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Laser-addressing rewritable optical information storage of (liquid crystalline side chain copolymer/liquid crystals/photo-responsive molecule) ternary composite systems

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Abstract

A laser-addressing rewritable optical information storage for (liquid crystalline side chain copolymer: LCcoP/low molecular weight nematic liquid crystals: nematic LCs/photo-responsive molecule: PM) ternary composite systems in a smectic state was investigated on the basis of a reversible and bistable electro-optical switching driven by ac electric fields with two different frequencies. In order to improve the response speed for the electro-optical switching for the ternary composite system, a LCcoP with the mesogenic side chain fraction of 52.5 mol% was synthesized. The ternary composite system with the LCcoP fraction of 36 wt% showed a smectic state over a wide range near room temperature. High speed reversible and bistable electro-optical switching (~ 100 ms) under an appropriate electric field, and a stable memory effect (~ y) were demonstrated upon irradiation of UV light of 355 nm by using a YAG laser for the ternary composite systems in a smectic phase at room temperature. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline side chain copolymer; Rewritable optical information storage; Photo-responsive molecule

1. Introduction

Recently, various kinds of liquid crystalline polymers (LCPs) were synthesized and their electro-optical properties were studied extensively. Thermotropic side chain type LCPs with various functional mesogenic side chain groups have focused intensively owing to their possibilities for applications as electro-optical devices, because LCPs exhibit both the mesomorphic inherent characteristics of low molecular weight liquid crystals (LCs) and the mechanical properties as polymeric materials. However, LCPs have not been the competitors to LCs for the purpose of fast switching electro-optical displays, because of their very slow response times [1]. Therefore, LCPs can be used for rewritable optical information storage devices. In order to realize the optical information writing and its stable storage at room temperature, writing informations at a temperature above T_g and storing the data in a glassy state at temperature below T_g were carried out for polymers with T_g above room temperatures [2–5]. However, there were some applications in optical data storage for smectic siloxane LCPs with T_g below room temperature, that is, the data might be stored in the viscous smectic state [6–9]. The integrity for the stable data storage was excellent in ambient conditions. Also, the photochemical phase transition induced by photoisomerization of azobenzene and spiropyran derivatives molecularly dispersed in nematic or smectic LCs and LCPs was extensively studied for optical image storage [10–16]. The working principle was photochemically induced isothermal phase transition of LCs at the irradiation site.

Since, in general, LCPs show slower responses with respect to external agencies like electric and magnetic fields and mechanical deformation owing to the higher magnitude of viscosity in comparison with LCs, the binary composite systems composed of LCP and LC which has the similar chemical structure to that of the mesogenic side chain in LCP were proposed in order to improve the electro-optical switching speed of LCPs [17–19]. The (LCP/LC) binary composite systems showed faster switching speed than LCP itself because of an effective decrease of viscosity by an addition of LC. Moreover, the authors reported a reversible and bistable electro-optical switching driven by ac electric fields with two different frequencies and stable memory effect for the (LCP/LCs) composite systems in a homogeneous smectic state [19–29]. A typical light-switching curve for the smectic composite system under electric

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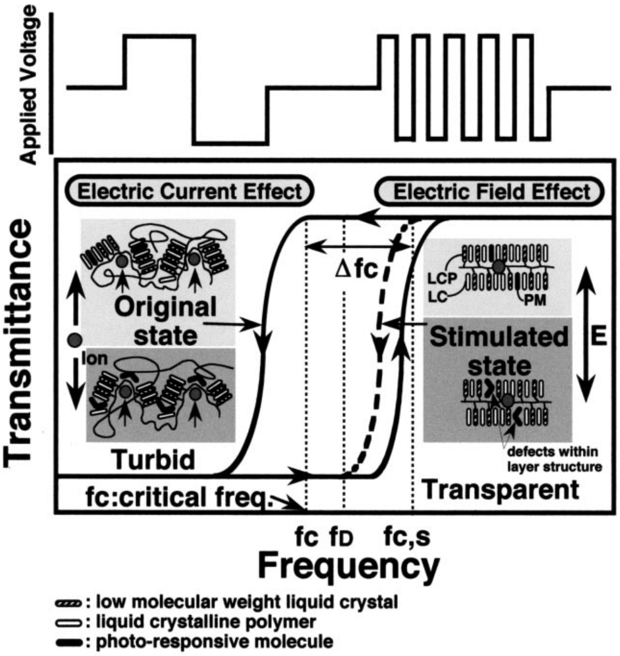


Fig. 1. Schematic illustration of the transmittance changes for the original and stimulated states of the smectic composite system under the application of an ac electric field with different frequencies and the relationship among fc, fc,s and f_D.

fields with high and low frequencies is schematically illustrated in Fig. 1. Though photo-responsive molecules are added to the (LCP/LC) composite in Fig. 1, the mechanism of the electro-optical switching might be considered to be in a similar manner to that of the (LCP/LC) binary system. The application of a high-frequency electric field made the transmission light intensity increased remarkably. Since a high-frequency field does not induce an ionic current, a large-scale homeotropic alignment of smectic layers is easily formed by a dielectric anisotropy of the mesogenic side chain group and LC. This molecular aggregation upon the application of a high frequency ac electric field might induce an remarkable increase of the transmittance up to 99% owing to a reduction of director fluctuations and/or optical boundaries. However, the transmitted light intensity decreased strikingly after the application of a low-frequency electric field, as schematically shown in Fig. 1. Since the application of a low-frequency electric field may induce an ionic current throughout the composite film, it is reasonable to consider that an induced turbulent flow of LCP main chains by an ionic current makes a fairly well organized large smectic layer collapse into many small fragments, resulting in an increase in light scattering, in other words, a decrease in transmittance below 1%. Then, the transparent (light-transmittance) and turbid (light-scattering) states appears based on the balance between hydrodynamic motion of the LCP main chain and dielectric anisotropy of the side chain group and LC. Also, each transparent and turbid state can be stably memorized after the removal of an electric field owing to the mechanical strength of the smectic layer.

In order to find the optimum smectic binary composite systems with respect to faster bistable switching speed and stable memory effect at room temperature, the induced smectic (nematic LCP/nematic LC) composite system or the (smectic liquid crystalline copolymer: LCcoP/nematic LC) one were investigated [21–29]. The response speed could be remarkably improved by an introduction of another LC as the third component to the induced binary composite system, since an addition of the another LC alternating the nematic LCP reduce effectively the magnitude of viscosity in the composite system by reducing the LCP fraction, maintaining an induced smectic state [23,24]. Also, an introduction of LCcoP with a small substituent fraction of mesogenic side chains into the induced smectic binary composite system was strikingly effective in reducing the electro-optical switching times with a stable memory effect at room temperature [27–29]. Moreover, a faster electro-optical switching with a bistable memory effect at room temperature was reported for the smectic (smectic LCcoP/nematic LCs) binary composite systems, because LCcoP showed remarkably high mobility on its main chain. Both rise and decay response times under an appropriate electric field condition were in a range of several 10–100 ms at room temperature [25,26].

A bistable and reversible light-switching between light scattering and transparent states can be performed by changing the frequency of an ac electric field, as discussed earlier. Then, the threshold frequency, fc, is defined as the critical frequency at which the electro-optical characteristics of the (LCP/LCs) composite system change from a transparent state to a turbid one when the frequency of an imposed ac electric field is gradually decreased, as shown in Fig. 1. If the magnitude of fc can be reversibly changed to fc, s by another external stimulation such as photoirradiation, the transmittance of the composite system must be switched by this stimulation upon the application of ac electric field with driving frequency, f_D, which is between fc and fc, s. This shows a possibility of a rewritable optical storage effect for the composite system. If photoresponsive molecules (PM) can change the molecular aggregation state in the composite system upon irradiation of lights with different wavelengths such as UV and visible lights, a rewritable optical storage effect might be realized under the application of an ac electric field at f_D. Then, a laser-addressing optical information storage of the (LCP/nematic LCs/azobenzene derivatives) ternary composite systems were investigated [30–33]. In the case of the (LCP/LC/azobenzen derivatives) ternary composite systems, fc corresponds to fc_{UV} upon irradiation with ultraviolet light (UV) and fc_{VIS} upon irradiation with visible light (VIS). Photoisomerizable molecules such as azobenzene derivatives can induce a variation in fc for the ternary composite systems upon photoirradiations with different light wavelengths. This indicates that the

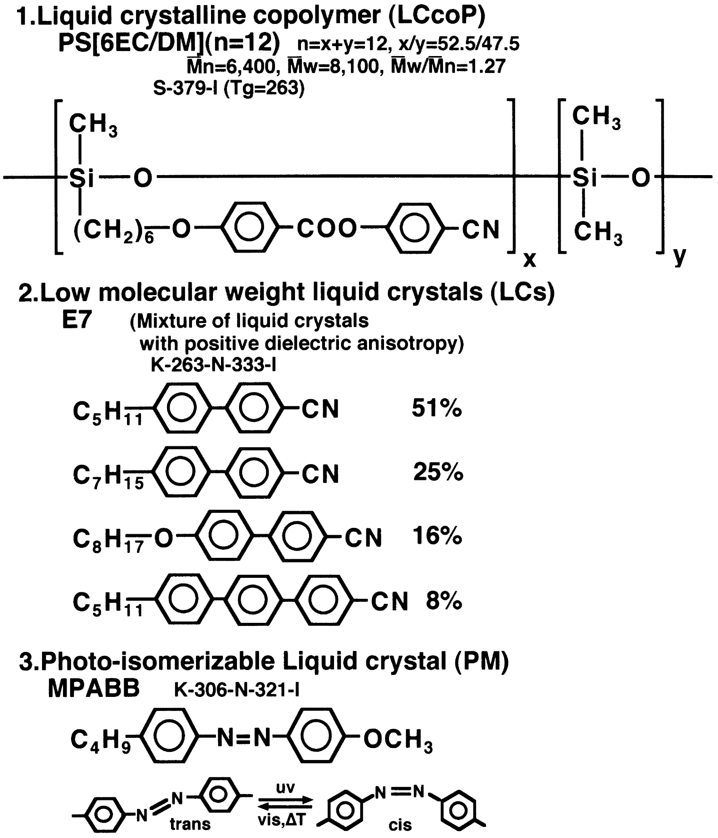


Fig. 2. Chemical structures and physical properties of smectic liquid crystalline copolymer (1), low molecular weight liquid crystals (2) and photoresponsive molecule (3).

transparent and turbid states can be switched by photoirradiation of UV and VIS, in the case of the application of an ac electric field with the driving frequency, f_D, between fc_{UV} and $fc_{VIS.}$

In the present study, the (LCcoP/LCs/PM) ternary composite system in a smectic state was investigated in order to improve the response switching speed at room temperature. A light-addressed optical information storage of the ternary composite system with the UV light of 355 nm generated from pulsed-YAG laser was demonstrated at room temperature, in order to improve a recording speed and/or memory resolution owing to depression of molecular thermal diffusion.

2. Experimental section

2.1. Materials

Fig. 2 shows the chemical structures and physical properties of smectic LCcoP, nematic LCs, and photo-isomerizable molecule (PM) used in this study. The LCcoP was poly[(((((4-cyanophenoxy)carbonyl)phenoxy)hexyl)-methylsiloxane)-*co*-(dimethylsiloxane)] copolymer (PS(6EC/DM)($n = 12$)). The degree of polymerization n was 12. The number of methylene group as a flexible alkyl spacer attached between polysiloxane main chain and mesogenic side chain was 6. The PS(6EC/DM)($n = 12$) was synthesized through hydrosilylation reaction reported by Finkelmann et al. [34]. The chemical structure and the substituent fraction of mesogenic side chains in a LCcoP chain were confirmed by NMR and FT-IR. The average molecular weight of the LCcoP were determined by gel permeation chromatography (GPC) in tetrahydrofuran using the polystyrene standards. The PM was 4-(4’-methoxyphenylazo)butylbenzene (MPABB) which isomerizes from *cis*- to *trans*-form upon irradiation of visible (VIS) light or thermal energy, and from *trans*- to *cis*-form upon irradiation of ultraviolet (UV) light. Also, the nematic LCs were commercially available E7 (MERCK Co. Ltd.), which was a eutectic nematic mixture of cyanobiphenyl, oxycyanobiphenyl, and cyanoterphenyl derivatives with a positive dielectric anisotropy. The PS(6EC/DM)($n = 12$), E7, and MPABB exhibited a smectic, nematic, and nematic phase, respectively. The ternary composite films were prepared from an acetone solution of (PS(6EC/DM)($n = 12$)/E7/MPABB) by a solvent casting. The weight ratios of (PS(6EC/DM)($n = 12$)/E7/MPABB) were 39/58/3 and 36/55/9.

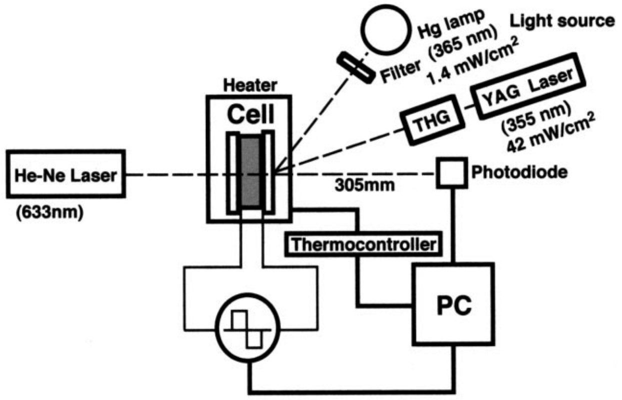


Fig. 3. Schematic illustration of the measuring system for electro-optical properties of the composite system.

2.2. Characterization of the ternary composite systems

The thermal properties, the phase transition behavior and the aggregation states of the ternary composites were investigated on the basis of differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (WAXD) studies. 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 by an X-ray generator (Rigaku Co. Ltd., RU-200) equipped with a temperature controller of ± 0.1 K accuracy, using Ni filtered Cu-Kα ($\lambda = 0.1542$ nm). The absorption spectra were measured with a spectrophotometer (SHIMADZU Co. Ltd., MPS-2000).

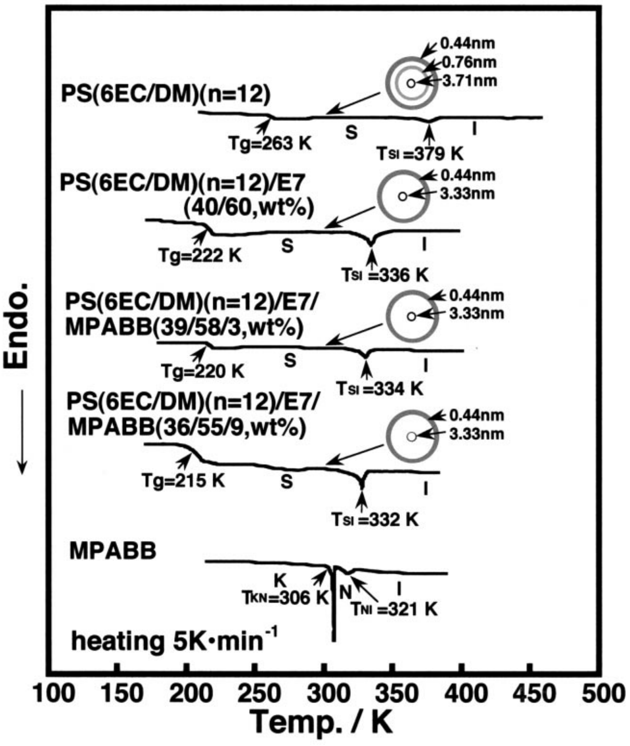
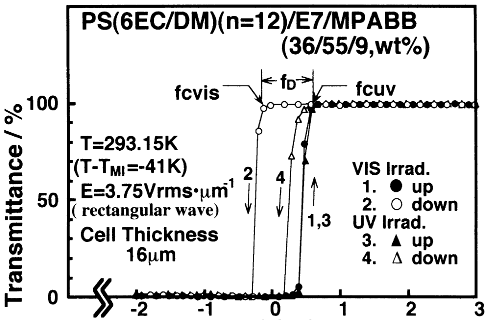


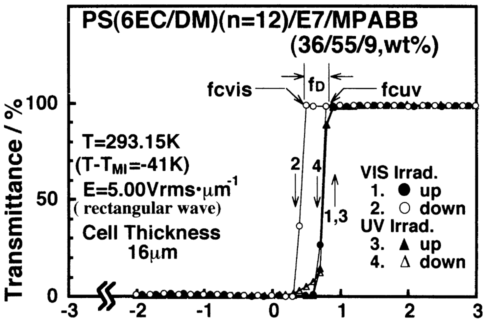
Fig. 4. DSC curves and X-ray diffraction patterns of PS(6EC/DM)($n = 12$), the [PS(6EC/DM)(n = 12)/E7,40/60 wt%] binary composite system, the [PS(6EC/DM)(n = 12)/E7/MPABB,39/58/3 wt%] and the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite systems and MPABB.

2.3. Measurement of the Electro-optical Effect for the Ternary Composite Systems

The experimental setup for electro-optical switching measurements of the characteristics is illustrated in Fig. 3. The composite film was 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 computer using a custom made nichrom heating system attached to a thermo-controller with a resolution of ± 0.04 K. A He–Ne laser (Uniphase Co. Ltd., 1103p) of 2 mW at 632.8 nm with a beam 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 intensities were measured without any polarizers under the modulation of an ac electric field with a photodiode (HAMAMATSU Co. Ltd., S1223) 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 required for a 90–10% transmittance change. The elapsed time dependence of the transmitted light intensity was recorded with a digital storage oscilloscope (HITACHI Co. Ltd., VC-6045) to evaluate a memory effect for the composite systems. The distance between cell and photodiode was 305 mm. Ultraviolet light (UV) with the wavelength of 365 nm and visible light (VIS) with the wavelength longer than 420 nm were generated from a 100 W high-pressure Hg lamp. The color filters (Toshiba Co. Ltd., UV-D35 and L-42) were used to select the specific bright lines of the Hg lamp. The illuminance of the UV light (1.4 mW·cm^{-2}) was measured with a UV illumination photometer (ORC Co. Ltd., UV-MO2). Also, UV with the wavelength of 355 nm was gained as a third harmonic generation (THG) of a YAG laser. The Nd:YAG laser (Continuum Co. Ltd., NY-60) used was a Q-SW attached pulse laser with the power of 20 mJ per pulse and the pulse width of 10 ns. The flashing frequency of the YAG laser was 50 Hz. The beam diameter of 6 mm was spread to 50 mm ϕ with a concave lens in order to prevent a temperature rise of the sample owing to heat effect of the YAG laser. The illuminance of the UV light was 42 mW·cm^{-2}.



(a) $E = 3.75$ Vrms•μm^{-1}



(b) $E = 5.00$ Vrms•μm^{-1}

Fig. 5. Frequency of applied electric field dependence of the light transmittance for the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite system upon irradiation with UV and VIS lights and the relationship among fc_{VIS}, fc_{UV} and f_D under ac electric field of $E = 3.75$ Vrms · μm^{-1} (a) and $E = 5.00$ Vrms · μm^{-1} (b) at 293 K.

3. Results and discussion

It was reported that the mixture of LCcoP and LCs form a more compatible smectic mesophase than that of LCP and LC [25–29]. This means that an introduction of LCcoP with an appropriate substituent fraction of mesogenic side chains into the binary composite system is extremely effective to construct the smectic binary composite with a lower LCcoP fraction, maintaining a wide smectic mesophase range in the vicinity of room temperature. The lower fraction of LCcoP might lead to faster bistable switching as well as a stable memory effect at room temperature owing to the lower viscosity in the binary composite system. The [PS(6EC/DM,52.5/47.5 mol%)(n = 12)/E7] composite system exhibited a smectic phase over a wide range of both mixing concentration (approximately above 30 wt% (above 20 mol%) of the LCcoP fraction) and temperature (250 ~ 340 K) [25]. The optically homogeneous smectic phase played an important role in realizing an excellent memory effect as well as a reversible and bistable light switching with a high contrast owing to its high viscosity in comparison with that of a nematic state.

Fig. 4 shows DSC curves and schematic X-ray diffraction patterns of PS(6EC/DM)(n = 12), the [PS(6EC/DM)(n = 12)/E7,40/60 wt%] binary composite system, the [PS(6EC/DM)(n = 12)/E7/MPABB,39/58/3 wt%] and [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite systems, and MPABB. In the case of the PS(6EC/DM, 52.5/47.5 mol%)(n = 12), the DSC curve showed a deviation from the base line corresponding to the glass transition temperature, T_g at 263 K, as shown by the arrow in Fig. 4, and only one endothermic peak corresponding to the mesophase-isotropic phase transition, T_{MI} at 379 K. POM observation of the PS(6EC/DM, 52.5/47.5 mol%)(n = 12) under crossed polarizers showed the fan-shape texture which was characteristic of smectic phase over a temperature range above T_g and below T_{MI}. Also, the X-ray pattern of the PS(6EC/DM, 52.5/47.5 mol%)(n = 12) at 293 K exhibited one sharp Debye ring corresponding to the spacing of 3.71 nm in a small Bragg angle region and one diffuse Debye ring corresponding to the spacing of 0.44 nm in a wide Bragg angle region. The sharp small-angle X-ray scattering might be attributed to the smectic layer structure. Therefore, the T_{MI} of the PS(6EC/DM, 52.5/47.5 mol%)(n = 12) should be assigned as a smectic-isotropic phase transition temperature, T_{SI}. The DSC curves of the binary and the two ternary composite systems showed a deviation from the base line corresponding to T_g at 222, 220, and 215 K, respectively, and a single endothermic peak which was assigned to T_{SI} at 336, 334, and 332 K, respectively. The magnitude of T_g decreased with an increase in the E7 fraction owing to the plasticizing effect of E7 to the LCcoP chains. Since an endothermic peak assigned to the T_{MI} was measured by the DSC measurement and no phase-separated texture was recognized in the mesomorphic state under POM observation and also, the observed X-ray diffraction pattern apparently showed Debye rings corresponding to a single component in the mesomorphic state, it is apparent that the binary composite systems might be in a homogeneously mixed mesomorphic phase with respect to optical scale [19,20]. Therefore, it is reasonable to consider that E7 in both isotropic and mesomorphic states is miscible to PS(6EC/DM)(n = 12). Also, the magnitudes of T_g and T_{SI} for the ternary composite systems decreased with an increase of the MPABB fraction used as a photoisomerizable molecule owing to the plasticizer and impurity effect of MPABB. In the weight fraction range of 3 and 9 wt% of MPABB, only one endothermic peak attributed to the smectic-isotropic phase transition was observed and also, no phase separated texture was recognized in the smectic phase under POM observation for the [PS(6EC/DM)(n = 12)/E7/MPABB,39/58/3 wt%] and the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite systems. Moreover, the ternary composite systems exhibited a sharp Debye ring in a small Bragg angle region. These DSC, POM, and X-ray results apparently indicate that the ternary composite system is in a homogeneous smectic phase at room temperature in a similar fashion to the binary one. The optically homogeneous smectic phase in the ternary composite systems is necessary to realize a bistable electro-optical

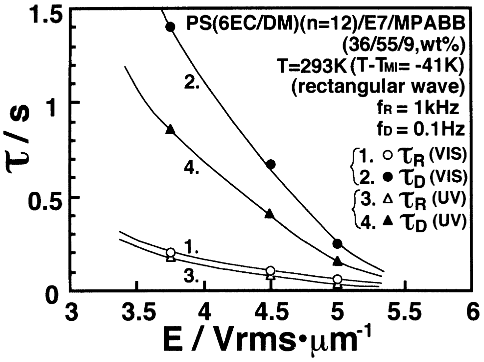


Fig. 6. Relationship between rise and decay response times (τ_R and τ_D) and the applied electric field for the [PS(6EC/DM)($n = 12$)/E7/MPABB,36/55/9 wt%] ternary composite system under the irradiation with UV and VIS lights at 293 K.

effect with a high contrast, that is, a stable memory effect.

Figs. 5 (a) and (b) show the frequency dependence of the light transmittance for the [PS(6EC/DM)($n = 12$)/E7/MPABB,36/55/9 wt%] ternary composite system upon irradiation with UV and VIS lights at 293 K under the application of an ac electric field of $E = 3.75$ Vrms·μm^{-1} and $E = 5.00$ Vrms·μm^{-1}, respectively. To photoisomerize the MPABB, UV light (365 nm, 1.4 mW·cm^{-2}) and VIS light ($>$ 420 nm) from a high-pressure Hg lamp were irradiated to the cell for 30 min. An ac electric field was applied to the cell for several periods at each frequency. The ternary composite system exhibited the hysteresis in the increasing (curve 1) and decreasing (curve 2) processes of an electric field frequency upon irradiation of VIS light. This may arise from the difference of structural stability between laterally large smectic homeotropic alignment and aggregation of small smectic fragments [27–29]. The hysteresis decreased upon irradiation of UV light since the difference of structural stability was improved owing to the structural defect caused by cis-azo-molecules in the smectic layer, as shown in Figs. 5 (a) and (b). The magnitude of the critical frequency, fc were difined as the starting point of decreasing transmittance upon irradiation of VIS light, fc_{VIS} in the decreasing process of an electric field frequency from high-frequency region and also, as one upon irradiation of UV light, fc_{UV} in a similar manner as earlier, as shown in Figs. 5 (a) and (b). The threshold frequency, fc, for the ternary composite system is governed by the balance between the electric field effect and the electric current effect. The fc is an important parameter which exhibits the mechanical strength of the smectic layer structure in the ternary composite system to the ionic current. MPABB used as a photoisomerizable molecule (PM) could induce a change in the fc of the LC phase for the ternary composite system by photoirradiation. These results indicate that the transparent and turbid states for the ternary composite system can be switched by photoirradiation of UV and VIS under the application of an ac electric field with the driving frequency, f_D, between fc_{UV} and fc_{VIS}, as shown in Figs. 5 (a) and (b). Also, it was recognized that the magnitude of the fc increased and the driving frequency range decreased according as an applied ac electric field strength or a driving temperature was increasing. However, the [PS(6EC/DM)($n = 12$)/E7/MPABB,39/58/3 wt%] ternary composite system exhibited the same hysteresis as the [PS(6EC/DM)($n = 12$)/E7/MPABB,36/55/9 wt%] in the increasing and decreasing processes of the electric field frequency upon irradiation with VIS light. However, the decrease in the hysteresis was smaller upon irradiation with UV light, that is, the increase in the magnitude of fc from fc_{VIS} to fc_{UV} was smaller, and hence the driving frequency range decreased, compared with the [PS(6EC/DM)($n = 12$)/E7/MPABB,36/55/9 wt%].

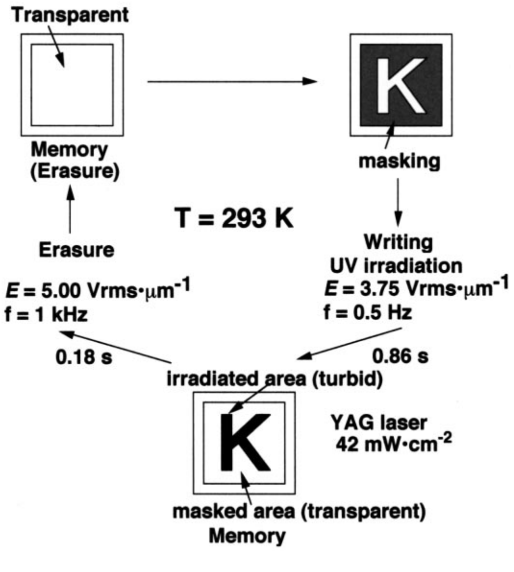


Fig. 7. Schematic illustration of the rewritable light-addressed optical information storage effect for the ternary composite system.

Fig. 6 shows the plots of rise and decay response times (τ_R and τ_D) against the magnitude of an applied ac electric field for the [PS(6EC/DM)($n = 2$)/E7/MPABB,36/55/9 wt%] ternary composite system under irradiations of UV and VIS lights at 293 K. Under an appropriate ac electric field, it was recognized that the switching speed of the ternary composite system was several hundred milliseconds. The magnitudes of τ_R and τ_D upon UV light irradiation were shorter than those upon VIS one owing to the difference of a mechanical strength and a viscosity of the smectic layer based on a structural change of PM. When the ternary composite system was irradiated with UV light, azo-molecules with the trans form in the smectic layer photoisomerized to the cis one. Since the cis-azo-molecules is remarkably bulky in comparison with the trans one, the cis-azo-molecules serve as a structural defect in the smectic layer. Therefore, UV light irradiation might lead to the formation of a less-order mesophase and finally, mechanical strength of the smectic layer upon the application of a low frequency electric field apparently decreases upon

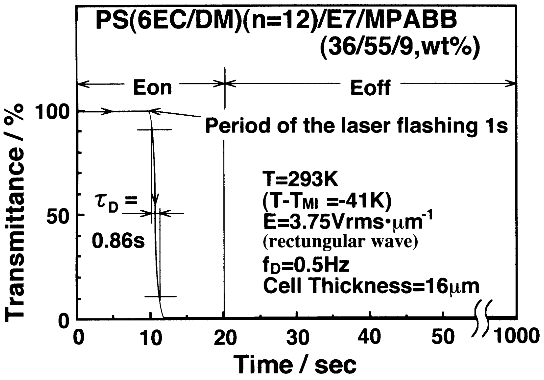


Fig. 8. Light switching curve of laser-image addressing for the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite system.

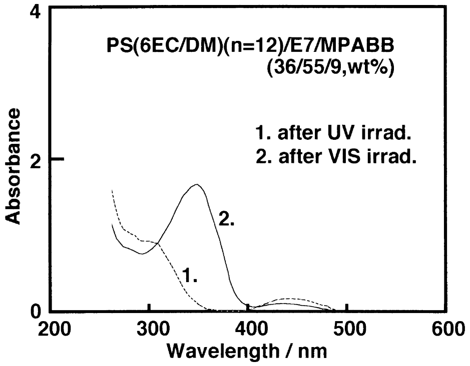


Fig. 10. UV-visible absorption spectra of the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite system at 293 K owing to *trans*/*cis* photoisomerization of MPABB.

irradiation of UV light. Consequently, the mesogenic side chain groups and polymer backbones would have a higher mobility in the less-ordered mesophase. This situation under irradiation of UV would favor faster switching of the mesogenic group under an applied electric field, compared with that under irradiation of VIS light.

Actually, a laser-addressing optical storage of the ternary composite system was demonstrated at room temperature. In order to improve a recording speed and resolution by depression of molecular heat diffusion, the third harmonic generation (THG) of Nd:YAG laser (355 nm) was used as a UV light source. The beam diameter was spread to 50 mm ϕ with a concave lens in order to prevent the heating effect of the YAG laser. The intensity of the UV radiation was 42 mW·cm^{-2}. Fig. 7 shows a schematic illustration of the rewritable optical information storage effect based on both the light-image addressing and the electric field-effect erasure modes for the ternary composite system at room temperature. To begin with, the cell of the composite system was prepared to be transparent state at 293 K by the application of an ac electric field of $E = 3.75$ Vrms·μm^{-1} with frequency of 1 kHz. Then, the cell was irradiated with UV light from the YAG laser for one second through a photomask of the letter ‘‘K’’ to the transparent composite system under the application of an ac electric field with driving frequency, $f_D = 0.5$ Hz. Finally, the UV light irradiated part was selectively changed into a turbid state, that is, the turbid letter ‘‘K’’ was clearly recorded on the transparent composite system. Fig. 8 shows a light switching curve of laser-image addressing for the[PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite system. The transmittance of a He–Ne laser (633 nm) was observed at room temperature. The decay response time, τ_D, of the recording process was 0.86 second. The recorded letter remained unchanged even after the ac electric field at f_D was removed at room temperature. The turbid state could be reversibly returned to the transparent one when an ac electric field with frequency of 1 kHz was imposed. The rise response time, τ_R, of the erasing process was 0.18 s. That is, the several hundred miliseconds were taken to record at room temperature by the laser irradiation for one second under the application of an ac electric field with f_D and the optical information could be rewritable and erasable by light or electric stimulation at room temperature. Fig. 9 shows a photograph of the writing and erasure memory states for the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite system, and the photomask written the letter ‘‘K’’. A clear memorized image was observed. A resolution of the ternary composite system was approximately 20 μm, that is the nearly same as the thickness of the cell (16 μm). A reading contrast ratio of 300 was realized. The stored image could be kept very stable for a long period (more than one y) at room temperature.

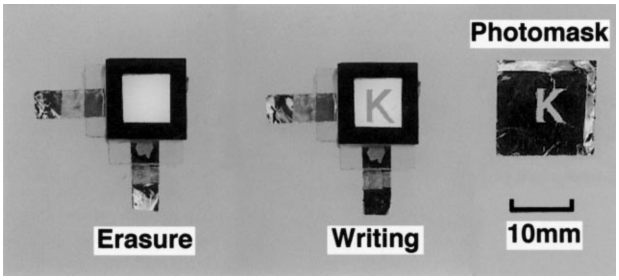


Fig. 9. Photograph of the writing and erasure memory states for the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite system and the photomask written the letter ‘‘K’’.

To check the photoisomerization and the thermal decomposition of the MPABB by irradiation of YAG laser, UV-visible absorption spectra of the cell were measured. Fig. 10 shows the UV-visible absorption spectra of the [PS(6EC/DM)(n = 12)/E7/MPABB,36/55/9 wt%] ternary composite system at 293 K owing to trans/cis photoisomerization of MPABB. The reproducibility of the UV-visible spectra was confirmed after the irradiation with the UV and the VIS lights was repeated several times. Therefore, it was apparent that the thermal decomposition of the MPABB never occurred.

Compared with the previous ternary composite systems using LCP homopolymer [30–33], we can conclude from

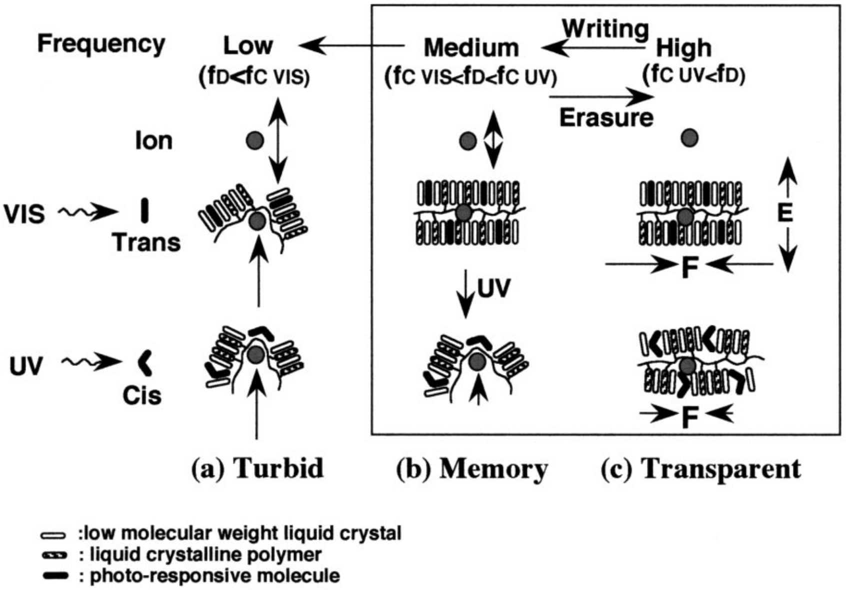


Fig. 11. Schematic representation of molecular aggregation changes in a smectic layer upon irradiation with UV and VIS lights.

the results mentioned earlier that a faster light-addressed optical information storage with the UV light of 355 nm by YAG laser, high speed optical switching, and stable memory effect for the ternary composite systems using LCcoP was recognized at room temperature.

Let us now look at a mechanism of light-addressing effect for the ternary composite systems in detail. Fig. 11 shows the schematic representation of molecular aggregation changes in a smectic layer upon irradiation with UV and VIS lights for the ternary composite system. If azo-molecules are trans in the smectic layer upon irradiation of VIS light and also, the magnitude of f_D is higher than that of fc_{VIS}, the initial state of the ternary composite system exhibits a homeotropic alignment of the smectic phase under the application of ac electric field at f_D owing to the electric field effect based on the dielectric anisotropy of LC molecules and mesogenic side chain part of the LCcoP, as shown in Fig. 11 (c). Therefore, the initial composite system is in a highly transparent state under the application of ac electric field with frequency of f_D ($f_D > fc_{VIS}$). When the composite system is irradiated with UV light, azo-molecules photoisomerize from trans-form into *cis*-one in the smectic layer. Since the *cis*-azo-molecules serve as a structural defect in the smectic layer, mechanical strength of the smectic layer against ion current decreases upon irradiation of UV light. Therefore, the magnitude of fc changes from fc_{VIS} to higher than f_D upon exposure of UV light ($f_D < fc_{UV}$), so that an induced turbulent flow caused by an ionic current collapses a fairly well organized large smectic layer into many small fragments, and the irradiated part of the transparent composite system selectively changes into the turbid state owing to the electric current effect based on the electrohydrodynamic motion of the LCcoP main chain, as shown in Fig. 11 (b). Moreover, when VIS light is irradiated to the composite film under the application of ac electric field at f_D or the magnitude of f_D changes higher than that of fc_{UV} ($f_D > fc_{UV}$), the turbid composite system changes into the initial transparent one. In this manner, a light information can be reversibly recorded and erased as the variation of molecular alignment of liquid crystals controlled by both photon and electric modes.

One might suspect that a rise in driving temperature of the ternary composite system by irradiation of UV light changes the magnitude of the threshold frequency, fc, higher. Fig. 12 shows the rise in temperature of the [PS(6EC/DM)($n = 12$)/E7/MPABB,36/55/9 wt%] ternary composite system measured by an emission thermometer as a function of UV irradiation time. The intensities of the UV radiation generated by YAG laser were 25 and 45 mW·cm^{-2}, respectively. It was apparent that the rise in temperature of the ternary composite system by irradiation of UV light was below 2 K. Therefore, it must be concluded that the laser-addressed rewritable optical information storage of this ternary composite system was demonstrated

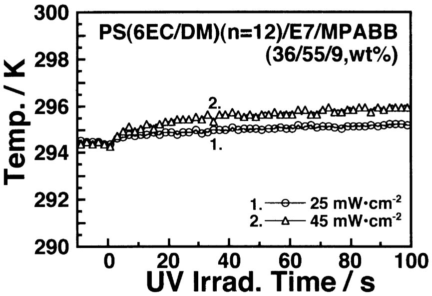


Fig. 12. The rise in temperature of the [PS(6EC/DM)($n = 12$)/E7/MPABB,36/55/9 wt%] ternary composite system as a function of UV irradiation time.

at room temperature by irradiation of UV light on the basis of not thermal mode but both photon and electric modes.

4. Conclusions

The rewritable optical storage by light irradiation to the (LCcoP/LCs/PM) ternary composite system was investigated on the basis of a reversible and bistable electro-optical switching driven by ac electric field with two different frequencies at room temperature. An introduction of LCcoP with small mesogenic side chain fraction of 52.5 mol% into the ternary composite system was effective to induce a smectic phase exhibiting an excellent stable memory effect based on the mechanical strength of smectic layers at room temperature widely. The threshold frequency, fc, was defined as the critical frequency at which the electro-optical characteristics of the composite system change from a transparent state to a turbid one when the frequency of an imposed ac electric field is gradually decreased. In the case of the ternary composite system, the magnitude of fc increased upon irradiation with ultraviolet light (UV) and reverted to the original state upon irradiation with visible light (VIS) at room temperature. MPABB used as photoisomerizable molecule could induce a change in fc of LC phase by photoirradiation at room temperature. Therefore, the transparent and turbid states for the ternary composite system can be switched by photoirradiation of UV and VIS under the application of an ac electric field with the frequency, f_D, between fc_{UV} and fc_{VIS}. Moreover, a light-addressed optical information storage with the UV light of 355 nm by YAG laser, high speed optical switching (several 100 ms), and stable memory effect (more than one y) of the ternary composite system was recognized at room temperature. Thus, we believe that the ternary composite system is promised as a optical information storage film which is capable of reversible writing and erasing the information on the basis of various external stimulations such as electric mode, photon mode, and heat mode, and that it is useful as a novel type of ‘‘light valve’’ exhibiting an excellent stable memory effect based on mechanical strength of a homogeneous smectic phase.

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