

Bistable electro-optical switching with memory effects of (liquid crystalline polymer/low molecular weight liquid crystal) composite systems

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Nematic liquid crystal (LC) is miscible over a whole range of smectic liquid crystalline polymer (LCP) in isotropic and mesomorphic states. The composite system formed a smectic phase in an LCP weight fraction range above 60%. Reversible and bistable electro-optical effects based on light scattering were recognized for a smectic phase of the binary composite composed of LCP and LC. A light scattering state appeared in the case of the application of an a.c. electric field below a threshold frequency (f_c). Furthermore, the application of an a.c. electric field above f_c made the transmission intensity increased. Such a phenomena were induced in conjunction with the two type of effects: one is an electric field effect based on the dielectric anisotropy ($\Delta\epsilon$) of the mesogenic group and the other is an electric current effect based on the electro-hydrodynamic motion of the main chain. Each turbid and transparent state can be memorized after removal of an electric field due to the mechanical stability of the smectic layer. Similar electro-optical effect was observed for the (LCP/LC) system with an induced smectic state. Also, rewritable information storage effects have been realized for (LCP/LC/ photoresponsive molecule) ternary composite system by utilizing a photo-induced change in mechanical stability of the smectic layer.

1. INTRODUCTION

Various types of (polymer/low molecular weight liquid crystal: LC) composite system have been reported as large area and flexible light-intensity controllable films[1-7]. The term of "Dynamic Scattering" was introduced to describe the phenomenon of a light scattering state which was generated by hydrodynamic shear forces leading to turbulent flow to nematic material with negative dielectric anisotropy upon the application of an a.c. electric field. The dynamic scattering phenomenon has potential usefulness in a variety of devices, such as shutters, matrix displays, reflective TV and so on. A strong interfacial interaction between polymeric walls and LC molecules generates a light scattering state without any application of an a.c. electric

field. The optical heterogeneity in the (polymer/LC) composite film may be mainly induced by a compulsorily distorted nematic directors as well as mismatch in refractive indices. Therefore, a light scattering state of the polymer/LC composite system under an off- a.c. electric field can be characteristically termed "Static Scattering State" [7,8].

Thermotropic liquid crystalline polymers (LCP) with mesogenic side chain groups have been arousing much interest due to their possibilities for applications such as electro-optical devices, because LCP exhibits both the mesomorphic inherent properties of LC and the excellent mechanical characteristics of polymeric materials. Recently, various kinds of LCP have been synthesized and their electro-optical properties have been studied extensively. Since LCP in a mesomorphic state is more viscous than LC, the magnitude of

the response time of LCP to an external stimulation such as electric and magnetic fields is much greater than that of LC. It is, therefore, reasonable to consider that the viscosity of LCP in a mesomorphic state can be decreased by mixing of LC, in order to reduce the magnitude of the response time in the composite system. The purpose of this study is to reveal the electro-optical switching behavior of (LCP/LC) composite system. And also, rewritable information storage effects have been investigated for (LCP/LC/ photoresponsive molecule) ternary composite system.

2. EXPERIMENTAL

2.1 Materials

The chemical structures of side chain type liquid crystalline polymers (LCPs), liquid crystals (LCs), and photoresponsive molecule (PM) are given in Figure 1. PS6EC has a cyano group in the side chain mesogenic group which has a strong dielectric anisotropy. PS3EM has a methoxy terminal group in the side chain mesogenic group. Nematic LCs used were CPHOB, 5OCB and HPPB. CPHOB and 5OCB have a cyano group which exhibit a positive dielectric anisotropy. HPPB has similar functional groups to that of PS3EM. Photoresponsive molecule (PM, 9Az9) with azo group was used in order to change the mechanical stability of smectic layer upon photoirradiation of visible and ultra-violet (UV) lights.

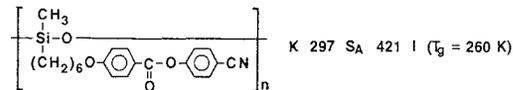
(LCP/LC) and (LCP/LC/PM) composite films were prepared by a solvent-casting method. The thickness of the film was about 15-20 μm .

2.2 Measurement

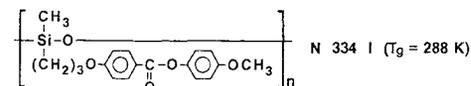
The phase transition behavior and the aggregation states of the (LCP/LC)

1. Liquid Crystalline Polymer

PS6EC

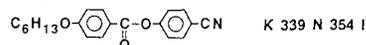


PS3EM

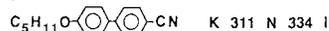


2. Low Molecular Weight Liquid Crystal

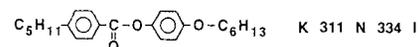
CPHOB



5OCB



HPPB



3. Photo-Responsive Molecule

9Az9

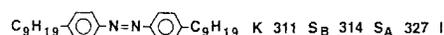


Figure 1. Chemical structures of liquid crystalline polymers (LCPs), low molecular weight liquid crystals (LCs) and photoresponsive molecule (PM).

composites were investigated on the basis of differential scanning calorimetry(DSC), polarizing optical microscopy(POM) and X-ray diffraction study.

In order to investigate the electro-optical effect, the (LCP/LC) composites were sandwiched between two ITO-coated glass plates which were transparent electrodes. The distance between the two electrodes was maintained by a 10 μm thick PET spacer. An incident light source was He-Ne laser. The electro-optical effect of the composite films based on light scattering was investigated under various conditions of the magnitude and the frequency of an a.c. electric field.

3. RESULTS AND DISCUSSION

3.1. The (LCP/LC) composite system in smectic phase

The chemical structure of CPHOB is similar to the mesogenic side group of PS6EC. (PS6EC/CPHOB) composite film was prepared to investigate a bistable light switching. The phase diagram of the (PS6EC/CPHOB) composite was obtained on the basis of DSC, POM and X-ray studies. Figure 2 shows the phase diagram of the (PS6EC/CPHOB) composite system. The glass transition temperature, T_g of PS6EC decreased with an increase in the CPHOB fraction. The decrease in T_g might be caused by the plasticizing effect of CPHOB. Since only one endothermic peak attributed to the mesophase-isotropic transition was observed, it is apparent that the composite forms a homogeneously mixed mesomorphic phase (molecularly dispersed state). Therefore, CPHOB is miscible over a whole concentration range of PS6EC in both isotropic and mesomorphic states. Since sharp low angle X-ray diffraction with a d-spacing of about 3.06 nm corresponding to a smectic layer spacing, was observed in a CPHOB weight fraction range below 40 wt%, a smectic phase certainly exists in a mesophase region above 60 wt% of PS6EC.

The as-cast (PS6EC/CPHOB:60/40) composite film of 10 μm thick in a smectic state transmitted 86 % of an incident light of He-Ne laser. A typical light-switching curve for the smectic composite system under electric fields with high and low frequencies is schematically illustrated in Figure 3. The transmittance to an incident light strikingly decreased to after applying an a.c. 100 V electric field of 1 Hz due to a remarkable increase of light scattering. Furthermore, the application of an a.c. 100 V electric field of 1 kHz made the transmittance increased to 94 %

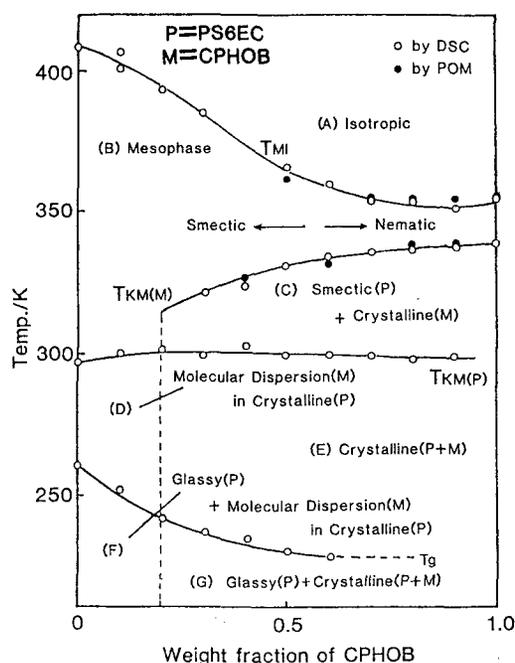


Figure 2. Phase diagram of (PS6EC/CPHOB) composite system.

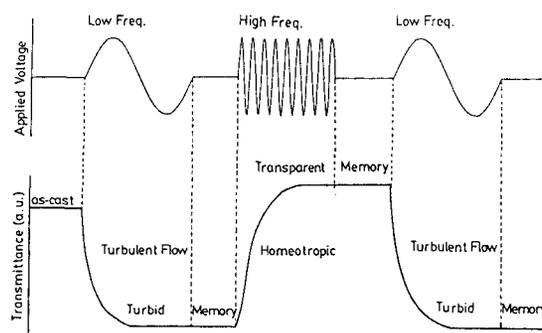


Figure 3. Schematic illustration of the typical light-switching curve for the smectic composite system under high- and low-frequency electric fields.

within a few seconds. The degree of light intensity difference (contrast) between the light scattering (turbid) and transparent states

the side chain group of PS3EM and 5OCB molecules. The sharp low angle X-ray diffraction rings resulting from an induced smectic phase were observed for the (PS3EM/5OCB) mixture system in the range of 80/20-20/80 (mol%). Therefore, PS3EM is fairly miscible with 5OCB and the binary mixture exhibits an induced smectic phase over a wide range of component fraction.

The electro-optical effect of the (PS3EM/5OCB) mixture based on light scattering was also investigated under various conditions of an a.c. electric field. In the case of electro-optical measurement of PS3EM and 5OCB, there have been observed no distinguishable optical change and a little change of transmittance of about 8 % upon on- and off- electric fields, respectively. On the other hand, the (PS3EM/5OCB: 50/50 mol%) composite exhibited a bistable and reversible light switching driven by an a.c. electric field with two different frequencies, being in a similar fashion to the (PS6EC/CPHOB) composite system. An induced smectic phase of the (PS3EM/5OCB) composite system makes us expect that its electro-optical effect is promising as the novel type of memory display (bistable light switching) with a high speed response characteristic [11,12].

When the molar ratio of (PS3EM/5OCB) varied from 70/30 to 30/70, the rise response time, τ_R decreased with about three decade. The variation of τ_R cannot be explained only by the change of the magnitude of dielectric anisotropy, $\Delta\epsilon$ for the composite system, because $\Delta\epsilon_S$ of PS3EM and 5OCB are about 1 and 12, respectively. Therefore, it is reasonable to consider that the decrease of viscosity contributes remarkably to the decrease of τ_R with an increase of the LC fraction. Then, in order to decrease τ_R , it may be effective to reduce the fraction of PS3EM in the composite system. HPPB has been added to the (PS3EM/5OCB) composite

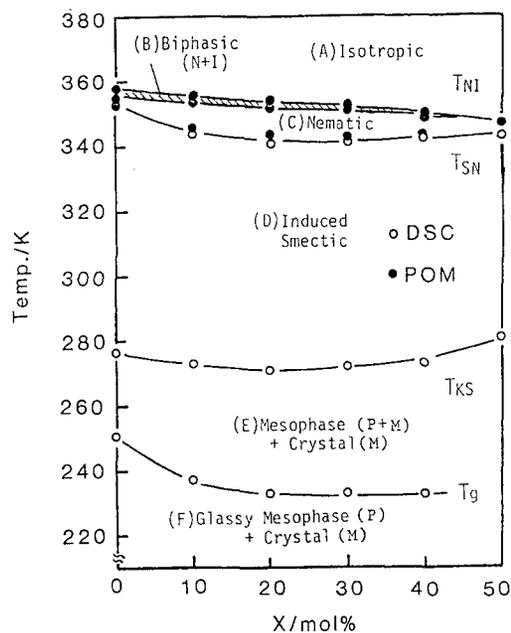


Figure 5. Phase diagram of the (PS3EM/HPPB/5OCB:50-X/X/X, mol%) composite system

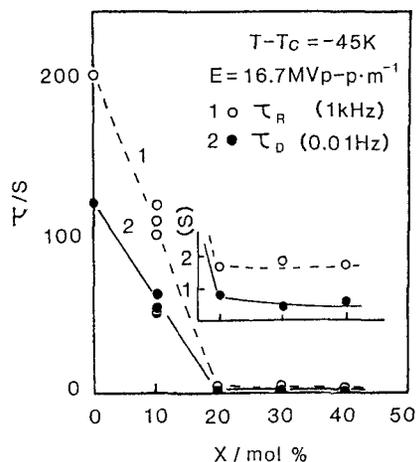


Figure 6. Variations of response time with HPPB molar fraction for (PS3EM/HPPB/5OCB:50-X/X/X, mol%) composite system.

system in order to prepare the ternary system. The HPPB has weak polar terminal group and the structure is similar to that of the side

mesogenic group of PS3EM. Figure 5 is the phase diagram of the (PS3EM/HPPB/5OCB) ternary system which was obtained on the basis of DSC, POM and X-ray studies. An induced smectic phase appears on a whole range of the component fraction and a wide range of temperature. Therefore, in the case of the (PS3EM/HPPB/5OCB) ternary composite system, the fraction of PS3EM can be reduced with maintaining the characteristic of an induced smectic phase by mixing HPPB of which chemical structure is similar to that of the side group of PS3EM.

Figure 6 shows the variation of the response time of the (PS3EM/HPPB/5OCB:50-X/X/50mol%) ternary composite system with mol% of PS3EM, 50-X and HPPB,X. The response time could be attained below 1 sec. in the case that X is above 20mol%. Each light scattering and light transmittance state was remained unchanged as it was, even after electric fields with low and high frequencies was removed, respectively. The response speed of bistable light switching can be remarkably improved by reducing the LCP fraction for the ternary induced smectic system.

3.3. Rewritable optical storage effect for the (LCP/LC/PM) ternary composite system

The threshold frequency, f_c is defined as the critical frequency at which the electro-optical characteristics of the (LCP/LC) composite system change from a transparent state to a turbid one when the frequency of an imposed a.c. electric field is gradually decreased. This case is schematically shown in Figure 7. If the magnitude of f_c can be reversibly changed to $f_{c,s}$ by an external stimulation such as photoirradiation, a rewritable optical storage effect for the composite system must be realized. Then,

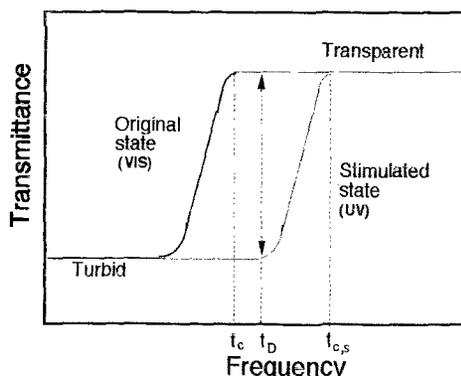


Figure 7. Transmittance changes for the original and stimulated states, and relationship among f_c , $f_{c,s}$ and f_D .

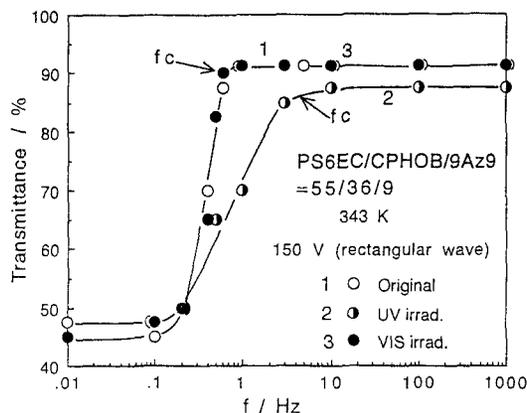


Figure 8. Frequency dependence of light transmittance for the (PS6EC/CPHOB/9Az9) composite system upon irradiation of UV and VIS light.

the rewritable optical storage by light irradiation to the (PS6EC/CPHOB/9Az9) ternary composite system has been investigated [13, 14]. Figure 8 shows the frequency dependence of light transmittance for the (PS6EC/CPHOB/9Az9) composite system upon irradiation of UV and VIS lights. In the case of the (PS6EC/CPHOB/9Az9:55/36/9 wt%) ternary composite system, the magnitude of f_c increased upon irradiation with UV light and reverted to the original state upon

irradiation with VIS light. These results indicate that the transparent and turbid states can be switched by photoirradiation of VIS and UV, in the case of the application of an a.c. electric field with the frequency, f_D between f_C and $f_{C,S}$. The molecular aggregation changes in a smectic layer upon photoirradiations of VIS and UV is schematically shown in Figure 9. Thus, the (LCP/LC/PM) ternary composite system is promised as a novel information storage film based on various external stimulations such as electric mode, photon mode and heat mode.

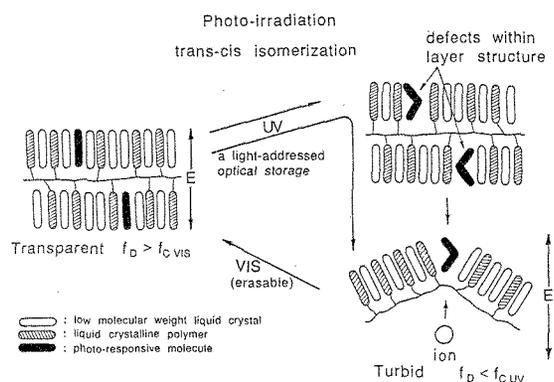


Figure 9. Molecular aggregation changes in smectic layer upon irradiation with VIS and UV light.

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