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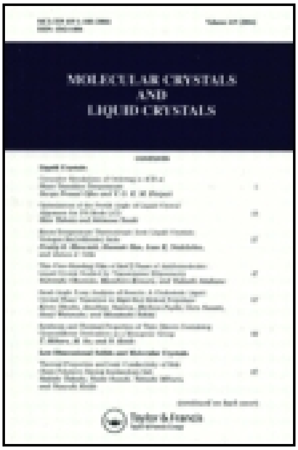

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Spacer Length Dependence of Mesomorphic Characteristics and Bistable Electro-Optical Effects for Smectic (Liquid Crystalline Copolymer/Liquid Crystals) Composite Systems

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Spacer Length Dependence of Mesomorphic Characteristics and Bistable Electro-Optical Effects for Smectic (Liquid Crystalline Copolymer/Liquid Crystals) Composite Systems

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Mesomorphic characteristics and bistable electro-optical switching effects of smectic composite systems composed of side chain liquid crystalline copolymer (LCcoP) with a weak polar methoxy terminal group in a side chain and low molecular weight nematic liquid crystals (nematic LCs) with each strong polar cyano end group have been investigated. The spacer length of the mesogenic side chain in LCcoP has strongly affected the mesomorphic characteristics and the electro-optical effects of the (LCcoP/LCs) composite systems. The response speed of the binary composite systems became faster with a decrease of the spacer length. The binary composite systems showed reversible and bistable electro-optical switching characteristics with response time of ~100 ms, that is, a light scattering state and a transparent one upon the application of ac electric fields with low frequency (up to ~ Hz) and high one (10–10^5 Hz), respectively. However, a light scattering state was also observed due to the sign reversal of dielectric anisotropy upon the application of an ac electric field above ~10^5 Hz.

Keywords: side chain liquid crystalline copolymer; pseudo liquid crystalline copolymer; induced smectic; binary composite system; spacer length; bistable electro-optical switching

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INTRODUCTION

Side chain liquid crystalline polymers (LCPs) which exemplify the dual nature of polymers and low molecular weight liquid crystals (LCs) are widely recognized as one of the electro-optical materials to store information optically[1]. The introduction of LCP materials into LC matrices has been the focus of much interest to improve the switching speed of an electro-optical effect for LCP[2-4]. The (LCP/LC) composite systems show faster switching speed than LCP itself, because of a decrease in viscosity. Furthermore, the binary composite systems exhibit reversible and bistable electro-optical switching, in the case that the composites show a homogeneous smectic phase[4-6].

The approach to build the optimum smectic binary composite system with a faster bistable switching speed and a stable memory effect at room temperature has been tried by using the composite systems being composed of various LCPs or side chain liquid crystalline copolymer (LCcoPs) with dimethylsiloxane groups in the main chain and nematic LCs, which exhibit a nematic state at room temperature[7-9]. Also, it has been reported that the binary mixtures of nematic LCs with a weak polar terminal group and a strong polar one exhibit an induced smectic phase[10,11]. Then, this concept was applied to the binary composite system of nematic LCP with a weak polar terminal group in the side chain part and nematic LCs with a strong polar end group, in order to reduce the response time for the bistable and reversible light switching[8,12-15].

This paper describes the influence of the spacer length of mesogenic side chain in LCcoP with a weak polar terminal group on mesomorphic characteristics and electro-optical effects for the smectic (LCcoP/LCs) composite systems in order to improve the switching speed. When a certain amount of LCcoP is introduced into LCs matrices, the mesophase characteristics change from nematic to smectic mesophase dramatically with significantly altering the electro-optic properties of the LC. We suggest that the composite systems can be used for fast response materials with a stable memory function for practical applications.

EXPERIMENTAL SECTION

Figure 1 shows the chemical structures and physical properties of a pseudo LCcoP, LCcoPs, and nematic LCs used in this study. The pseudo LCcoP means that the copolymer does not exhibit a mesophase but the composite

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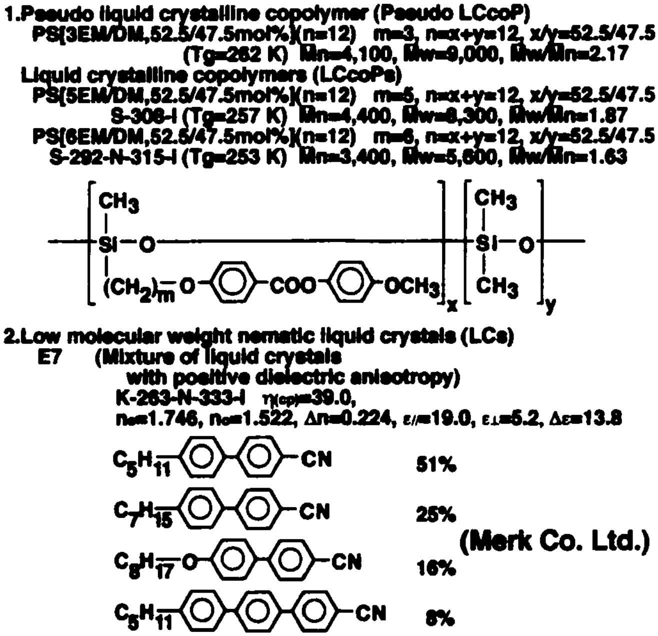

FIGURE 1 Chemical structures and physical properties of a pseudo liquid crystalline copolymer with weak polar terminal groups and liquid crystalline copolymers with weak polar terminal groups (1) and low molecular weight nematic liquid crystals with each strong polar terminal group (2).

system with LCs forms a mesophase. The pseudo LCcoP and LCcoPs were poly[(((((4-methoxyphenoxy)carbonyl)phenoxy)hexyl)methylsiloxane)-*co*-(dimethylsiloxane)], PS(3EM/DM, 52.5/47.5 mol %)(n = 12), and PS(5EM/DM, 52.5/47.5 mol %)(n = 12) and PS(6EM/DM, 52.5/47.5 mol %)(n = 12), respectively. n is the average degree of polymerization. The number of methylene group as a flexible alkyl spacer was m = 3, 5 and 6. The siloxane copolymers were synthesized by a standard method reported by Finkelmann *et al.*[16]. Their chemical structures were confirmed by NMR and FT-IR, and their 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 in tetrahydrofuran using polystyrene standards. Also, nematic LCs were commercial liquid crystals of

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E7, a eutectic nematic mixture. E7 showed a positive dielectric anisotropy. The binary composite systems were prepared from an acetone solution 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 obtain the phase diagrams of the binary composite systems. DSC thermograms were obtained by using a Rigaku DSC 8230 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 Nikon POM AFM equipped with a Leitz 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-Ka (λ = 0.15405 nm).

For electro-optical studies, the composite film was sandwiched between two ITO -coated glass plates (dimensions 5 mm × 5 mm) which were separated by the PET film spacer of 10 μm thick. All samples were measured in an unaligned state. A He-Ne laser 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 were measured with a photodiode without any polarizers under the modulation of an ac 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 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 90-10 % transmittance change. The intensity of transmitted light with an elapse of time was recorded with a digital storage oscilloscope to evaluate a faculty of memory effect for the composite systems.

RESULTS AND DISCUSSION

Effect of the Spacer Length of Mesogenic Side Chain on the Mesomorphic Characteristics of (Pseudo LCcoP or LCcoP/E7) Composite Systems

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Figures 2 (a), (b), and (c) show the phase diagrams of the [PS(3EM/DM, 52.5/47.5 mol %)(*n* = 12)/E7] (a), the [PS(5EM/DM, 52.5/47.5 mol %)(*n* = 12)/E7] (b), and the [PS(6EM/DM, 52.5/47.5 mol %)(*n* = 12)/E7] (c) composite systems. These phase diagrams were obtained on the basis of the DSC and X-ray studies, and POM observations. The phase diagrams are mainly divided into six regions, that is, (A) isotropic state, (B) biphasic (mesophase + isotropic) state, (C) mesophase (smectic, induced smectic or nematic) state, (D) crystalline (LCcoP + LCs) state, (E) crystalline (LCcoP + LCs) + mesophase (LCcoP + LCs) state, and (F) crystalline (LCcoP + LCs) + glassy mesophase (LCcoP + LCs) state. In the case of the [PS(3EM/DM)(*n* = 12)/E7], a homogeneous mesophase was formed over the mixing range below 78 mol % (85 wt %) of the pseudo LCcoP fraction. On the other hand, in the cases of the [PS(5EM/DM)(*n* = 12)/E7] and the [PS(6EM/DM)(*n* = 12)/E7] composites, homogeneous mesophases were formed over the whole mixing range of the LCcoPs. As shown in Figures 2 (a), (b) and (c), these composite systems formed a homogeneous smectic phase in the 33-78 mol % (45-85 wt %) range of PS(3EM/DM)(*n* = 12), in the 24-100 mol % (35-100 wt %) range of PS(5EM/DM)(*n* = 12), and in the 23-100 mol % (35-100 wt %) range of PS(6EM/DM)(*n* = 12), respectively. The homogeneous smectic or induced smectic phase played an important role in realizing an excellent memory effect with a fairly high response speed due to its high viscosity in comparison with that in a nematic phase[12,13].

Although PS(3EM/DM)(*n* = 12) did not show any mesophase states in the temperature range studied here, the [PS(3EM/DM)(*n* = 12)/E7] composite system formed the homogeneous induced smectic phase, as shown in Figure 2 (a). Then, in this paper, the pseudo LCcoP is defined as the amorphous

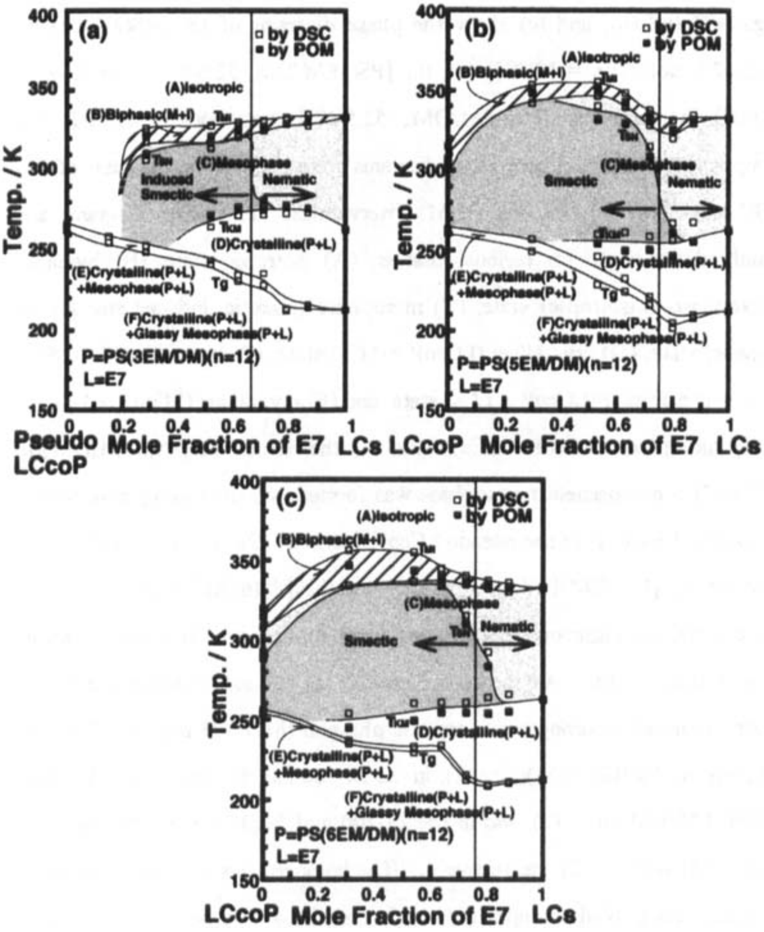

FIGURE 2 Phase diagrams of the [PS(3EM/DM)(n = 12)/E7] (a), the [PS(5EM/DM)(n = 12)/E7] (b), and the [PS(6EM/DM)(n = 12)/E7] (c)

polymer which has the possibility of forming the induced smectic phase when the LCs are mixed to the amorphous LCcoP as the binary composite component. Also, in the case of the pseudo LCcoP or the LCcoPs fraction

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lower than 40 wt % (33~19 mol %), the mesophase temperature ranges for the binary composite systems were almost independent of the spacer length, that is, 270~330 K.

Influence of the Spacer Length of Mesogenic Side Chain on Electro-optical Properties for Smectic Binary Composite Systems

Figure 3 shows the frequency dependence of the transmittance for the [PS(3EM/DM)(*n* = 12)/E7, 38/62 mol %(50/50 wt %)] under the conditions of ac electric field of 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 an apparent hysteresis in the increasing and decreasing processes of an electric field frequency. On the other hand, at E=5.00 Vrms•μm^{-1}, the composite system did not show hysteresis. This may be due to the balance between electric current effect and electric field effect and also, the difference between aggregation stability of the random orientation of smectic layer fragments and the homeotropic alignment composed of laterally large smectic layers. 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 system changed to a light scattering state in the higher frequency region above *ca.* 100 kHz in a similar fashion to the low frequency region, as shown in Figure 3. Also, characteristics of both [PS(5EM/DM)(*n* = 12)/E7, 28/72 mol %(40/60 wt %)] and [PS(6EM/DM)(*n* = 12)/E7, 27/73 mol %(40/60 wt %)] composites exhibited very similar light switching behaviors to the case of the [PS(3EM/DM)(*n* = 12)/E7, 38/62 mol %(50/50 wt %)] composite described above. Since the dielectric anisotropy of both LCs molecules and the side

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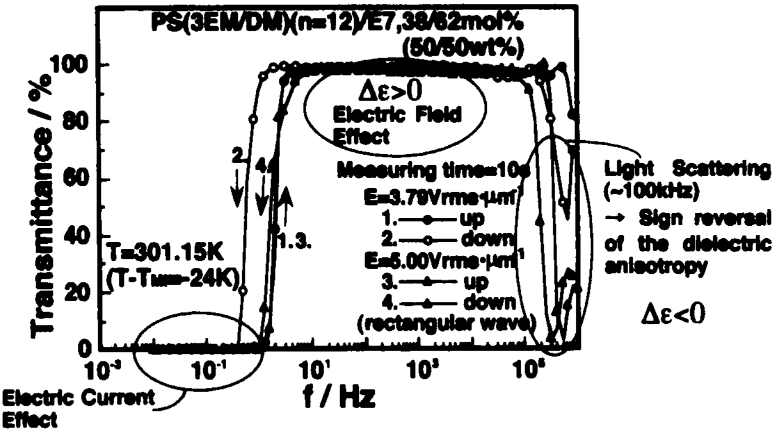

FIGURE 3 Frequency dependence of the transmittance for the [PS(3EM/DM)(*n* = 12)/E7, 38/62 mol %(50/50 wt %)] composite system.

chain part of the pseudo LCcoP was reversed from positive to negative value in the higher frequency region above *ca.* 100 kHz, it is reasonable that a light scattering state appeared in this ac frequency region. The bistable and reversible light switching driven by ac electric fields with high (~ kHz) and higher frequencies (~100 kHz), as mentioned above, 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 shows the relationship between rise and decay response times (τ_R and τ_D) and the spacer length (*m*) in PS(*m*EM/DM) for [PS(*m*EM/DM)(*n* = 12)/E7] upon the application of ac electric fields of 6.25 Vrms•μm^{-1} with low- (0.1 Hz) and high- (1 kHz) driving frequencies at 301 K. A reversible and bistable electro-optical switching with a high contrast at room temperature was

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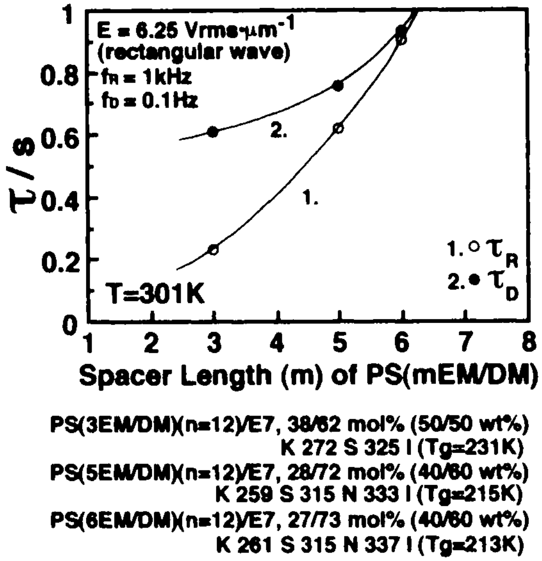

FIGURE 4 Relationship between response times (τ_R and τ_D) and the spacer length (*m*) in PS(*m*EM/DM) for [PS(*m*EM/DM, 52.5/47.5 mol %)(*n* = 12)/E7].

realized for the smectic binary composites, the [PS(3EM/DM)(*n* = 12)/E7, 38/62 mol %(50/50 wt %)], [PS(5EM/DM)(*n* = 12)/E7, 28/72 mol %(40/60 wt %)] and [PS(6EM/DM)(*n* = 12)/E7, 27/73 mol %(40/60 wt %)]. The smectic binary composite systems showed faster switching characteristics with a decrease in the spacer length of mesogenic side groups in LCcoP, may be due to a decrease in intermolecular interaction among mesogenic side chain groups and LC molecules. Though the turbid (light scattering) and the transparent states for the composite system were stable for a long period (more than three years) without any application of ac electric fields with low and high driving frequencies at room temperature owing to the mechanical strength of the smectic phase, the response speed between these states was quite slow and the magnitudes of τ_R and τ_D ranged in several 100 ms. Furthermore, in the case of the application of high- (1 kHz) and higher- (300 kHz) driving frequency ac electric fields, the binary composite systems showed a reversible and bistable electro-optical switching with much the same response times (~100 ms) at room temperature.

CONCLUSIONS

The influence of the spacer length of mesogenic side chain in LCcoP with a weak polar terminal group on mesomorphic characteristics and electro-optical effects for the smectic (LCcoP/LCs) composite systems has been investigated in order to improve the switching speed. In the case of the pseudo LCcoP with a short spacer length, *m* = 3, the binary composite systems showed a compatible induced smectic phase with nematic LCs at room temperature in the 45-85 wt %(33-78 mol %) range of the pseudo LCcoP. On the other hand, in the case of the LCcoPs with long spacer lengthes, *m* = 5 and 6, the binary composite systems showed smectic one in the 35-100 wt %(24-100 mol %) range of the LCcoPs. The response speed of the smectic binary composite systems became faster with a decrease in the spacer length of mesogenic side chain in LCcoP, maybe due to the change in molecular packing of the smectic phase. Also, the smectic binary composite systems showed reversible and bistable electro-optical switching characteristics with response time of ~100 ms based on the sign reversal of dielectric anisotropy upon the application of ac electric fields with high- (~ kHz) and higher- (~100 kHz) driving frequencies.

References

[1] C. B. McArdle, Ed. In *Side Chain Liquid Crystal Polymers* (Blackie: Glasgow and London, Chapman and Hall, Inc., New York, 1989).

[2] A. I. Hopwood and H. J. Coles, *Polymer*, **26**, 1312 (1985).

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[3] M. S. Sefton and H. J. Coles, *Polymer,* **26,** 1319 (1985).
[4] T. Kajiyama, H. Kikuchi, A. Miyamoto, S. Moritomi, and J. C. Hwang, *Chem. Lett.,* **1989,** 817–820 (1989).
[5] H. Kikuchi, S. Moritomi, J. C. Hwang, and T. Kajiyama, *Polym. Adv. Tech.,* **1,** 297–300 (1990).
[6] T. Kajiyama, H. Kikuchi, J. C. Hwang, A. Miyamoto, S. Moritomi, and Y. Morimura, *Progr. Pacific Polym. Sci.,* Springer-Verlag Berlin Heidelberg, 343–354 (1991).
[7] H. Yamane, H. Kikuchi, and T. Kajiyama, *Polymer Preprints, Japan,* **41,** 3719–3721(1992).
[8] T. Kajiyama, H. Yamane, H. Kikuchi, and J. C. Hwang, In *Liquid-Crystalline Polymer Systems Technological Advances* (A.I. Isayev, T. Kyu, S. Z. D. Cheng, ACS Symp. Series No. 632; American Chemical Society: Washington, DC, 1996) Chap. 12, p. 190–200.
[9] H. Yamane, H. Kikuchi, and T. Kajiyama, *Macromolecules,* **31,** 23, 8100–8109 (1998).
[10] A. C. Griffin and J. F. Johnson, *J. Am. Chemm.. Soc.,* **99,** 4859(1977).
[11] B. Engelen, G. Heppke, R. Hopf, and F. Schnider, *Ann. Phys.,* **3,** 403(1978).
[12] T. Kajiyama, H. Kikuchi, A. Miyamoto, S. Moritomi, and J. C. Hwang, *Mat. Res. Soc. Symp. Proc.,* **171,** 305–313 (1990).
[13] J. C. Hwang, H. Kikuchi, and T. Kajiyama, *Polymer,* **33,** 1822–1825 (1992).
[14] T. Kajiyama, H. Yamane, and H. Kikuchi, *Proc. SPIE,* **3015,** 125–133 (1997).
[15] H. Yamane, H. Kikuchi, and T. Kajiyama, *Macromolecules,* **30,** 11, 3234–3241 (1997).
[16] H. Finkelmann, H. Kock, and G. Rehage, *Makromol. Chem., Rapid. Commun.,* **2,** 317 (1981).

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