) and high frequencies (~ kHz), it is easy to predict the damage of the cell for the binary composite system because of the electric current effect accompanying an ionic current upon the application of a low frequency electric field. Therefore, it is apparent that the bistable and reversible light switching driven by a.c. electric fields with high (~ kHz) and higher frequencies (~100 kHz) should be useful to construct the binary composite systems having an excellent durability, because the ionic current should not be induced in the higher frequency region above ~ kHz.

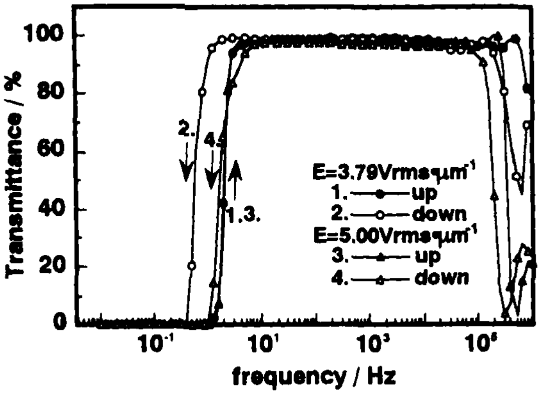


FIGURE 4 Frequency dependence of the transmittance for the [PS(3EM/DM)(n=12)/E7,38/62mol%(50/50wt%)] composite system at 301 K.

Figure 5 shows the relationship between rise and decay response times (τ_R, τ_D) and magnitude of applied electric field for the [PS(3EM/DM)(n=12)/E7,38/62mol%] composite system upon the application of a.c. electric fields with low- (0.1 Hz) and high- (1 kHz) driving frequencies. A reversible and bistable electro-optical switching with quite shorter response times (~100 ms) at room temperature was realized for the [PS(3EM/DM)(n=12)/E7,38/62mol%] composite system under the application of an a.c. electric field above 4 Vrms•μm^{-1}, as shown in Figure 6. Also, in the case of the application of high- (1 kHz) and higher- (300 kHz) driving frequency a.c. electric fields, the binary composite system showed a reversible and bistable electro-optical switching with the similar response times (~100 ms) at room temperature. The turbid (light scattering) and the transparent states for the composite system could be stably maintained 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 strength at room temperature. Then, it is concluded from the results mentioned above that the introduction of pseudo LCcoP for the induced smectic composite systems is strikingly effective to reduce the electro-optical switching times with a stable memory effect at room temperature.

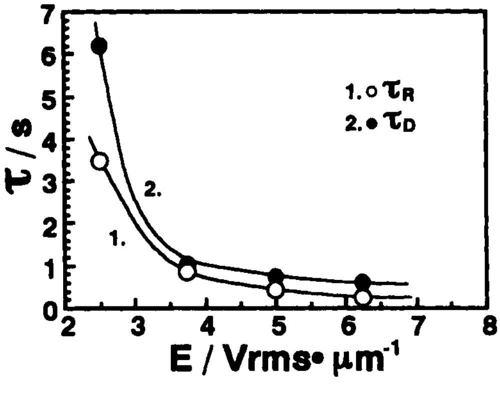


FIGURE 5 Relationship between rise and decay response times (τ_R, τ_D) and magnitude of applied electric field for the [PS(3EM/DM)(n=12)/E7,38/62mol%(50/50wt%)] composite system at 301 K upon application of electric field with 1kHz and 0.1Hz, respectively.

CONCLUSIONS

A pseudo liquid crystalline copolymer (pseudo LCcoP) with weak polar methoxy terminal groups in the side chains 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 chains 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 (22-67 mol% of LCs) and temperature (250~320 K). A novel type of induced smectic (pseudo LCcoP with weak polar methoxy terminal groups / nematic LCs with each strong polar cyano terminal group) composite system was developed. 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. Also, the binary composite system showed a reversible and bistable electro-optical switching based on the sigh reversal of the dielectric anisotropy upon the application of a.c. electric fields with high- (~kHz) and higher- (~100 kHz) driving frequencies. Introduction of pseudo LCcoP with a small substituent fraction of mesogenic side chains to the induced smectic binary composite system is extremely effective for an improvement of the switching speed of the binary composite system.

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