

High speed switching of (liquid crystalline copolymer / low molecular weight liquid crystal) composite systems with memory functions

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Bistable light switching characteristics of the composite system composed of side chain type liquid crystalline polymer (LCP) and low molecular weight liquid crystals (LCs) have been investigated. The reversible turbid (light scattering)-transparent switching was observed upon the application of electric fields with low and high frequencies, respectively. Both transparent and turbid states of the binary composite could be maintained stably, even though an electric field was turned off. The response speed for bistable light switching could be remarkably improved by reducing the LCP fraction maintaining a smectic state. The novel types of the (LCP/LCs) composite systems and the (LC copolymer : LCcoP/LCs) composite systems with a short response time as well as bistable and reversible light switching characteristics at room temperature were investigated. High speed switching with bistable and reversible light switching characteristics was realized under the conditions of (1) reduction of the LCP fraction, (2) formation of an induced smectic state, (3) introduction of LC copolymer and (4) optimum flexible segment fraction to form an induced smectic state.

1. INTRODUCTION

Various types of (polymer/LC) composite systems have been reported as large area and flexible light-intensity controllable films [1-4]. Since thermotropic liquid crystalline polymers (LCPs) with mesogenic side chain groups exhibit both inherent mesomorphic properties of LC and excellent mechanical characteristics of polymeric materials, LCPs have attracted a major attention due to their promising applications as electro-optical devices [5]. However, since LCPs in a mesophase state are more viscous than LCs, the response time of LCPs to an external stimulation such as an electric or magnetic field is fairly longer than that of LCs. A (LCP/LC) mixture in which LC takes a role of solvent or diluent to LCP has been studied in order to reduce the magnitude of viscosity of LCP, in other words, to reduce the magnitude of response time [6-9]. A bistable and reversible light switching of the (LCP/LC) composite system in an smectic phase could be realized by the balance between electric current effect based on the electrohydrodynamic motion of the LCP main chain and electric field effect based on the dielectric anisotropy of the smectic layer being composed of LC molecules and the side chain part of LCP.

Other efforts have been done to reduce the rise and decay response times as well as the long-term excellent memory by using liquid crystalline copolymers (LCcoP) for the composite systems of

(1) (smectic-LCcoP/nematic-LCs) in a smectic state, (2) (nematic-LCcoP/nematic-LCs) in an induced smectic and (3) (smectic-LCcoP/nematic-LCs) in a flexible segment-induced smectic state.

2. BISTABLE ELECTRO-OPTICAL SWITCHING OF (SMECTIC-LCcoP/NEMATIC-LCs) COMPOSITE SYSTEMS IN SMECTIC STATE

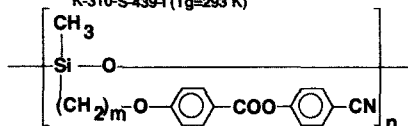
A bistable and reversible light switching of the (LCP/LC) composite system in a smectic phase could be realized by the balance between electric current effect of the LCP main chain and electric field effect of LC molecules and side chain part of LCP.

Figure 1 shows the chemical structures of LCPs, LCcoPs and LCs used in this study. LCcoPs with siloxane backbone were synthesized through poly(hydrosilation) reaction between poly(hydrogenmethyl-dimethylsiloxane) copolymer [P(HM/DM)S] backbone and appropriate alkene. The degree of polymerization of a starting copolymer was 12, 40, 120. The degree of polymerization (n) and the degree of molecular weight distribution, M_w/M_n of LCcoPs were determined on the basis of GPC. The phase transition behaviors, the thermodynamic properties and the aggregation states of the binary composites were investigated on the basis of DSC measurement,

1. Liquid crystalline polymers

PS6EC(n=35) Mn=15,130, Mw=35,920, Mw/Mn=2.37
K-311-S-444-I (Tg=292 K)

PS6EC(n=24) Mn=13,050, Mw=25,790, Mw/Mn=1.98
K-310-S-439-I (Tg=293 K)



2. Liquid crystalline copolymers and pseudocopolymer

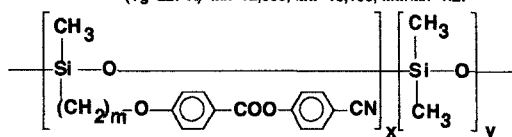
PS[3EC/DM](n=12) m=3, n=x+y=12, x/y=52.5/47.5
S-311-I (Tg=271 K) Mn=4,880, Mw=6,250, Mw/Mn=1.28

PS[3EC/DM](n=120) m=3, n=x+y=120, x/y=1/1
S-316-I (Tg=270 K) Mn=8,820, Mw=21,600, Mw/Mn=2.45

PS[6EC/DM, 52.5/47.5 mol%](n=12) n=x+y=12, x/y=52.5/47.5
S-379-I (Tg=263 K) Mn=6,370, Mw=8,080, Mw/Mn=1.27

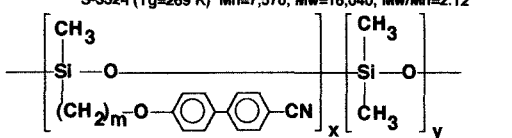
PS[6EC/DM, 32.5/67.5 mol%](n=27) n=x+y=27, x/y=32.5/67.5
S-337-I (Tg=252 K) Mn=14,320, Mw=21,430, Mw/Mn=1.50

PS[6EC/DM, 16.5/83.5 mol%](n=29) n=x+y=29, x/y=16.5/83.5
(Tg=227 K) Mn=12,660, Mw=16,100, Mw/Mn=1.27

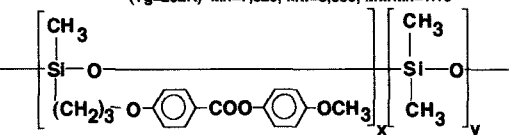


PS[4BC/DM](n=12) m=4, n=x+y=12, x/y=52.5/47.5
S-337-I (Tg=254 K) Mn=8,000, Mw=10,270, Mw/Mn=1.28

PS[4BC/DM](n=40) m=4, n=x+y=40, x/y=1/1
S-352-I (Tg=269 K) Mn=7,570, Mw=16,040, Mw/Mn=2.12



PS[3EM/DM, 52.5/47.5 mol%](n=12) n=x+y=12, x/y=52.5/47.5
(Tg=262 K) Mn=7,820, Mw=8,830, Mw/Mn=1.13



3. Low molecular weight liquid crystal
4-cyanophenyl 4'-n-heptyloxy benzoate (CPHOB)

K-339-N-354-I



E7 (Mixture of liquid crystals with positive dielectric anisotropy)
K-263-N-333-I

C₉H₁₇ 51%

C₇H₁₅ 25%

C₈H₁₇ 16%

C₅H₁₁ 8%

Figure 1. Chemical structures and physical properties of samples.

polarizing optical microscopic observation and X-ray diffraction study.

The temperature-composition phase diagram for the binary composite system using LCcOP with n=120 exhibited a phase-separated mesophase, smectic LCcOP and nematic LCs, over a whole composite fraction at room temperature. On the

other hand, the mesomorphic phase of the composite system using LCcOPs with n=12 and 40 showed a compatible mixture, smectic or nematic phases depending on the weight fraction of the components at room temperature, as shown in Figure 2. The phase diagrams of the composite systems revealed that the (PS6EC/CPHOB) composite system and the [PS(6EC/DM)/CPHOB] one were in a smectic phase above 60 wt% of LCP and 50wt% of LCcOP, respectively. This smectic phase is necessary to realize an excellent memory effect for the composite system, as discussed previously.

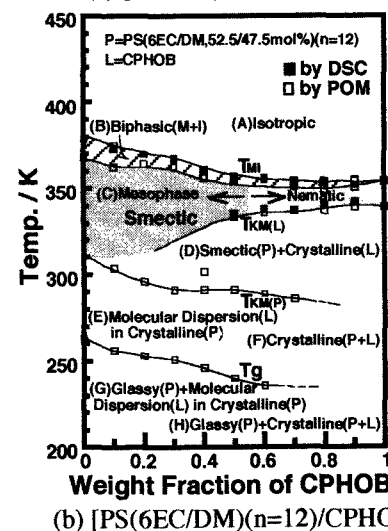
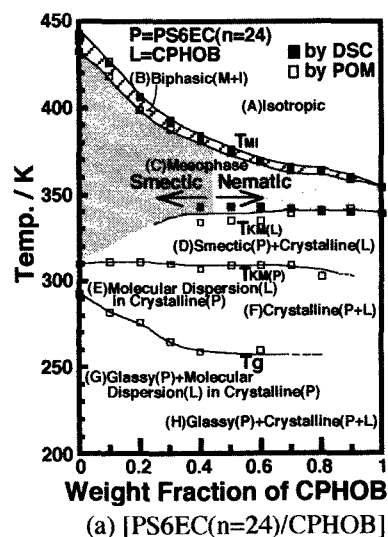


Figure 2. Phase diagrams of [PS6EC(n=24)/E7] (a) and [PS(6EC/DM)(n=12)/E7] (b) composite systems.

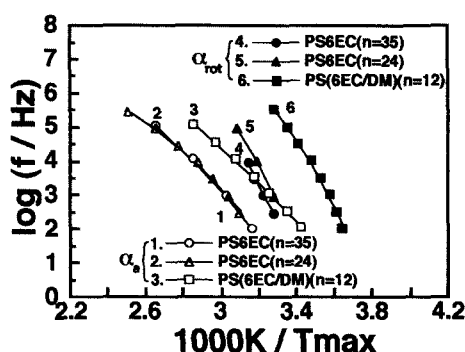


Figure 3. Arrhenius plot for relaxation frequencies of the liquid crystal side chain polymers as a function of reciprocal temperature .

Figure 3 shows the Arrhenius plot, $\log f$ vs $1/T_{max}$, for the α_a - and the α_{rot} - relaxation processes of LCPs or LCcoP. It is apparent from the dielectric relaxation studies that molecular mobility for the LCP or LCcoP main chain increased with a decrease in the degree of polymerization. Since, in particular, PS(6EC/DM) showed remarkably high mobility of its main chain, it is reasonable to conclude that molecular mobility was further enhanced by using LCcoP with a dimethylsiloxane group.

It is expected that the higher electro-optical response speed is realized for the composite system composed of LCP exhibiting higher molecular mobility. The bistable and high speed optical switching with memory effect could be realized at room temperature for the [PS(6EC/DM)/CPHOB, 50/50wt%] composite system in a smectic state at a higher temperature range by 30~40 K than room temperature.

3. BISTABLE ELECTRO-OPTICAL SWITCHING OF (NEMATIC-LCcoP/NEMATIC LCs) COMPOSITE SYSTEM IN INDUCED SMECTIC

It was reported that the binary mixtures of LCs with a strong polar cyano or nitro terminal group and a weak polar one induced a smectic phase [10,11]. This concept could be 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 to reduce the rise (τ_R) and the decay (τ_D) response times for bistable and reversible light switching [12-14]. Then, the (LCcoP/LCs) mixture in an induced smectic state is expected as a novel

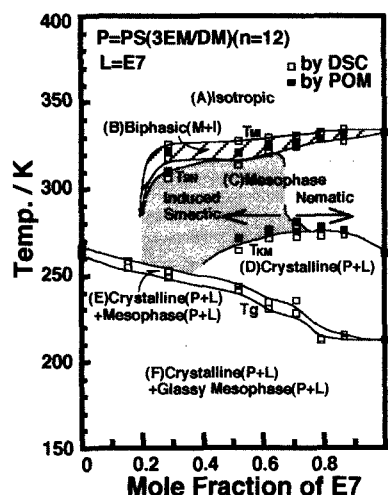


Figure 4. Phase diagram of [PS(3EM/DM)(n=12)/E7].

type of "light valve" exhibiting bistable and reversible light switching characteristics, that is, a memory effect. The binary composite system of pseudo LCcoP with a weak polar methoxy terminal group in the side chain (PS(3EM/DM,52.5/47.5 mol%)) and nematic LCs with a strong polar cyano end (E7) exhibited an induced smectic phase as shown in Figure 4. PS(3EM/DM) with substituted mesogenic side chain of 52.5 mol% did not exhibit any mesophase characteristics. However, Figure 4 shows apparently that the binary composite showed an induced smectic phase over wide ranges of both mixing concentration (35~75 mol% of LCcoP) and temperature (250~320 K). Figure 5 shows the applied electric field dependence of τ_R and τ_D for the [PS(3EM/DM)(n=12)/E7,38/62mol%] composite. A

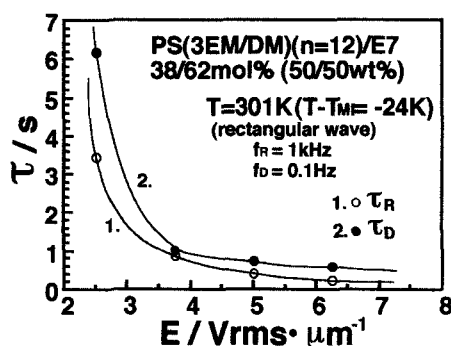


Figure 5. Relationship between response times (τ_R , τ_D) and applied electric field for [PS(3EM/DM)(n=12)/E7].

reversible and bistable electro-optical switching with a short response time (~ 100 ms) at room temperature was realized for the binary composite system.

4. FLEXIBLE SEGMENT-INDUCED SMECTIC TRANSFORMATION FOR [PS(6EC/DM)/E7,30/70wt%] COMPOSITE

The influence of the substituent fraction of the mesogenic side chain of LCP on the electro-optical effect was discussed for the (LCcoP/LCs) composite systems in order to improve the switching speed. The glass transition temperature (T_g) and the mesophase temperature range of LCcoP decreased with a decrease of mesogenic side chain fraction in LCcoP. As discussed above, it is necessary to reduce the weight fraction of LCcoP in the (LCcoP/LCs) composite system in order to improve the electro-optical switching speed. Figure 6 shows that the [PS6EC/E7] composite was not in a smectic phase but in a nematic one in the case of the lower weight fraction of LCP than 60 wt%. An appropriate introduction of a flexible dimethylsiloxane segment to a rigid LCP chain induced a smectic phase in the case of the [PS(6EC/DM)/E7,30/70wt%] composite as shown in Figure 7. Figure 7 clearly indicates that a flexible segment-induced smectic phase in the [LCcoP/LCs,30/70wt%] composite is remarkably effective to realize a higher speed electro-optical switching ($\tau_R \sim 250$ ms, $\tau_D \sim 100$ ms) as well as a stable memory effect at room temperature.

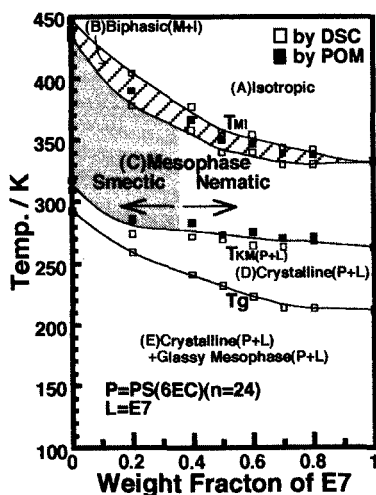


Figure 6. Phase diagram of [PS6EC($n=24$)/E7].

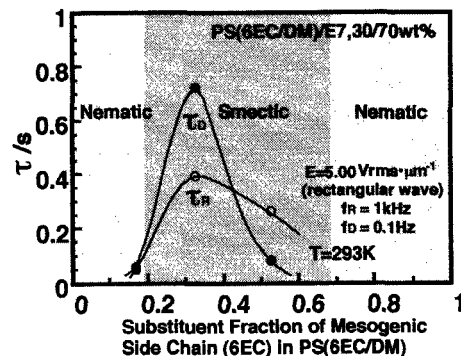


Figure 7 Relationship between response times (τ_R , τ_D) and substituent fraction of mesogenic side chain in PS(6EC/DM) for [PS(6EC/DM)/E7,30/70wt%].

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