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Thermo-recording in (side chain type smectic A liquid crystal polymer/nematic liquid crystal/chiral dopant/dichroic dye) composite with a low power laser

HUAI YANG, HIROKAZU YAMANE, HIROTSUGU KIKUCHI
and TISATO KAJIYAMA*

Department of Materials Physics and Chemistry, Graduate School of Engineering,
Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

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Thermo-recording in a [side chain type smectic A liquid crystal polymer (SmA-LCP)/nematic liquid crystal (N-LC)/chiral dopant/dichroic dye] composite has been realized by using 2 mW of power from a He-Ne laser. The laser irradiation-induced phase transitions of smectic A (SmA) → chiral nematic (N*) → SmA formed the dominant thermo-recording mechanism in the composite. Thermo-recording in the (SmA-LCP/N-LC/chiral dopant/dichroic dye) composite exhibited a higher contrast when compared with the non-polymeric (SmA-LC)/N-LC/chiral dopant/dichroic dye composite.

1. Introduction

Laser addressing liquid crystal display (LALCD) modes based on a light-transmittance to light-scattering change have attracted much attention because of their unique characteristics; these include a high density information display, no cross-talk effect, a rewritable memory effect, no viewing angle problem and a large area projection, etc [1–4]. Chiral nematic liquid crystals (N*-LCs) [1, 2] or smectic A liquid crystals (SmA-LCs) [3, 4] are currently important candidate LALCD materials. The SmA-LC is a better candidate in terms of display contrast, memory effect life and the magnitude of energy necessary for writing and erasing information. For practical applications, a small amount of dichroic dye is usually doped into the mixture to increase the absorbing efficiency of the laser beam [5].

When a SmA-LC with positive dielectric anisotropy is homeotropically sandwiched between glass substrates, surface treated to induce homeotropic alignment, the optical axis in the SmA phase orients perpendicular to the substrate surfaces in a single-domain state. This texture is optically very uniform and scatters little light. When the homeotropically aligned SmA phase is locally heated to the isotropic (I) phase by laser irradiation and then, cooled back to the SmA phase, an unoriented polydomain texture, the so-called focal-conic texture, is formed in the SmA phase where the SmA-LC is heated. The focal-conic texture generally scatters light strongly because of its optically heterogeneous structure. The laser-addressed light-scattering pattern then appears on the clear background of the cell and thermo-recording is realized. When the light-scattering texture formed in the SmA phase is further heated to the isotropic phase, and then cooled in the presence of an electric field along the substrate surface normal, the homeotropically aligned SmA-LC becomes transparent again. The thermo-recorded state is thus erased.

In general, SmA-LCs with a narrow N phase or a narrow N* phase between the SmA and I phases can be used for the LALCD. Since SmA-LC does not respond to an applied electric field as readily as a N-LC (or a N*-LC), it is difficult to form the homeotropically aligned SmA phase upon cooling even in the presence of an electric field if the N (or N*) phase does not appear between SmA and I phases [5]. Thus, the process of thermo-recording, i.e. the process of laser-addressing information storage, is based on the SmA → N (N*) → I → N(N*) → SmA phase transitions. From the industrial and technical viewpoints, thermo-recording should be achieved with a low power laser; up to now, however, LC thermo-recording has been reported only by using a 3 ~ 4 mW He-Ne laser.

Side chain type LCP/LC composites have been studied extensively [6, 7], and unique characteristics have been found [8–12]. The reversible and bistable electro-optical effect based on light-scattering was recognized for the smectic (Sm) LCP/LC mixture [7, 8]. A light-scattering

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* Author for correspondence;
e-mail: tkajitcf@mbox.nc.kyushu-u.ac.jp

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state appeared upon the application of an a.c. electric field below a threshold frequency (f_c). It was concluded that the light-scattering state might arise from an electric current effect based on the electro-hydrodynamic motion of the backbones of the LCP. Since the backbones effectively disturb the uniform alignment of the LC, and furthermore can form randomly oriented small smectic fragments, the light-scattering intensity of the Sm phase in the LCP/LC mixture was much stronger than that of a Sm-LC. Thus, the light-scattering intensity of the LC could be improved remarkably by mixing with the LCP.

Recently, it was reported that when a SmA-LCP/N-LC/chiral dopant ternary composite was sandwiched between substrates inducing a homeotropic alignment, an extremely sharp change from a transparent state (the homeotropic state of the SmA phase) to a strongly light-scattering one (the focal-conic state of the N* phase) was observed with the heat-induced SmA → N* phase transition [13]. Upon rapid cooling, the strongly light-scattering state of the N* phase was frozen into the SmA phase. The strongly light-scattering intensity of the N* phase might be enhanced from the existence of the SmA-LCP for the reason mentioned above. It is well known that the latent heat of the SmA → N* phase transition is very small since this is a very weak first order or second order transition [14, 15]. Thus, it is expected that the SmA → N* phase transition, that is, the change from the transparent SmA phase to the strongly light-scattering N* phase, could be induced by a low power laser. If this is correct, a novel LC material for a laser-addressing information storage will be possible. In this study, therefore, high contrast thermo-recording based on the SmA → N* phase transition has been investigated for a SmA-LCP-N-LC/chiral dopant/dichroic dye composite irradiated by a He-Ne laser of only 2 mW power.

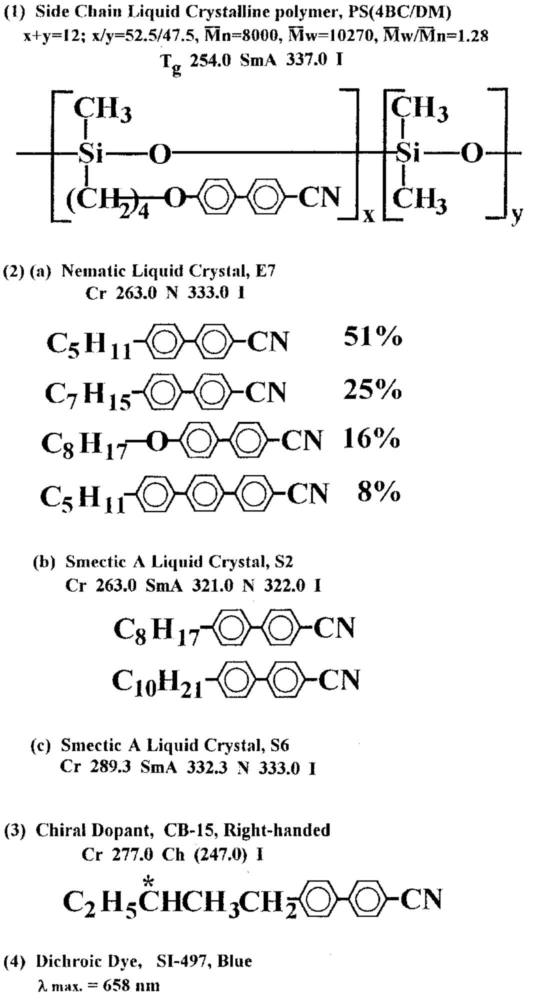

Figure 1. The chemical structures and some physical properties of the materials used.

2. Experimental

2.1. *Materials*

The side chain liquid crystal polymer PS(4BC/DM) was synthesized following the method proposed by Finkelmann *et al.* [16]; its chemical structure and some physical properties are shown in figure 1. The purity and the average molecular weight of PS(4BC/DM) were evaluated by GPC, and the block ratio was determined by NMR and FTIR. The N-LC (E7), the SmA-LCs (S2 and S6) and the chiral dopant (CB-15) are commercially available (Merck Co., Ltd.), and were used without further purification. Also, 2.0 wt% of the dichroic dye SI-497 (Mitsui Co., Ltd.) was doped into the S2/E7/CB-15 mixture, the PS(4BC/DM)/E7/CB-15 composite, and into S2 and S6, to increase the efficiency of energy absorption of the laser beam when thermo-recording experiments were performed. The table lists the components, the compositions, the phase transition temperatures, the latent heats of the SmA → N* (N) and the N → I phase transitions for the samples A–D. It also lists the pitch lengths of the N* phases of samples A and B, and the space thickness of the cells for samples A–D. The samples A–D were prepared by a solvent case method from acetone solutions.

2.2. *Fabrication of the cells*

The inner surfaces of the ITO-coated cell substrates were homeotropically treated following the method proposed by Kahn by using dimethyloctadecyl[3-(trimethoxysilyl)-propyl]ammonium chloride (Fluka Co., Ltd.) [17]. A PET film of 14 μm thickness was used as a cell spacer and the mixtures (samples A–D) were filled into the cells by capillary action in their isotropic phases.

Table. Components, compositions, phase transition temperatures, latent heats of phase transitions, pitch lengths of N* phases and thicknesses of spacers of cells for the samples A–D.

				Latent heat of phase transition/J g^{-1}			
Sample	Component	Composition/ wt %	Phase transition temperature/K	SmA → N* (N) transition;	N → I transition	Pitch length of N* phase/ μm	Spacer thickness of cell/ μm
A	[a]LCP/E7/CB-15/ SI-497	37.3/56.0/4.7/2.0	g219.0SmA313.5 N*327.3I	0.02	—	3.8	14
B	S2/E7/CB-15/ SI-497	60.7/32.6/4.7/2.0	K264.0SmA304.4 N*322.2I	0.02	—	3.5	18
C	S2/SI-497	98.0/2.0	K270.0SmA319.8 N*320.7I	0.08	0.67	—	14
D	S6/SI-497	98.0/2.0	K286.4SmA330.9 N*331.8I	0.13	0.81	—	12

[a] LCP = PS(4BC/DM).

2.3. *Measurements*

The phase transition temperatures and aggregation structures of the samples A–D were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and wide angle X-ray diffraction (WAXD). The latent heats of the SmA → N* (N) and the N → I phase transitions of these samples were also measured by DSC. The DSC thermograms were obtained by using a Rigaku DSC8230B instrument at a heating rate of 5.0 K min^{-1} under dry nitrogen. POM observations under crossed Nicols were carried out using a Nikon polarizing optical microscope equipped with a hot stage calibrated to an accuracy ± 0.05 K. WAXD studies used Ni filtered CuK_α ($\lambda = 0.15405$ nm) radiation from a M18XHF (Macscience Co., Ltd.) X-ray generator.

The Cano wedge technique [18] was used to measure the pitch lengths of the N* phases of samples A and B. Rubbed poly(vinylalcohol) (PVA) films were used to obtain planar alignments of the LC molecules. The thermo-recording characteristics of samples A–D were investigated with the home-made instrument schematically shown in figure 2. The direct beam without lenses 1 and 2, and the focused beam with lenses 1 and 2, of a He-Ne laser (2 mW, 632.8 nm) were used as incident light. The intensity of the transmitted light was recorded with a photodiode. The transmittance of the blank cell was normalized as 100%.

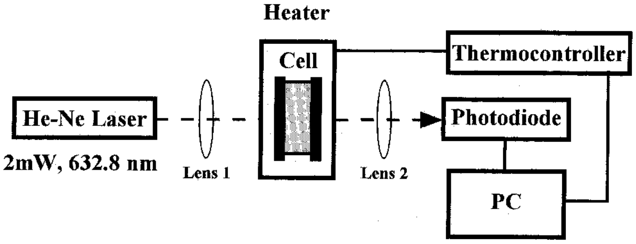

Figure 2. The set-up for thermo-recording experiments.

3. Results and discussion

It was confirmed from POM observations that a light-scattering focal-conic texture was formed in the N* phase of sample A when it was heated from the SmA to the N* phase. When sample A was then cooled very slowly (< 1 K min^{-1}) from a temperature above the SmA–N* phase transition temperature of 313.5 K to room temperature of about 290 K, the optic axis of the LC molecules in the SmA phase aligned perpendicular to the substrate surfaces; this was due to an anchoring effect of the surface agent which induces uniform homeotropic orientation of the LC molecules. Since the homeotropically oriented SmA phase was optically uniform, the slowly cooled sample A was transparent. On the other hand, if sample A was cooled rapidly (> 1 K min^{-1}), a focal-conic texture with a light-scattering characteristic was formed in the SmA phase as mentioned in § 1. The transparent or light-scattering states in the SmA phase can therefore be selectively obtained by controlling the cooling rate from the N* to the SmA phase.

In order to heat sample A locally, it was irradiated by a direct beam or a focused beam of a 2 mW laser at 311.5 K, a temperature lower than the SmA–N* phase transition temperature by 2.0 K. Sample A was doped with 2.0 wt % of SI-497 to increase the energy absorption efficiency of the laser beam. The irradiation time dependences of transmittance for the direct and focused systems are shown in figure 3. After the irradiation times of 28.4 and 3.5 s, respectively, the transmittance of sample A started to decrease with the direct beam and the focused beam. The drastic decrease in transmittance may be attributed to the change from the transparent SmA phase to the light-scattering N* phase, a transition that was induced by a laser irradiation of only 2 mW power. The time periods for the transmittance change from 90% to 10% were 14.1 and 1.9 s with the direct beam

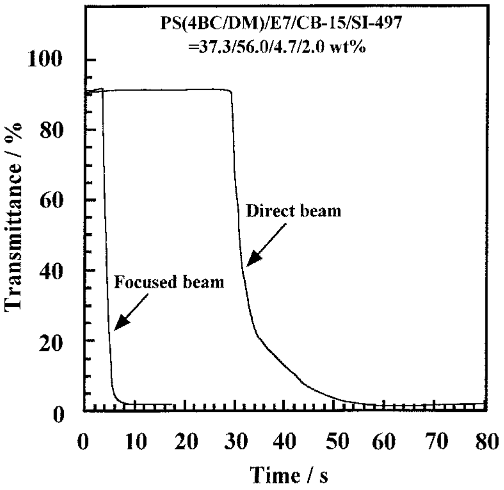

Figure 3. Plot of laser irradiation time versus transmittance for a cell of sample A.

and the focused beam, respectively. A high contrast ratio of about 40:1 between the transparent SmA phase and the light-scattering N* phase was achieved.

After the laser was turned off, the light-scattering state of the N* phase was frozen into the SmA phase due to rapid cooling to an ambient temperature. Figure 4 shows the POM photomicrograph of the frozen focal-conic texture formed with the direct beam. The circular shape of recorded pattern shown in figure 4 corresponds to the incident beam shape of the He-Ne laser. The frozen light-scattering focal-conic texture was so stable that little change in the texture was observed over a time period of one year. When the sample A cell was heated above the SmA–N* phase transition temperature of 313.5 K, and then cooled very slowly ($< 1\ \mathrm{K\ min^{-1}}$) to room temperature, it reverted to the homeotropically oriented SmA phase with an optically uniform structure. Thus the laser-addressed light-scattering texture appeared to be easily erased. Of course, the laser-addressed light-scattering texture frozen into the SmA phase could also be transformed into the transparent homeotropic texture when an electric field of 1 kHz was applied to the cell directly in the temperature range of the SmA phase, due to the positive dielectric anisotropy of sample A.

Figures 5 and 6 show, respectively, the irradiation time dependences of transmittance of sample B and the POM photomicrograph of the frozen light-scattering texture formed with the direct beam. The results of figures 5 and 6 were obtained under the same experimental conditions as figures 3 and 4, respectively. Since sample B was a mixture of low molecular weight compounds, resulting in lower viscosity than sample A, the time being necessary for the SmA → N* phase transition of sample B might be shorter than that for sample A. However, the contrast ratio between the homeotropically aligned SmA phase and the laser irradiation-induced

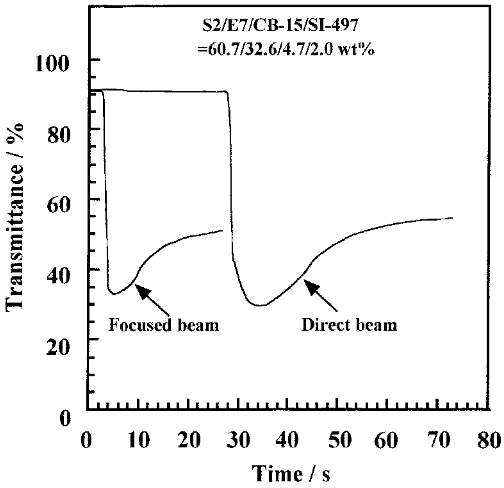

Figure 5. Plot of laser irradiation time versus transmittance for a cell of sample B.

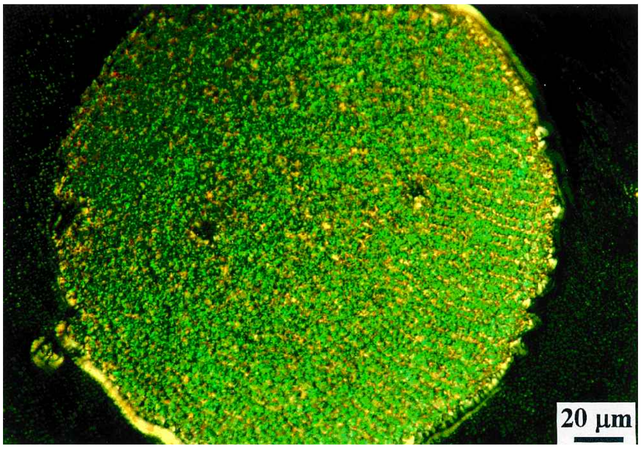

Figure 4. POM photomicrograph of the frozen laser-addressed texture in sample A.

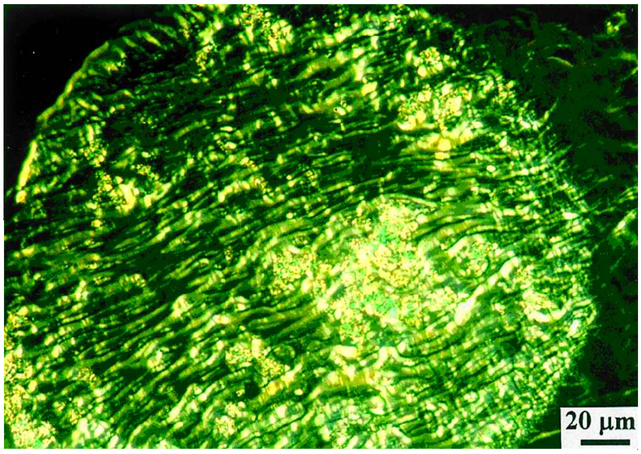

Figure 6. POM photomicrograph of the frozen laser-addressed texture in sample B.

N* phase for sample B, as shown in figure 5, was lower than that for sample A as shown in figure 3. The image contrast between the homeotropically aligned SmA phase and the thermo-recorded light-scattering texture for sample B, as shown in figure 6, was somewhat lower than that for sample A, as shown in figure 4. These results apparently indicate that the PS(4BC/DM) played a major role in the effective formation of the strongly light-scattering N* phase. The efficacy of LCP in obtaining an excellent laser-addressing characteristic for the composite system will be discussed in detail more elsewhere.

The cells of the homeotropically aligned samples C and D were irradiated by the focused laser beam at 318.7 and 329.8 K, respectively. These temperatures were lower than the N → I phase transition temperature of samples C and D by 2.0 K. However, even though these samples were irradiated for a very long period at temperature, the N → I phase transitions could not be achieved. This might be attributed to the fact that the latent heat for the N → I phase transition in samples C and D was considerably larger than that for the SmA → N* phase transition in samples A and B, as listed in the table. That is, the N → I phase transition is first order, the SmA → N* transition is very weak first order or second order [14, 15]. Since the energy of a 2 mW He-Ne laser was insufficient to induce the SmA → N → I phase transition in samples C and D, thermo-recording could not be achieved.

From above discussion, it is seen that the composite system with the SmA↔N* phase transition and containing the LCP forms the basis for a high contrast laser-addressing material which can be addressed with a 2.0 mW He-Ne laser.

4. Conclusion

Laser-addressing thermo-recording with high contrast and durable memory effect has been realized for a PS(4BC/DM)/E7/CB-15/dichroic dye composite. The thermo-recording could be achieved with only 2.0 mW of He-Ne laser power. The laser-addressed information storage process was based on SmA → N* → SmA phase transitions, and not on the SmA → N (N*) → I → N (N*) → SmA phase transitions conventionally used for the laser-addressing mode. Thus, a novel material for the laser-addressing memory effect which could be addressed with a low laser power has been demonstrated.

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