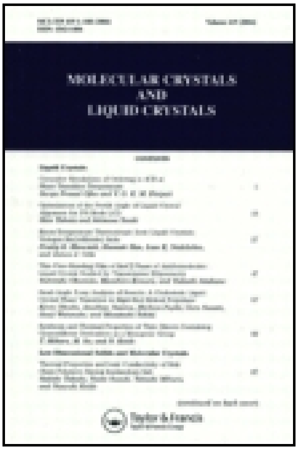

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Fast Bistable Switching Composite Systems of Side-chain Liquid-crystalline Copolymer and Low Molecular Weight Liquid Crystals

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Fast Bistable Switching Composite Systems of Side-chain Liquid-crystalline Copolymer and Low Molecular Weight Liquid Crystals

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Mesomorphic characteristics and bistable light switching properties of the composite system composed of various side chain type liquid crystalline copolymers (LCcoPs) which includes the flexible dimethylsiloxane segment as one constituent of the copolymer and low molecular weight nematic liquid crystals (nematic LCs) have been investigated in order to construct the optimum smectic binary composite system with both fast light switching characteristics and stable memory effects at room temperature. Two types of novel (LCcoP/nematic LCs) composite systems in a smectic phase studied were (1) (pseudo LCcoP with weak polar methoxy terminal groups/nematic LCs with strong polar cyano terminal groups) and (2) (smectic LCcoP with strong polar cyano terminal groups/nematic LCs with the same terminal groups). The response speed of bistable light switching for the binary composite system could be remarkably improved by reducing the LCcoP fraction maintaining a smectic state at room temperature due to an increase of the optimum flexible segment fraction.

Keywords: Side chain liquid crystalline copolymer; pseudo liquid crystalline copolymer; induced smectic binary composite system; induced smectic phase; bistable and reversible electro-optical switching; memory effect

INTRODUCTION

Side chain liquid crystalline polymers (LCPs) are fascinating materials as a constituent component for technologically important electro-optical devices

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[1]. The application of LCPs in a glassy phase for an optical data storage, that is, the write-once and erasable thermo-optical recording has been demonstrated by some researchers since 1983 [2-4]. There were also some applications in optical data storage for smectic polysiloxanes, that is, the data might be stored in the viscous smectic state [5-8]. Though the combination of polymeric and liquid crystal (LC) properties is very unique, LCPs are inferior to LCs in their applications as fast switching electro-optical displays since LCPs response very slowly to external stimulations such as electric or magnetic fields due to their high viscosities.

The binary composite systems composed of LCP and LC which has the similar chemical structure to that of the mesogenic side chain in LCP have been extensively investigated in order to improve the switching speed of an electro-optical effect for LCPs [9-11]. The (LCP/LC) composite systems show faster switching speed than LCP itself because of a decrease in viscosity. Furthermore, the smectic composite systems composed of nematic or smectic side chain type and nematic LCs exhibit reversible and bistable electro-optical switching if the binary systems show a homogeneous smectic phase [11-13]. As schematically shown in Figure 1, the reversible turbid

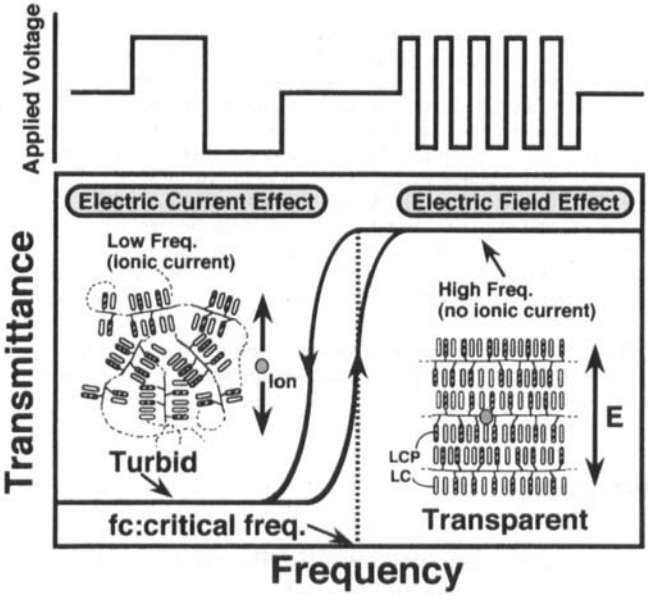

FIGURE 1 Schematic illustration of the turbid and transparent states for the smectic (LCP/nematic LCs) composite system under the application of an ac electric field with different frequencies.

(light scattering)-transparent switching with a high contrast is observed upon the application of ac electric fields with low and high frequencies, respectively. The novel characteristic of the binary systems is that both transparent and turbid states can be maintained stably due to mechanical strength of the smectic phase, even though an electric field is turned off. Similar phenomena have been reported for a dynamic scattering mode of smectic A LCs doped with some charged impurities (S_ADSM) [14–16]. Compared with the S_ADSM, the (LCP/LC) binary composite systems exhibited a faster decay response because a more effective electric current effect occurred due to the presence of LCP [17, 18].

The smectic binary composite systems are mainly divided into two types, (1) the induced smectic binary composite system of nematic LCP with a weak polar methoxy terminal group in the side chain and nematic LCs with a strong polar cyano end: (nematic LCP/nematic LCs) and (2) the smectic binary composite system of smectic LCP with a strong polar cyano terminal group in the side chain and nematic LCs with a strong polar cyano end: (smectic LCP/nematic LCs) [19, 20]. In order to construct the smectic or induced smectic binary composite system which exhibit reversible and bistable electric-optical switching with a short response time at room temperature as well as a stable memory effect, a compatible smectic phase is required over wide ranges of concentration and temperature. For this purpose, the optimum composite systems might be realized by using the smectic LC copolymer (smectic LCcoP) with dimethylsiloxane groups in the main chain and nematic LCs. Faster electro-optical switching with a bistable memory effect at room temperature might be expected by the introduction of LCcoP into the smectic (smectic LCcoP/nematic LCs) composite systems due to a reduction of the LCcoP fraction than LCP one, maintaining a smectic state, because LCcoP showed a smectic phase at room temperature widely and remarkably high mobility of its main chain [21]. LCcoP with a small fraction of substituted mesogenic side chain did not exhibit mesophase characteristics, which was named as pseudo LCcoP in the present study. However, the (pseudo LCcoP/nematic LCs) composite system showed an induced smectic phase over a wide range of mixing concentration and temperature. Also, 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 [22, 23].

In this paper, two novel types of binary composite systems including LCcoPs and pseudo LCcoPs with a small fraction of substituted mesogenic side chain have been proposed to improve the response speed for bistable electro-optical switching at room temperature. The influence of the substituent fraction of mesogenic side chain on the electro-optical characteristics has been investigated to increase the switching speed for the binary composite systems.

EXPERIMENTAL SECTION

Materials

Figure 2 shows chemical structures and physical properties of nematic or smectic LCP, smectic LCcoPs, pseudo LCcoPs, and nematic LCs used in this study. The nematic LCP and the pseudo LCcoPs with a weak polar terminal group (n-LCP-OMe and pseudo LCcoP-OMes) were poly[((((4-methoxyphenoxy)carbonyl)phenoxy)propyl)methylsiloxane] (PS3EM(n = 24)) and poly[(((((4-methoxyphenoxy)carbonyl)phenoxy)propyl)methylsiloxane)-*co*-(dimethylsiloxane)] (PS(3EM/DM, 52.5/47.5 mol%)(n = 12) and PS(3EM/DM, 27.5/72.5 mol%)(n = 25)). The smectic LCP, the smectic LCcoPs, and the pseudo LCcoP with a strong terminal group (s-LCP-CN, s-LCcoP-CNs, and pseudo LCcoP-CN) were poly[((((4-cyanophenoxy)carbonyl)phenoxy)hexyl)methylsiloxane] homopolymer (PS6EC(n = 24)), poly-[(((((4-cyanophenoxy)carbonyl)phenoxy)hexyl)methylsiloxane)-*co*-(dimethylsiloxane)] copolymers (PS(6EC/DM, 52.5/47.5 mol%)(n = 12), PS(6EC/DM, 32.5/67.5 mol%)(n = 27), and PS(6EC/DM, 16.5/83.5 mol%)(n = 29)), respectively. These LCP, LCcoPs, and pseudo LCcoP with the same mesogenic unit and the siloxane backbone were synthesized through a hydrosilylation reaction between poly[(methylsiloxane) homopolymer (PHMS) or poly[(methylsiloxane)-*co*-(dimethylsiloxane)] copolymer (PHDS) and appropriate alkene terminated mesogenic group by a conversional method [24]. The chemical components or structures and the mesogenic side chain fraction in the LCPs, the LCcoPs, and the pseudo LCcoPs were confirmed by both NMR and FT-IR. The average degrees of polymerization n, number- and weight-average molecular weights M_n and M_w, the polydispersity M_w/M_n, and purities were determined by gel permeation chromatography (GPC) in tetrahydrofuran using the polystyrene standards. Nematic LCs are commercial liquid crystals, E7 (MERCK Co. Ltd., an eutectic nematic mixture). E7 exhibites a positive dielectric anisotropy, and is reported to be comprised of cyanobiphenyl, oxycyanobiphenyl, and cyanoterphenyl derivatives.

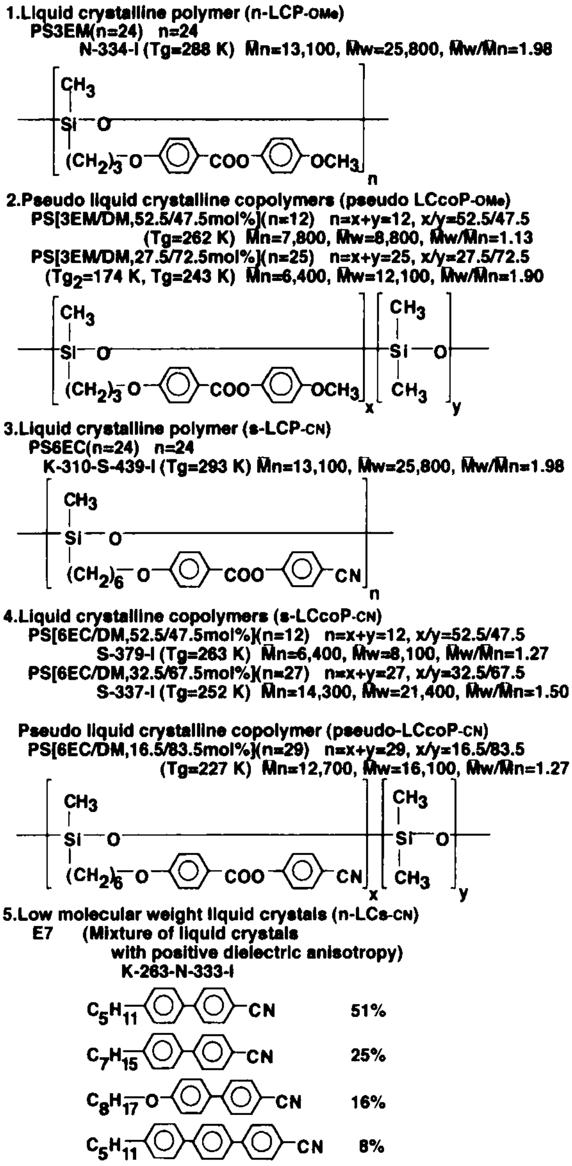

FIGURE 2 Chemical structures and physical properties of (1) nematic liquid crystalline polymer with weak polar terminal groups, (2) pseudo liquid crystalline copolymers with weak polar terminal groups, (3) smectic liquid crystalline polymer with strong polar terminal groups, (4) smectic liquid crystalline copolymers and pseudo liquid crystalline copolymer with strong polar terminal groups, and (5) low molecular weight nematic liquid crystals with each strong polar cyano terminal group.

Characterization of the Binary Composite Systems

The binary composite films were prepared by solvent casting from an acetone solution of (LCP/LCs), (LCcoP/LCs), and (pseudo LCcoP/LCs). The thermal properties, 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 obtain the temperature-composition phase diagrams for the binary composite systems. DSC thermograms were obtained under nitrogen purge. In order to obtain the reproducible DSC data, the 3rd heating curves were used. POM observation was carried out under crossed polarizers by using a hot stage. The heating and cooling rates for DSC studies and POM observations were 5 and 1 K • min^{-1}, respectively. X-ray diffraction patterns were taken on an imaging plate by using Ni filtered Cu-Kα (λ = 0.15405 nm).

Measurement of Electro-optical Effect for the Binary Composite Systems

The experimental setup used for electro-optical switching measurements is illustrated in Figure 3. The composite films were sandwiched between two indium-tin oxide (ITO)-coated glass plates of 5 mm × 5 mm which were separated by a PET film spacer of 10 μm thick. All samples were measured in an unaligned state. The temperature of the sample was controlled by using a home-made nichrom heating system attached a thermocontroller with a resolution of ±0.04 K. A He-Ne laser of 2 mW at 632.8 nm with a beam

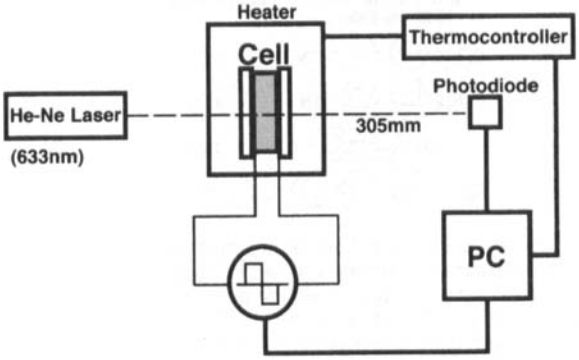

FIGURE 3 Schematic illustration of the measuring system for electro-optical properties of the composite system.

diameter of 0.63 mm was used as an incident light being transmitted normal to the film surface and an external ac electric field was applied across the composite film. The transmitted light intensity was measured with a photodiode without any polarizers under the modulation of an ac electric field and its effective light detectable area was 6.6 mm^2. The rise response time, τ_R was evaluated as the time period required for a 10–90% transmittance change. Similarly, the decay response time, τ_D was also evaluated as the time period required for a 90–10% transmittance change. The elapse time dependence of the transmitted light intensity was recorded with a digital storage oscilloscope to evaluate a memory effect of the composite systems. The distance between cell and photodiode was 305 mm.

RESULTS AND DISCUSSION

Mesomorphic Characterization of (n-LCP-OMe/n-LCs-CN) and (pseudo-LCcoP-OMe/n-LCs-CN) Composite Systems

Figures 4(a), (b) and (c) show the phase diagrams of the [PS3EM(n = 24)/E7] (a), the [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7] (b), and the [PS(3EM/DM, 27.5/72.5 mol%)(n = 25)/E7] (c) composite systems. These phase diagrams were obtained on the basis of the DSC and X-ray studies and also POM observations. The phase diagrams are mainly divided into 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, (F) crystalline (LCP or pseudo LCcoP + LCs) + glassy mesophase (LCP or pseudo LCcoP + LCs) state, and (G) phase-separated (isotropic pseudo LCcoP + mesophase pseudo LCcoP and LCs) state. In the case of [PS3EM(n = 24)/E7], a homogeneous mesophase was formed over the whole mixing concentration of LCP. On the other hand, in the cases of [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7] and [PS(3EM/DM, 27.5/72.5 mol%)(n = 25)/E7], homogeneous mesophases were formed over the mixing ranges below 78 mol% (85 wt%) and 60 mol% (75 wt%) of pseudo LCcoP fraction, respectively. These [PS3EM(n = 24)/E7], [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7], [PS(3EM/DM, 27.5/72.5 mol%)(n = 25)/E7] composite systems formed a homogeneous induced smectic phase in the 29–81 mol% (35–85 wt%) range of PS3EM(n = 24), in the 33–78 mol% (45–85 wt%) range of PS(3EM/DM, 52.5/47.5 mol%)(n = 12), and in the

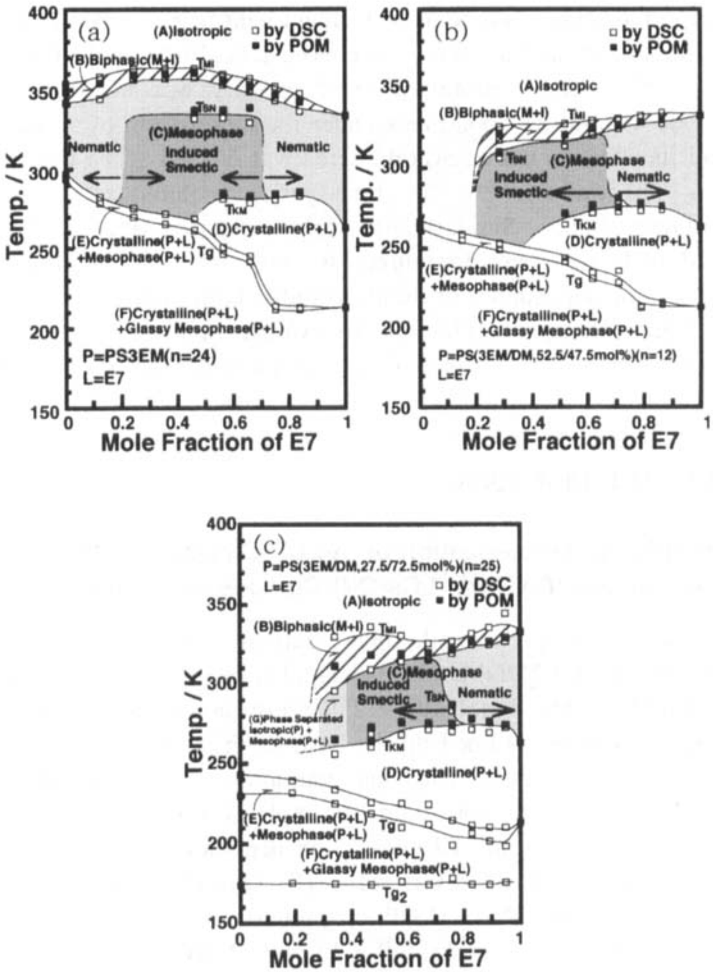

FIGURE 4 Phase diagrams of the [PS3EM($n=24$)/E7] (a), the [PS(3EM/DM, 52.5/47.5 mol%)($n=12$)/E7] (b), and the [PS(3EM/DM, 27.5/72.5 mol%)($n = 25$)/E7] (c) composite systems.

29–60 mol% (45–75 wt%) range of PS(3EM/DM, 27.5/72.5 mol%) ($n = 25$), respectively. In the series of these induced smectic binary composite systems composed of nematic LCP or pseudo LCcoPs with weak polar methoxy terminal groups and nematic LCs with each strong polar cyano terminal group, LCP or pseudo LCcoPs of approximately 30–80 mol% is necessary to construct the induced smectic phase, in analogy with the binary mixtures of nematic LCs [25–28]. The homogeneous induced smectic phase played an important role in realizing an excellent memory effect due to its remarkable high viscosity in comparison with that in a nematic state [16, 17]. Although PS(3EM/DM, 52.5/47.5 mol%) ($n = 12$) and PS(3EM/DM, 27.5/72.5 mol%)($n = 25$) did not show any mesophases states in the temperature range studied here, as shown in Figures 4(b) and (c), the [PS(3EM/DM, 52.5/47.5 mol%)($n = 12$)/E7] and the [PS(3EM/DM, 27.5/72.5 mol%)($n = 25$)/E7] composite systems formed the homogeneous induced smectic phases. Then, in this paper, the pseudo LCcoPs are defined as the amorphous polymers which have the possibility of forming the induced smectic phase when LCs are mixed to the amorphous LCcoPs as the binary composite component. The temperature ranges of the induced smectic state for both the [PS(3EM/DM, 52.5/47.5 mol%)($n = 12$)/E7] and [PS(3EM/DM, 27.5/72.5 mol%)($n = 25$)/E7] composites were lower than that for the [PS3EM($n = 24$)/E7] one, maybe, due to an copolymer effect.

Electro-optical Properties of Induced Smectic (n-LCP-OMe/n-LCs-CN) and (pseudo-LCcoP-OMe/n-LCs-CN) Composite Systems

In the case of the induced smectic (nematic LCP/nematic LCs) composite systems studied here, the mechanical strength or stability of an induced smectic layer might be controlled by means of varying the mixing concentration in order to improve the electro-optical switching speed. That is, polar balance between weak polar terminal groups of LCP and strong polar terminal groups of LCs can be changed depending on the variation of the component fractions and also, the polar balance might be closely related to the mechanical strength of the induced smectic layer. Then, the wide ranges of 33–78 mol% (45–85 wt%) of PS(3EM/DM, 52.5/47.5 mol%) ($n = 12$) and 29–60 mol%(45–75 wt%) of PS(3EM/DM, 27.5/72.5 mol%) ($n = 25$) were used to obtain the induced smectic composite systems at room temperature, as shown in Figures 4(b) and (c).

Figure 5 shows the frequency dependence of the transmittance for [PS(3EM/DM, 52.5/47.5 mol%)($n = 12$)/E7] with the different component fractions under the application of an electric field of $E = 5.00\,\mathrm{Vrms} \bullet \mu\mathrm{m}^{-1}$ at 301 K. A reversible and bistable light switching was recognized for the [PS(3EM/DM, 52.5/47.5 mol%)($n = 12$)/E7, 48/52 mol% (60/40 wt%)] and the [PS(3EM/DM, 52.5/47.5 mol%)($n = 12$)/E7, 38/62 mol% (50/50 wt%)] composite systems in the induced smectic state at room temperature. Each composite system exhibited a highly transparent state upon the application of a high-frequency ac electric field (1 kHz) due to the electric field effect based on the dielectric anisotropy of the LC molecules and the side chain

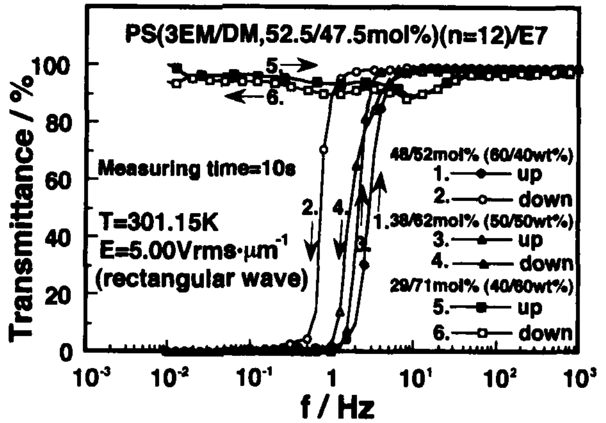

FIGURE 5 Frequency dependence of the transmittance for the [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7] composite system.

part of the pseudo LCcoP and also, a remarkable light scattering state upon the application of a low-frequency ac 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 stable, even though ac electric fields were turned off. The [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7, 48/52 mol% (60/40 wt%)] composite exhibited some hysteresis in the increasing and decreasing processes of electric field frequency. This may be due to the difference of molecular aggregation stability between laterally large smectic layer and small fragment of smectic layer. In the case of the nematic [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7, 29/71 mol% (40/60 wt%)] composite, a light scattering state was not observed, even under the application of a low-frequency ac electric field (0.1 Hz), as shown in Figure 5. The composite system also showed a low contrast and did not show a memory effect due to a homogeneous nematic state. The frequency dependence of the transmittance for [PS(3EM/DM, 27.5/72.5 mol%)(n = 25)/E7] with the different component fractions was similar to that for the [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7] described above. These results indicate that since the change in the mixing concentration of pseudo LCcoP and LCs for the binary composite system directly corresponds to the change in the polar balance between terminal groups of the two components, the viscosity of the binary composite system and the mechanical strength of the smectic layer depend strongly on the components fraction.

Figure 6 shows a variation of rise and decay response times (τ_R and τ_D) with the magnitude of applied electric fields of low (0.1 Hz) and high (1 kHz) driving frequencies, respectively, for the [PS(3EM/DM, 52.5/47.5 mol%) (n = 12)/E7, 38/62 mol% (50/50 wt%)] composite. A reversible and bistable electro-optical switching with quite shorter response times (~ 100 ms) was realized under the application of an ac electric field above 4 Vrms • μm^{-1} at room temperature for the [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7, 38/62 mol%] composite, as shown in Figure 6. The turbid (light scattering) and the transparent states for the composite system were stable for a long period (more than 3 years) at room temperature. Similarly [PS(3EM/DM, 27.5/72.5 mol%)(n = 25)/E7, 33/67 mol% (50/50 wt%)] composite exhibited a reversible and bistable electro-optical switching with a high contrast at room temperature. However, the magnitudes of the response times, about one second were longer than that of the PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7, 38/62 mol%]. The electro-optical switching of the binary composite systems needs the reorientation of polymer segments, as shown in Figure 1. The viscosity and mobility of polymer segments in the binary composites may be closely related to the length of polymer segments [18]. On the other hand, the [PS3EM(n = 24)/E7] composite did not show a fast bistable electro-optical switching, but the response times at room temperature ranged above several seconds under the corresponding electric field strength

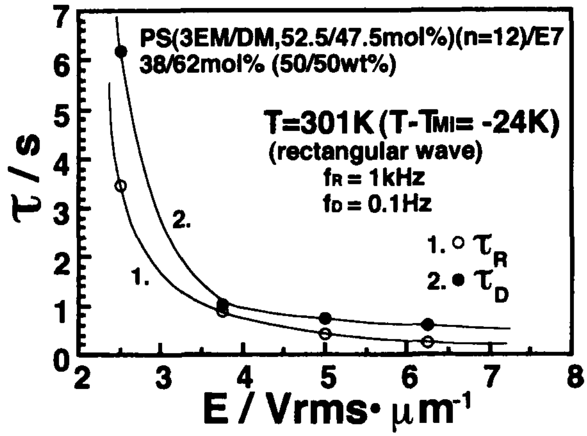

FIGURE 6 Relationship between rise and decay response times (τ_R and τ_D) and the magnitude of applied electric fields for the [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7, 38/62 mol% (50/50 wt%)] composite system.

to the cases of [PS(3EM/DM, 52.5/47.5 mol%)(n = 12)/E7] and [PS(3EM/DM, 27.5/72.5 mol%)(n = 25)/E7].

Therefore, it is reasonable to conclude from the results mentioned above that the introduction of pseudo LCcoP into the induced smectic composite systems is strikingly effective in reducing the electro-optical bistable switching times with stable turbid and transparent memories at room temperature.

Substituent Fraction Dependences of Mesogenic Side Chain on Mesomorphic Phases of (s-LCP-CN/n-LCs-CN), (s-LCcoP-CN/n-LCs-CN), and (pseudo-LCcoP-CN/n-LCs-CN) Composite Systems

Figures 7(a) ~ (d) show the phase diagrams for the [PS6EC(n = 24)/E7], the [PS(6EC/DM, 52.5/47.5 mol%)(n = 12)/E7], the [PS(6EC/DM, 32.5/67.5 mol%)(n = 27)/E7], and the [PS(6EC/DM, 16.5/83.5 mol%)(n = 29)/E7] composite systems. These phase diagrams were drawn in a similar manner for the former composite systems as mentioned above. The phase diagrams were mainly divided into the six regions, that is, (A) isotropic state, (B) biphasic (mesophase + isotropic) state, (C) mesophase (smectic or induced smectic or nematic) state, (D) crystalline (LCP or LCcoP or pseudo LCcoP + LCs) + mesophase (LCP or LCcoP or pseudo LCcoP + LCs) state, (E) crystalline (LCP or LCcoP or pseudo LCcoP + LCs) + glassy mesophase (LCP or LCcoP or pseudo LCcoP + LCs) state, and (F) phase-separated (isotropic pseudo LCcoP + mesophase pseudo LCcoP and LCs) state. In these phase diagrams, the magnitude of Tg for the binary composite systems decreased with an increase in the E7 fraction due to the plasticizing effect of E7 to the polymeric chains. The (C) region was a homogeneous mesophase (smectic or nematic) state, in which the mixture composed of the smectic LCP, the smectic LCcoPs or the pseudo LCcoP and the nematic LCs was sufficiently compatible, because of the following experimental results; (1) only one endothermic peak assigned to the mesophase-isotropic transition, T_{MI} was obtained by DSC measurement, (2) no phase-separated texture was recognized in the mesomorphic state under POM observation, and (3) the observed X-ray diffraction pattern apparently showed Debye rings corresponding to a single component in the mesomorphic state. The former three phase diagrams of the binary composite systems except the [PS(6EC/DM, 16.5/83.5 mol%)(n = 29)/E7] one showed a homogeneous mesophase over the whole mixing concentration of the LCP and the LCcoPs.

The [PS6EC(n = 24)/E7] composite system showed a smectic phase in a range of LCP above 70 wt% (62 mol%), while both the [PS(6EC/DM, 52.5/47.5 mol%)(n = 12)/E7] and the [PS(6EC/DM, 32.5/67.5 mol%)(n = 27)/E7] composite systems exhibited a smectic phase over a wide range of both the LCcoP concentration (approximately 25– 100 wt% (15– 100 mol%)) and the temperature (250– 340 K), as shown in Figures 7(a) ~ (c). As discussed in our previous reports [17–23], a homogeneous smectic phase played an important role in realizing an excellent bistable memory effect on an electro-optical switching due to its considerably high viscosity in

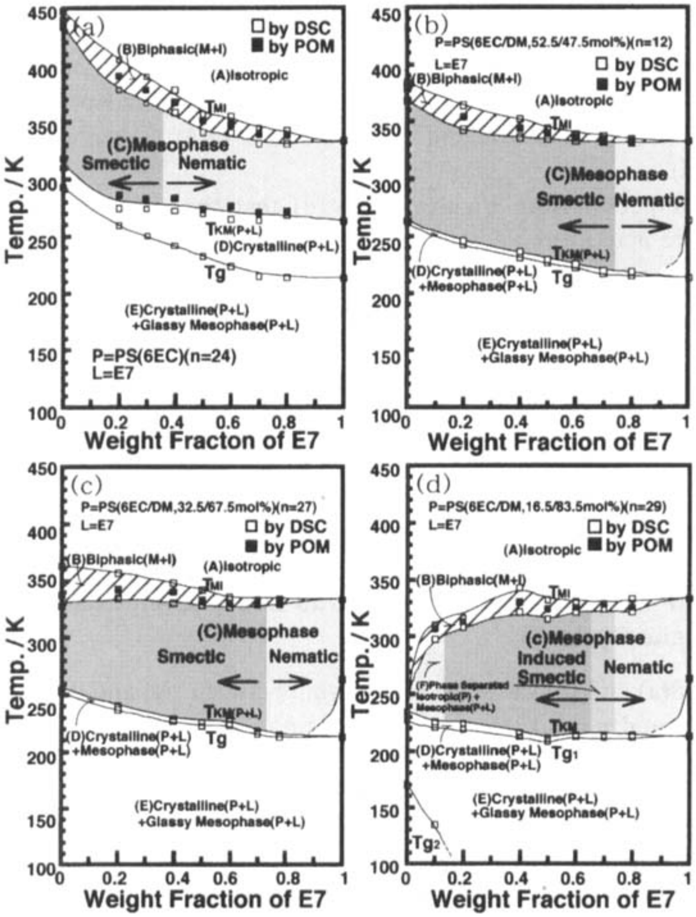

FIGURE 7 Phase diagrams of the [PS6EC(n = 24)/E7] (a), the [PS(6EC/DM, 52.5/47.5 mol%) (n = 12)/E7] (b), the [PS(6EC/DM, 32.5/67.5 mol%)(n = 27)/E7] (c), and the [PS(6EC/DM, 16.5/83.5 mol%)(n = 29)/E7] (d) composite systems.

comparison with that in a nematic state. Though the PS(6EC/DM, 16.5/83.5 mol%)($n = 29$) did not exhibit any mesophase characteristics in a temperature range studied here as mentioned in Figure 7(d), the [PS(6EC/DM, 16.5/83.5 mol%)($n = 29$)/E7] composite system showed a homogeneous induced smectic phase over a range of both the pseudo LCcoP concentration (35–85 wt% (16–67 mol%)) and the temperature (250–340 K). Therefore, it is apparent from Figure 7(d) that though the pseudo LCcoP is amorphous, its composite system can form an induced smectic phase when E7 is mixed to the amorphous pseudo LCcoP. Consequently, this indicates that a novel type of the induced smectic binary composite system could be realized. Additionally, in the case of the binary composite system composed of the LCP, the LCcoPs and the pseudo LCcoP lower than about 40 wt% (19–32 mol%), the mesophase temperature ranges (220–340 K) for the binary composite system was independent of the mesogenic side chain fraction in the PS(6EC/DM), as shown in Figures 7(a) ~ (d).

It is apparent from Figures 7(a) ~ (d) that the (LCcoP/nematic LCs) composite may form a compatible smectic mesophase in wider component and temperature ranges in comparison with the (LCP/nematic LCs) one. This indicates that an introduction of LCcoP with an appropriate substituent fraction of mesogenic side chain into the binary composite system is extremely effective in order to construct the smectic binary composite, even though the LCcoP fraction is extremely reduced, maintaining a smectic mesophase near room temperature widely.

Substituent Fraction Dependence of Mesogenic Side Chain on Electro-optical Properties of Smectic (s-LCP-CN/n-LCs-CN), (s-LCcoP-CN/n-LCs-CN), and (pseudo-LCcoP-CN/n-LCs-CN) Composite Systems

Figures 8(a) and (b) show the relationship between rise and decay response times, τ_R and τ_D and mesogenic side chain (6EC) fraction of PS(6EC/DM) for the [PS(6EC/DM)/E7, 40/60 wt%] and the [PS(6EC/DM)/E7, 30/70 wt%] composite systems at 293 K under the electric field strengthes of 6.25 and 5.00 Vrms • μm^{-1}, respectively. The driving frequencies were low-(0.1 Hz) and high-(1 kHz) ones. In the case of the [PS(6EC/DM)/E7, 40/60 wt%] composite systems, since the binary composite systems composed of LCcoPs with the mesogenic side chain fractions of 52.5, 32.5, and 16.5 mol% formed a compatible smectic phase as mentioned in Figures 7(b) ~ (d), the composite systems exhibited a reversible electro-optical switching with a high contrast (approximately 1–99% transmittance change) as well as a stable memory effect (~years) at room temperature, in a similar fashion to the smectic (LCP/LC) composite systems [11–13]. Also, since the [PS(6EC(n = 24)/E7, 40/60 wt%] composite system formed a compatible nematic phase, as shown in Figure 7(a), this binary composite did not exhibit a memory effect at room temperature. The appearance of the peak on τ_R and τ_D, as shown in Figure 8(a), might be attributed to more regularly organized smectic molecular packing in the [PS(6EC/DM, 32.5/67.5 mol%)(n = 27)/E7, 40/60 wt%] composite system, in comparison with that in another composite systems, as discussed on the basis of X-ray studies [12, 23]. Since the magnitude of response times is generally proportional to that of viscosity in the binary composite system, the viscosity for the reorientational arrangement of the smectic layer fragments might be considerably higher than that of another two composite systems, maybe due to the formation of more ordered smectic layer. However, the magnitudes of τ_R and τ_D for the [PS(6EC/DM)/E7, 40/60 wt%] composites ranged in several seconds.

In the case of a dynamic scattering mode using smectic A LCs doped with a little charged impurities (S$_A$DSM), since it is reasonable to consider a homeotropic-random alignment change corresponding to the variation from laterally large smectic layers to smectic layer fragments was more difficult than the reverse change although the orientational rearrangement of smectic layers in the smectic composite systems was directly influenced by the balance between the electric field effect and the electric current effect, the magnitude of τ_D was longer than that of τ_R [14–16, 18]. This means that

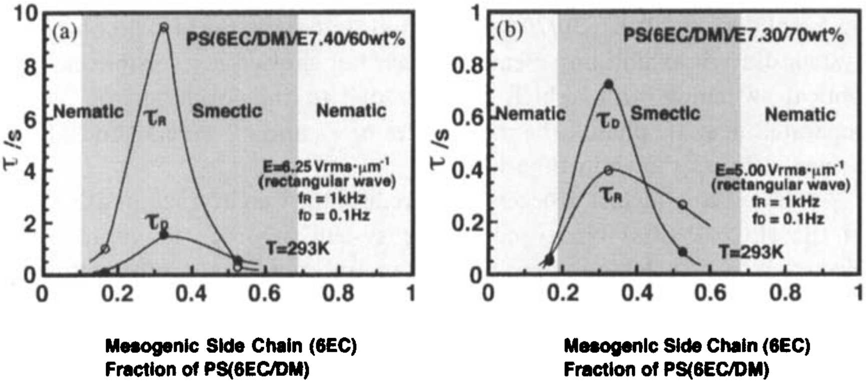

FIGURE 8 Relationship between rise and decay response times, τ_R and τ_D and mesogenic side chain (6EC) fraction of PS(6EC/DM) for the [PS(6EC/DM)/E7, 40/60 wt%] (a) and the [PS(6EC/DM)/E7, 30/70 wt%] (b) composite systems.

higher electrical power is necessary to collapse homeotropic laterally large smectic layers into small smectic fragments in comparison with the reverse aggregation change of the smectic layers. On the other hand, in the case of the [PS(6EC/DM)/E7, 40/60 wt%] binary composite systems composed of PS(6EC/DM)s with the mesogenic side chain fractions of 16.5 and 32.5 mol %, the magnitude of τ_D was shorter than that of τ_R, as shown in Figure 8(a). In particular, the magnitude of τ_D of the binary composite system composed of the pseudo LCcoP with the mesogenic side chain fraction of 16.5 mol%, 91 ms was much shorter than that of any other composite systems. This apparently indicates that an introduction of the pseudo LCcoP with fairly small mesogenic side chain fraction, that is to say, with the fairly large fraction of dimethylsiloxane groups in the main chain induces the formation of smectic layers with less-ordered molecular packing, resulting in the improvement of the decay response speed.

In the case of the [PS(6EC/DM)/E7, 30/70 wt%] composite systems, the binary composite systems composed of LCcoPs with the mesogenic side chain fractions of 32.5 and 52.5 mol% showed a compatible smectic phase, as shown in Figures 7(b) and (c), and exhibited a reversible electro-optical switching with a high contrast (approximately 1–99% transmittance change) as well as a stable memory effect (~years) at room temperature. In the case of the [PS(6EC/DM, 52.5/47.5 mol%)(n = 12)/E7, 30/70 wt%] composite system, the magnitudes of τ_R and τ_D were 267 and 86 ms, respectively, as shown in Figure 8(b). On the other hand, the (PS6EC(n = 24)/E7) and the (PS(6EC/DM, 16.5/83.5 mol%)(n = 29)/E7) composite systems showed a compatible nematic phase and a phase-separated one at room temperature, respectively. Both binary composite systems exhibited no memory effect at any temperature. In the case of the [PS(6EC/DM, 16.5/83.5 mol%)(n = 29)/E7, 30/70 wt%] composite system, the binary composite system did not exhibit any memory effect, but showed a reversible electro-optical switching with a high contrast due to the formation of phase-separated nematic phase. The magnitudes of τ_R and τ_D were 59 and 51 ms, respectively, as shown in Figure 8(b).

As discussed above, it is necessary to reduce the weight fraction of LCcoP in the (LCcoP/LCs) binary composite system in order to improve the electro-optical switching speed. Therefore, an appropriate introduction of flexible dimethylsiloxane segments into a LCcoP main chain might be permissible to reduce the magnitudes of τ_R and τ_D, because the smectic phase in the binary composite system can be formed in spite of the use of the small fraction of LCcoP. Then, it can be concluded that LCcoP with the optimum substituted fraction of mesogenic side chains is required to realize fairly fast electro-optical switching (~50 ms) as well as the stable memory (~years) at room temperature.

CONCLUSIONS

Reversible and bistable electro-optical switching characteristics of the two main types of binary composite systems have been investigated. The pseudo liquid crystalline copolymer (pseudo LCcoP) with weak polar methoxy terminal groups 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 mesogenic side chain fraction 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). The novel type of phase diagram for an induced smectic (pseudo LCcoP with weak polar methoxy terminal groups/nematic LCs with each strong polar cyano terminal group) composite system was developed. Introduction of pseudo LCcoP with minor mesogenic side chain fraction into the induced smectic binary composite system is extremely effective in order to improve the switching speed of the binary composite system. 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 influence of the mesogenic side chain fraction on the electro-optical effect for the smectic binary composite systems composed of LCcoP with a strong polar cyano terminal group was investigated in order to improve the switching speed. LCcoPs had a higher ability to form a compatible smectic mesophase than LCP. The pseudo LCcoP with minor mesogenic side chain fraction of 16.5 mol% did not exhibit any mesophase characteristics at any temperature. Nevertheless, the binary composite system showed an induced smectic phase over a range of both mixing concentration (35 – 85 wt% (16 – 67 mol%) of pseudo LCcoP) and temperature (250 – 340 K). The another novel type of phase diagram for an induced smectic (pseudo LCcoP with strong polar cyano terminal groups/nematic LCs with each strong polar cyano terminal group) was developed. The binary composite systems composed of 30 wt% (19 mol%) LCcoP with mesogenic side chain fractions of 32.5 and 52.5 mol% showed a compatible smectic phase at room temperature. A construct of the binary smectic composite with minor LCcoP fraction, maintaining a smectic mesophase range near room temperature widely is obviously realized for an introduction of LCcoP with an appropriate mesogenic side chain fraction into the binary composite system. This indicates that LCcoP with the optimum mesogenic side chain fraction is required to realize a high speed electro-optical switching (~50 ms) as well as a stable memory effect (~years) at room temperature.

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