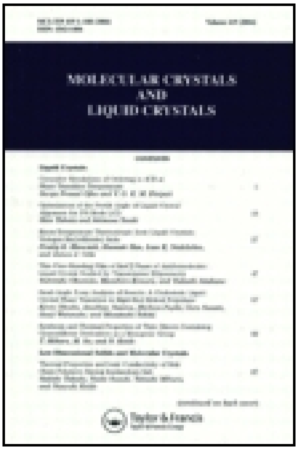

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(Homeotropically Oriented Polymer Network/Side Chain Type Liquid Crystalline Polymer/Liquid Crystals/Chiral Dopant) Composite with Thermally Addressed and Electrically Erasable Properties

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(HOMEOTROPICALLY ORIENTED POLYMER NETWORK/SIDE CHAIN TYPE LIQUID CRYSTALLINE POLYMER/LIQUID CRYSTALS/CHIRAL DOPANT) COMPOSITE WITH THERMALLY ADDRESSED AND ELECTRICALLY ERASABLE PROPERTIES

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A heat-induced drastic switching from a transparent smectic A (SmA) phase to a light-scattering nematic (N) one was achieved for a (homeotropically oriented polymer network (HOPN)/side chain type liquid crystalline polymer (SCLCP)/liquid crystals (LCs)/chiral dopant) quaternary composite. In the case that the composite was rapidly cooled from the heat-induced light-scattering N* phase to the SmA one, the SmA phase exhibited a strong light-scattering state. When an a.c. electric field above the threshold valve was applied to the composite in the light-scattering state, the strongly light-scattering SmA phase was changed into a transparent SmA one. Both the transparent and the light-scattering SmA states could be maintained for a long time (∼years) at room temperature. Thus, the composite with thermally addressable and electrically erasable characteristics was newly proposed.*

Keywords: polymer network; liquid crystalline polymer; smectic–chiral nematic phase transition; rewritable memory effect

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INTRODUCTION

A reversible light-transmitting light-scattering change based on the electrothermal reorientation of liquid crystal (LC) molecules with a positive dielectric anisotropy has been studied intensively in order to realize a thermally addressed and electrically erasable liquid crystal display (TAEELCD) mode [1–5]. This kind of mode attracts much attention because of the unique characteristics, such as exhibiting a rewritable memory effect, no cross-talk and viewing angle problem, etc. Chiral nematic liquid crystals (N*-LCs)[1–4] or smectic A liquid crystals (SmA-LCs)[3–5] are currently important candidates as TAEELCD materials. Furthermore, SmA-LCs offer advantages such as better bistability, higher resolution, and the possibility of selective erasure. Typically, SmA-LCs that possess a narrow nematic (N) or a narrow N* phase region, usually in the temperature range of 1–3 K, between the wide SmA phase and the isotropic (I) phase, are suitable for this application. When the SmA-LC is sandwiched between glass substrates of which the surface are treated to induce the homeotrophic alignment of LC molecules, the optical axis in the SmA phase is oriented in the direction perpendicular to the substrate surfaces in a single-domain state. This homeotropically aligned state is optically uniform and transparent. When the homeotropically aligned to the SmA phase, an unoriented polydomain structure, the so-called the focal-conic texture, is formed in the SmA phase at the position where the SmA-LC is heated. The focal-conic texture, in general, strongly scatters light because of its optically heterogeneous structure. Then the light-scattering characters of figures written thermally appear in the clear background in the LC cell. When the light-scattering texture formed in the SmA phase is heated again to the I phase and then cooled down to the SmA phase in the presence of an electric field along the substrate surface normal, the SmA-LC molecules are homeotropically aligned and the cell becomes transparent again. This means that the thermally written light-scattering characters or figures are erased. It may not be essential for this mode to have the N or the N* phase above the temperature region of the SmA phase. However, the presence of the N or N* phase makes the homeotropic alignment very easy since an SmA-LC does not respond to an applied electric field as readily as an N-LC or an N*-LC [3–5]. Thus, the thermal-writing process is based on the SmA →N(N*)→I→N(N*)→SmA phase transitions. This conventional TAEELCD material has one main shortcoming in that the time necessary for accomplishing the thermal-writing process is too long to meet practical requirements. Usually, the temperature range required to complete the N(N*)→I phase transition is large than 0.5 K. Meanwhile, since the LC is heated to the I phase by pulse heating, it is difficult to control the final temperature to which the LC is heated. It is very usual for it to be a few degrees higher than that of the N(N*)→I phase transition temperature. Furthermore, the super-cooling of the I→N(N*) phase transition for a few degrees relative to the N(N*)→ I phase transition is inevitable. Thus, in fact, the real temperature range necessary for accomplishing the SmA→ N(N*)→I→N(N*)→SmA phase transition is surely much greater than 1.0K and there's nothing strange for it to be 5.0 K ~ 10.0 K.

(Side chain type liquid crystalline polymer (SCLCP)/LC) composites have been studied extensively for their unique characteristics [6–16]. When the (SCLCP/LC/chiral dopant) composite system with the SmA↔N* phase transition was sandwiched between substrates of which the inner surfaces had been treated to induce a homeotropic alignment of the mesogenic groups of SCLCP and LC molecules, the composite exhibited an extremely sharp change from a transparent homeotropic state of the SmA phase to a strong light-scattering focal-conic one of the N* phase within a temperature range of 0.1 K due to a heat-induced SmA→N* phase transition. When the composite system was slowly cooled from the heat-induced light-scattering N* phase to the SmA one, the orientational state of the SmA phase turned into a homeotropic monodomain and became transparent again. On the other hand, in the case of rapid cooling of the composite system from the heat-induced light-scattering N* phase to the SmA phase, the SmA phase retained a polydomain structure to be a strong light-scattering state. Also, when an a.c. electric field above a threshold value was applied to the light-scattering SmA phase, the light-scattering SmA phase was changed to a transparent SmA one. The thermally and electrically induced transparent light-scattering change for the (SCLCP/LC/chiral dopant) composite makes us expect that thermal and electrical light switching is applicable or promising as TAEELCD with a much higher speed for memory switching compared with the conventional TAEELCD consisting of low-molecular-weight substances. Meanwhile, this novel TAEELCD also exhibited higher contrast and a more endurable memory effect than the conventional one [13,14]. Furthermore, the latent heat of the SmA→N* phase transition is very small, since the SmA→N* phase transition is a very weak first-order transition or a second-order one. Therefore, the change from the transparent state to the light-scattering one corresponding to the SmA→N* phase transition can be induced by low-power laser energy [15,16].

However, homeotropic orientation treatment on the inner surfaces of the substrates sandwiching the (SCTLCP/LC/chiral dopant) composite system was necessary for this novel TAEELCD. It gave rise to inconvenience in the fabrication of the TAEELCD, especially in the fabrication of the TAEELCD with a large area or one used with flexible substrates. In order to resolve this problem, the (polymer network/SCTLCP/LCs/chiral dopant) composite with an SmA↔N* phase transition, in which the polymer network has homeotropically oriented in the cell, sandwiching the composite and the inner surface of the cell which has not been subjected to any orientation treatment, is prepared, and the thermo-electro-optical properties of the composite are investigated.

EXPERIMENTAL

Materials

A photo-polymerizable LC monomer (MPBAHB), SCLCP (LCP93), an SmA-LC (S6), an N-LC (E48), a chiral dopant (ZLI-4572), and a photo-initiator (2, 2-dimethoxy-2-phenylacetophenone) were used. LCP93, S6, E48, and ZLI-4572 were purchased from Merck Co., Ltd., Japan, and 2, 2-dimethoxy-2-phenylacetophenone was from TCI Co., Ltd., Japan. The chemical structure and some physical properties of these materials are shown in Figure 1. MPBAHB was synthesized by the method proposed by D. J. Broer et al. [17]. The purity of MPBAHB was measured by NMR, FT-IR, and element analysis.

Sample Preparation

The (MPBAHB/LCP93/LCs (S6+E48)/ZLI-4572/photoinitiator, 0.5/2.0/91.4 (79.4+12.0)/6.0/0.1 wt%) mixture was prepared by a solvent-cast method from an acetone solution. The LC cell, of which the inner surfaces hadn't been treated for any orientation, was used for the measurements of thermo-electro-optical effects. The thickness of the cell was 18.0 μm. The (MPBAHB/LCP93/LCs (S6+E48)/ZLI-4572/photoinitiator) mixture was filled into a cell in an isotropic phase by capillary action.

Ultraviolet (UV) Light Irradiation

When an electric field above a critical value was applied to the (MPBAHB/LCP93/LCs (S6+E48)/ZLI-4572/photoinitiator) mixture in the temperature range of the SmA phase, the homeotropically oriented monodomain of the SmA phase was obtained. After the mixture in this molecular aggregation state was irradiated with UV light ($1.2\,\mathrm{mWcm^{-2}}$, 365 nm) for about 20.0 min, the homeotropically oriented polymer network (HOPN) was formed in the SmA phase by the photo-polymerization of MPBAHB and the (HOPN/LCP93/LCs (S6+E48)/ZLI-4572) composite was prepared.

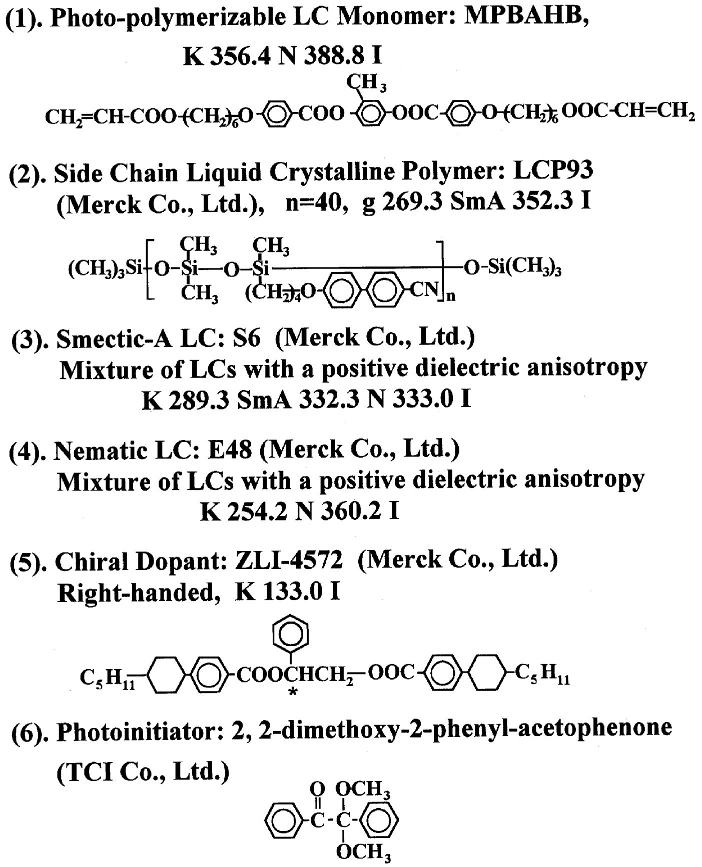

FIGURE 1 Chemical structures and some physical properties of the materials used.

Measurements

The phase transition temperatures and the aggregation structure of the samples were investigated on the basis of polarizing optical microscopic (POM) observations, differential scanning calorimetric (DSC) measurements, and wide-angle X-ray diffraction (WAXD) studies. The POM observations were carried out under crossed Nicols by using a Nikon polarizing optical microscope equipped with a hot stage calibrated to an accuracy of ±0.05 K. The DSC thermograms were obtained by using a Perkin Elmer (Pyris 1) at a heating rate of 5.0 K min^{-1} under dry He purge.

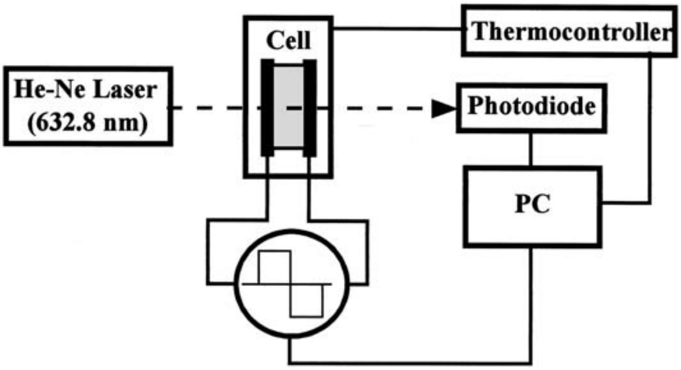

FIGURE 2 Experimental set-up for measuring the thermo-electro-optical effects.

The WAXD studies were done by using Ni-filtered Cu $K_\alpha(\lambda = 0.15405\,\text{nm})$ radiation from a M18XHF (Macscience Co., Ltd., Japan) X-ray generator.

The Cano wedge technique [18] was used to measure the pitch length of an N*-LC.

The thermo-electro-optical characteristics of the composites were investigated with the homemade instrument schematically shown in Figure 2. A He-Ne laser (2 mW, 632.8 nm) beam was used as incident light. The intensity of the transmitted light was recorded with a photodiode. The transmittance of the blank cell was normalized at 100%.

RESULTS AND DISCUSSION

It was characterized based on POM, DSC, and WAXD studies that the (MPBAHB/LCP93/LCs (S6+E48)/ZLI-4572)/photoinitiator, 0.5/2.0/91.4 (79.4+12.0)/6.0/0.1 wt%) mixture showed the crystalline (K)–SmA, SmA–N*, and N*–I phase transition temperatures at 270.0 K, 323.0 K, and 336.0 K, respectively. The pitch length of the mixture in the N* state was about 0.5 μm in the whole temperature range of the N* phase without coming near the SmA–N* and N*–I phase transition temperatures. Figure 3 shows the schematic representation of expected molecular alignments in the preparation process of the (polymer network/LCP93/LCs (S6+E48)/ZLI-4572) composite. After the (MPBAHB/LCP93/LCs (S6+E48)/ZLI-4572/photoinitiator, 0.5/2.0/91.4 (79.4+12.0)/6.0/0.1 wt%) mixture was filled into the cell in the isotropic phase and then cooled to the room temperature of about 298.2 K, the light-scattering focal-conic texture was formed in the SmA phase of the mixture as shown in Figure 3a. When an

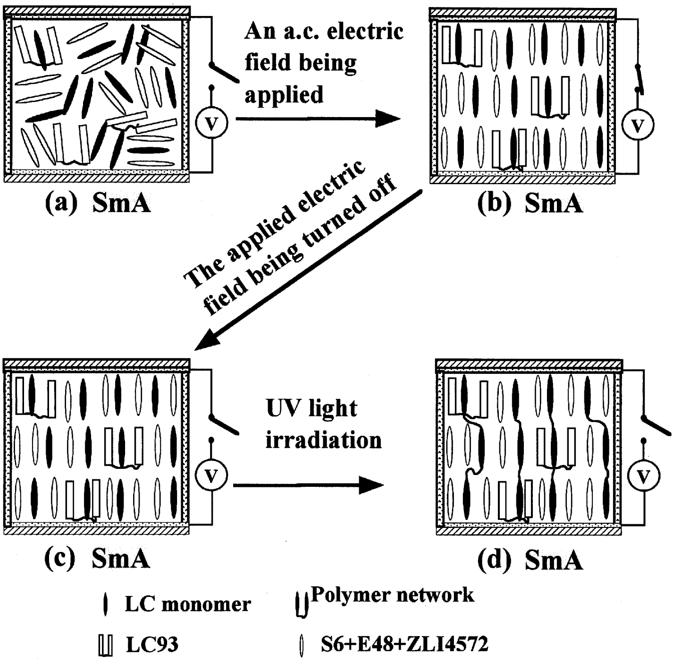

FIGURE 3 Schematic representation of the method to construct the (HOPN/LCP 93/LCs (S6+E48)/ZLI-4572) composite.

a.c. electric field above a threshold value was applied to the cell in the direction perpendicular to the cell surface at 298.2 K, the SmA phase of the mixture was homeotropically oriented due to a positive dielectric anisotropy of the LC molecules, as shown in Figure 3b, and the cell became transparent. After the electric field was turned off, the transparent state of the SmA phase maintained due to the mechanical characteristics of the SmA phase as shown in Figure 3c. Subsequently, the cell filled with the homeotropically oriented monodomain of the mixture in the SmA phase was irradiated with UV light at 298.2 K, and then the polymer network network was formed in the mixture by the photo-polymerization of MPBAHB. Since the polymer network was formed in the homeotropically oriented SmA phase of the mixture, it was also oriented homeotropically in the composite as shown in Figure 3d. The formation of the homeotropically oriented polymer network (HOPN) had been confirmed by scanning electron microscopic (SEM) observations [19]. Thus, the (HOPN/LCP93/LCs (S6+E48)/ZLI-4572) composite was prepared. The SmA phase of the composite was still transparent after UV irradiation. The K–SmA, SmA–N*, and N*–I phase transition temperatures of the composite were 270.1 K,

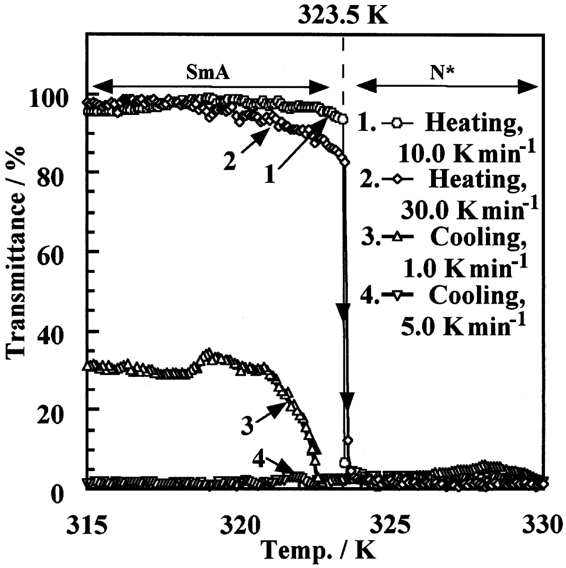

FIGURE 4 Plot of temperature versus transmittance for the composite.

323.5 K, and 334.9 K, respectively. The pitch length of the composite in the N* state was almost the same as that of the mixture before polymerization by UV irradiation.

Figure 4 shows the temperature dependence of the light transmittance for the composite in the absence of an electric field, and Figure 5 shows the schematic representation of the thermo-optical effects for the composite. It is apparent from curves 1 and 2 in Figure 4 that a drastic change from the transparent SmA state to the light-scattering N* one occurred upon heating the composite at a rate of 10.0 K min^{-1} and 30.0 K min^{-1}, respectively. The temperature range necessary for the drastic change of the transmittance was only about 0.1 K, being almost independent of the heating rate. The cell of the transparent SmA state showed a dark field, observed with a POM under crossed Nicols. Moreover, when the cell was rotated in the substrate surface plane perpendicular to the incident beam, the dark field always remained. This proved further that the LC molecules of the composite in the SmA state were homeotropically oriented, as schematically shown in Figure 3d or Figure 5a. When the composite was heated to a temperature above the SmA–N* phase transition temperature, 323.5 K, a fan-shape-like texture was exhibited. This indicated that the directions of the helical axes in the N* phase tended to be parallel to the cell surfaces, as schematically shown in Figure 5b, due to the interaction

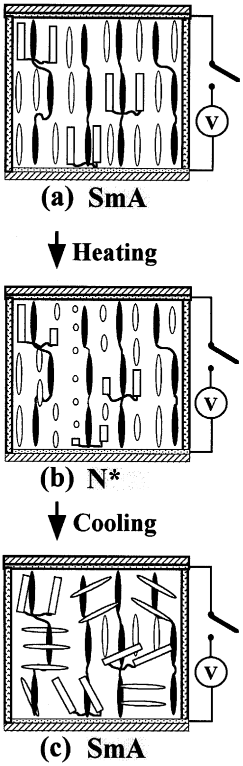

FIGURE 5 Schematic representation of the thermo-optical effects for the composite.

between the HOPN and LC molecules. It becomes clear from curve 3 in Figure 4 that, upon cooling the composite from the N* phase to the SmA one at a rate of 1.0 Kmin^{-1}, the transmittance of the cooling-induced SmA phase was about 32.0%, that is, a very low light-scattering intensity. This was because the LC molecules which were homeotropically oriented resulted somewhat from the interaction between the HOPN and the LC molecules. However, it becomes clear from curve 4 in Figure 4 that, upon cooling the composite at a rate of 5.0 K min^{-1}, the transmittance of the cooling-induced SmA phase was below 2.0% that is, a strong light-scattering state. POM observation demonstrated that a polydomain structure, as schematically shown in Figure 5c, formed in the SmA phase. This was because the cooling rate was so rapid that the light-scattering state of the N* phase had been frozen in the SmA one before the LC molecules could be homeotropically oriented, evidently by the interaction between the HOPN and the LC molecules.

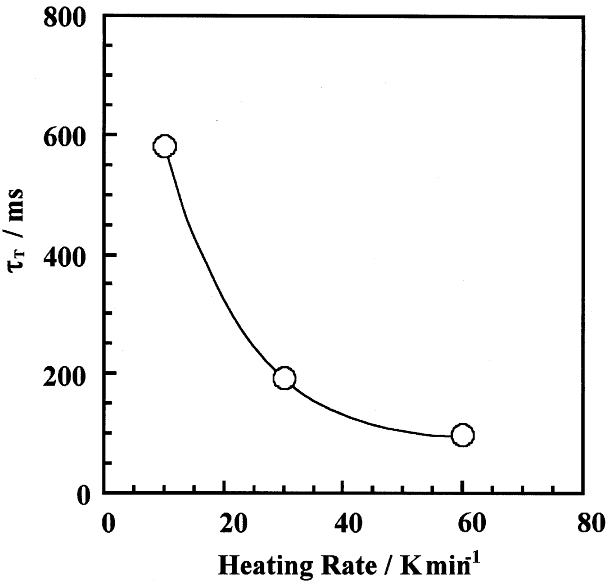

FIGURE 6 Plot of heating rate versus rise of response time τ_T for the composite.

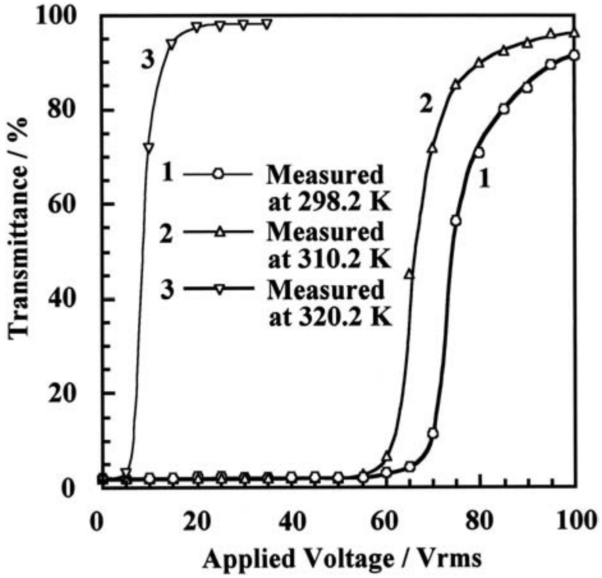

FIGURE 7 Plot of applied voltage versus transmittance for the composite.

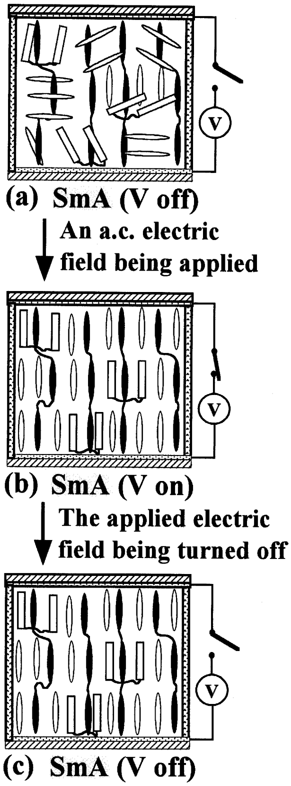

FIGURE 8 Schematic representation of the electro-optical effects for the composite.

Figure 6 shows the heating rate dependence of the response time, τ_T, for the heat-induced light-switching from the transparent SmA phase to the light-scattering N* one of the composite. The τ_T was defined as the time period required for a 9–10% transmittance change upon heating the composite at a certain rate. The magnitudes of τ_T were about 580 ms, 192 ms, or 98 ms upon heating the composite at a rate of 10.0 K min^{-1}, 30.0 K min^{-1} or 60.0 K min^{-1}, respectively.

Figure 7 shows the applied voltage (1.0 kHZ) dependence of the transmittance for the composite and Figure 8 shows the schematic representation of the electro-optical effects for the composite. It is apparent from curves 1, 2, and 3 in Figure 7 that the light-scattering SmA state as schematically shown in Figure 8a or 5c was changed into the transparent one when a voltage above a threshold value was applied to the cell. This is because the LC molecules were homeotropically oriented again, as schematically shown in Figure 8b, due to the positive dielectric anisotropy of the LC molecules. When V_{90} was defined as the voltage for the transmittance to increase of 90% the V_{90} was about 97.9 Vrms, 81.0 Vrms, and 13.5 Vrms measured at 298.2 K, 310.2 K, and 320.2 K, respectively. Apparently, the V_{90} decreased with increasing temperature of the composite; in other words, with increasing temperature of the composite near the SmA→N* phase transition temperature [20,21]. Thus, by adjusting the temperature of the composite or the SmA→N* phase transition temperature, V_{90} was changeable. After the applied electric field was turned off, the transparent state was maintained as schematically shown in Figure 8c due to both the mechanical characteristics of the SmA state and the interaction between the HOPN and the LC molecules.

Figure 9 shows the applied voltage dependence of the response time, τ_E, for the electric field-induced light switching from the light-scattering SmA state to the transparent SmA one of the composite. Here, τ_E was defined as the time period required for a 10–90% transmittance change upon the application of an a.c. electric field with a frequency of 1.0 kHz. As shown in Figure 9, τ_E decreased with increasing temperature at the

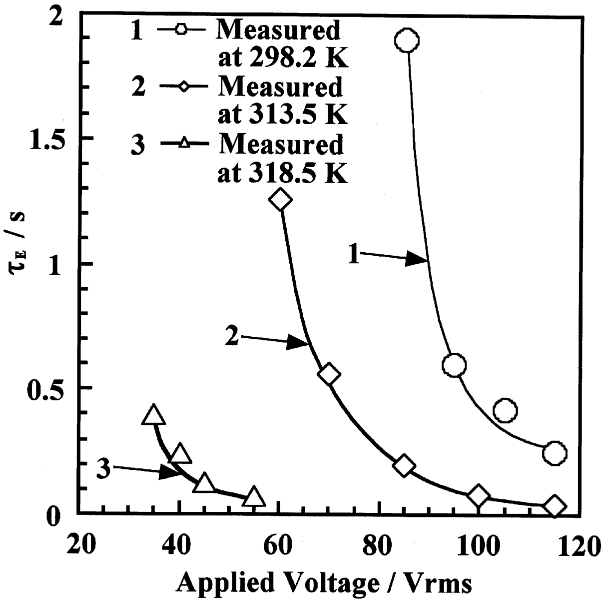

FIGURE 9 Plot of applied voltage versus rise of response time τ_E for the composite.

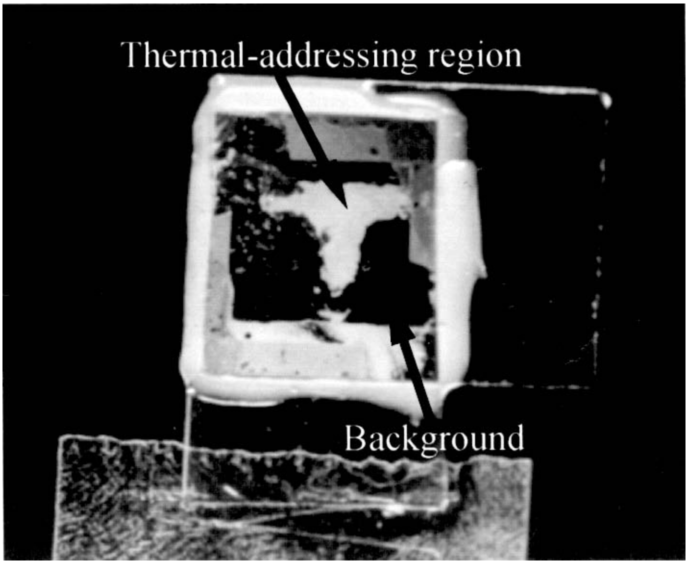

FIGURE 10 Photograph of the cell in which the light-scattering pattern T was thermally written in the transparent background.

same applied voltage since the viscosity of the composite decreased with increasing temperature and with increasing strength of the applied electric field at the same temperature. Thus, by adjusting the temperature of the composite and the strength of the applied electric field, τ_E could be adjusted.

Figure 10 shows the photograph of the cell in which a light-scattering pattern T was written in the transparent background with a hot pen scanning on the cell surface. In this experiment, the temperatures of the cell and hot pen were about 318.5 K and 338.5 K, being lower and higher than the SmA→N* phase transition temperature of the composite by about 5.0 K and 15.0 K, respectively. The scanning speed of the hot pen on the cell surface was about $2.5\,\mathrm{cm\,s^{-1}}$, and the thickness of the ITO glass substrates for the cell was 1.1 mm. No change had been observed in the transparent and light-scattering regions in the cell for about one year at room temperature since the pattern T was thermally written. It is easily understood that the light-scattering and the transparent regions became more stable and less stable with decreasing the content of the polymer network in the composite, and became less stable and more stable with increasing the content of the polymer network, respectively. By optimization of the content of the polymer network in the composite, these two regions can both be very stable. The light-scattering pattern T could be erased if an a.c. electric field above the threshold value was applied to the composite.

CONCLUSION

The (HOPN/LCP93/LCs (S6+E48)/ZLI-4572) composite which is applicable as a novel TAEELCD material was constructed. Like the (SCLCP/LC/chiral dopant) composite mentioned in the introduction, this novel composite had a high speed for memory thermal switching, a stable memory effect, and sufficient contrast. However, in comparison with the (SCLCP/LC/chiral dopant) composite, the inner surfaces of the cell containing this novel composite were unnecessary for any orientation treatment. This will make it very convenient to fabricate the TAEELCD, especially one with a large area or one used with flexible substrates.

The HOPN and LCP93 in the composite played a key role in the formation of the strong light-scattering N* phase and the strong light-scattering SmA one. This will be discussed in detail in future papers.

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