Investigation of the Electrothermo-Optical Effect of a Smectic LCP–Nematic LC–Chiral Dopant Ternary Composite System Based on $S_A \leftrightarrow N^*$ Phase Transition

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ABSTRACT: A sharp change in transmittance from a transparent state to a light scattering one within a tiny temperature range is induced accompanied with the heat-induced phase transition from a smectic-A (S_A) phase to a chiral nematic (N^*) one in a side-chain smectic-A liquid crystalline polymer (S_ALCP)–low-molecular-weight nematic liquid crystal (NLC)–chiral dopant ternary composite system with a homeotropic boundary condition. By adjusting the polymer ratio, an induced N^* phase exhibiting strong light scattering over a wide temperature region has been obtained. The resulting scattering texture retained in the S_A phase due to fast cooling from the N^* phase can be rather stable and can be easily erased by cooling slowly from the N^* phase to the S_A phase after the scattering texture being heated into the N^* phase again or by application of an alternating current electric field on the scattering texture directly. Based on these characteristics, it is very possible that this composite system will be used as a novel thermal addressed liquid crystal display material with respect to a fast response, a high contrast, and a durable memory effect. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 623–631, 1999

Key words: light scattering; NLC; LCD; electrothermo-optical effect

INTRODUCTION

Electrothermo-optical effect thermal addressed liquid crystal displays (LCD)[1] have attracted much attention because of the unique characteristics of displaying a large information content; no cross talk effect, even under a highly multiplexing drive; the existence of a certain memory effect; and no viewing angle problem. Although N^*LCs and S_ALCs can both be used as the LCD materials, considering that they (1) are able to be written

and erased by low power, (2) that there is enough contrast between the transparent and light scattering states, and (3) an adequate memory effect, S_ALCs are the best candidates and have been used in practice at present. When a S_ALC of a positive dielectric anisotropy is used as the LCD material, the initial state is clear since the inner surfaces of the cell has been treated homeotropically. After the S_ALC is heated to isotropic (I) phase and then cooled quickly, the focal conic texture of the S_A phase, which shows strong light scattering forms and information, is written. Usually, the focal conic texture exhibits a certain memory effect due to the high viscosity of a S_ALC. If the light scattering region is heated again into the I phase and

then cooled again with the existence of an electric field, the initial transparent state is obtained again, and the written information is erased. However, if no a narrow N phase exists between the S_A and I phase, it is difficult to obtain the transparent state on cooling. So the LCs with $S_A \leftrightarrow N \leftrightarrow I$ phase transitions should be used (since the N phase is very narrow, and the LC is still called as a S_ALC). Thus, in fact, the procedure of information being written is realized, based on $S_A \rightarrow N \rightarrow I \rightarrow N \rightarrow S_A$ phase transitions. If the N phase existing between S_A and I phases is wide, not only are more power and longer time necessary for the LC being heated over the clearing point, but strong light scattering state is also difficult to form on rapid cooling from the I phase because the twisting elastic constant k_{22} and the blending elastic constant k_{33} tend to be infinite with temperature dropping close to the $N - S_A$ transition since the transition is a second one.[2] If the temperature range is narrow, not only is the latent heat of the $N - S_A$ transition large due to the transition is a first one but the transparent state is difficult to form on cooling. Therefore, a LC with the $N - S_A$ phase transition is a weak first one; that is, the phase transition temperature near to the tricritical point of $S_A - N - I$ phase transitions, should be selected carefully.

If a chiral dopant is doped into a N phase, a $N*$ phase, locally being a N phase, will be induced. Hatoh[3] found that if a chiral compound is doped into a LC with $S_A \leftrightarrow N \leftrightarrow I$ phase transitions, a thermal addressed LCD based on $S_A \rightarrow N* \rightarrow I \rightarrow N* \rightarrow S_A$ phase transitions has a higher contrast because the twist force of the chiral dopant causes greater light scattering of the S_A phase forming on cooling rapidly from the I phase.

In this article, the electrothermo-optical effects of a S_ALCP–NLC–chiral dopant ternary composite system is studied, and it is found that it is very possible for this ternary composite system to be used as novel thermal addressed LCD material, whose procedure of information writing is based on $S_A \rightarrow N*$ phase transition, instead of the current thermal addressed LC materials, whose information writing is based on $S_A \rightarrow N \rightarrow I \rightarrow N \rightarrow S_A$ or $S_A \rightarrow N* \rightarrow I \rightarrow N* \rightarrow S_A$ phase transitions.

EXPERIMENTAL

Materials

A side-chain LC copolymer exhibiting S_A mesophase designated by the name of PS(4BC/DM),

1. Liquid crystalline copolymer

   PS(4BC/DM) (n=12) m=4; n=x+y=12; x/y=52.5/47.5

   Mn=8,000;   Mw=10,270;   Mw/Mn=1.28

   S_A-337-I (Tg=254K)

2. Low molecular weight liquid crystal

   E7 (Mixture of liquid crystals with positive dielectric anisotropy)

   K-263-N-333-I

3. Chiral dopant

   CB-15 right-handed helix $[\alpha]_D^{20} = +13$

   K-277-Ch(247)-I

Figure 1 The chemical structure and some parameters of the materials used.

the commercially available nematic mixture of cyanobiphenyl and cyanoterphenyl derivatives, E7 (Merck Co., Ltd.), and the commercially available chiral compound, CB-15 (Merck Co., Ltd.), were used as the three components of the S_ALCP–NLC–chiral dopant ternary composite system. The chemical structures and some physical parameters of the three components are shown in Figure 1. PS(4BC/DM) was synthesized following the method proposed by Finkelmann et al.[4] The purity and the molecular weights of PS(4BC/DM) were evaluated by gel permeation chromatography (GPC) and the block ratio was determined by nuclear magnetic resonance (NMR) and infrared (IR) analysis. Meanwhile, the phase transition behavior and the aggregate states were determined by polarizing optical microscopy (POM) observation, differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) measurements. The PS(4BC/DM)–E7–CB-15 composites were prepared by a solvent cast method from acetone solutions.

Investigation of the Phase Transition Behavior and the Aggregate States of the Ternary Composite System

The phase transition behavior and the aggregate states of the ternary composite system were inves-

tigated on the basis of the DSC calorimeter, POM, and X-ray diffraction studies (WAXD and SAXS). The DSC thermograms were obtained by using Rigaku DSC 8230B at a heating rate of 5.0 K min^{-1} under the protection of dry nitrogen purge, the POM microphotographs taken under crossed Nicole using Nikon polarizing optical microscope, and the WAXD and SAXS studies carried out using Ni-filtered CuKα(λ = 1.5405A) radiation from a M18XHF (Macscience Co., Ltd.) and a RU-300 (Rigku Co., Ltd.) X-ray generators, respectively.

Homeotropically Treated Method of the Inner Surfaces of a Tested Cell by a Surfacial Orientation Agent

Clearing of Substrates

Cleaning of solid substrates is still an art despite the considerable amount of work done on it.[5] Every reported method that could be found had been tried, but the molecules of the N^* phases couldn't be oriented very well when the ternary composites were sandwiched between the ITO substrates of a cell whose inner surfaces had been treated homeotropically after they had been cleaned by these cleaning methods. Thus, a new method of cleaning ITO substrates was established by us, as follows.

1. Dip the ITO substrates into distilled water and vibrate them ultrasonically for 5.0 min.
2. Keep the ITO substrates at 393.2 K for 30 min so that the water absorbed on them is evaporated completely.
3. Seal the ITO substrates in a glass tube with air existing in it and irradiate by ^{60}Co γ-ray for 500 kGy.

    The dependence of the resistance of the ITO film on radiation dose is shown in Figure 2. It is shown that the ITO film was very stable during the dose range studied. However, the substrates became somewhat black after irradiation.
4. Heat the ITO substrates by iso-propanol vapor until they get clear again.

It was demonstrated that very beautiful orientation was realized after the LC was sandwiched between the substrates, which had been cleaned with this new method and treated homeotropically.

Figure 2   The dependence of the resistance R of the ITO film of the substrate on the radiation dose D.

Method of the Treatment of Homeotropic Orientation

The method to obtain the homeotropic alignment was almost the same that was proposed by Kahn.[6] The substrates that had been cleaned by the above method were dipped into dilute solution of 0.5 wt % DMOAP [dimethy1-octadecy1-3-(trimethoxysily1) propylammonium chloride], and the solution was agitated at room temperature for about 5.0 min, then they were rinsed by distilled water to remove the excess DMOAP. Consequently, the excess water was blown free with clean N_2, and, finally, the DMOAP coating was further cured at 383.2 K for 1 hr in dry N_2.

Measurement of the Pitch Length of a N^* Phase

The Cano–Wedge technique[7] was used to measure the pitch lengths of the N^* phases of the system and the rubbed PVA films casted on the substrate surfaces were used to obtain the planar alignment.

Measurements of the Electrothermo-Optical Characteristics of the Ternary Composite System

The dependence of the transmittances of the cells sandwiching the ternary composites on temperature and on an electric field were carried out with the instrument, as schematically shown in Figure

Figure 3 The schematic representation of the instrument used to measure the electrothermo-optical characteristics of the ternary composite system.

3. A He-Ne laser (2 mW, 632.8 nm) was used as the incident beam, and the values were recorded by a photodiode. The transmittance of a blank cell was taken as 100%.

RESULT AND DISCUSSION

Phase Diagram of the Ternary Composite System

On the basis of POM observation, DSC, and WAXD and SAXS measurements, the phase diagram of PS(4BC/DM)–E7–CB-15 ternary composite system in which the CB-15 ratio is fixed as 4.8 wt % is determined, as shown in Figure 4, which has been discussed in another article.[8] It can be noted from the phase diagram that a S_A phase exists below the N^* one when PS(4BC/DM) ratio is between 18.0 and 47.6 wt %. Moreover, the $S_A \to N^*$ phase transition temperature increases with increasing PS(4BC/DM) ratio. Furthermore, smectic-like short-range ordering exists in a temperature range just above the transition.

Electrothermo-Optical Characteristics of the Ternary Composite System

Table I lists the compositions of the samples A–E and the thicknesses of the spacers of the corresponding cells sandwiching these samples. Figure 5(a)–(e) show the temperature dependence of the transmittances of the cells sandwiching samples A–E, respectively. For each sample in the temperature range of the S_A phase, the cell exhibits stable and high transmittance. This should be considered as the fluctuation of the molecules be-

ing limited by the rigidity of the layer structure of the S_A phase. When each cell is heated, a sharp change in the transmittance from a transparent S_A phase to a light scattering N^* one occurs in each sample within a tiny temperature range accompanied with the $S_A \to N^*$ phase transition. It has been understood that, different from some other phase transitions, $S_A \leftrightarrow N^*$ phase transitions are usually rather sharp. Lubensky[9] has showed that the relative shift of the transition temperature $\Delta T / T^*$ is estimated to be $\sim 10^{-3}$ (T^* is the second-order transition point). On cooling from the N^* to the S_A phase, near the transition, the free energy of the N^* phase may be written as

$$F = \tfrac{1}{2}(\mathrm{k}_{22}^0 + \delta\mathrm{k}_{22})q^2 - \mathrm{k}_{22}^0 q_0 q$$

where q_0 is the equilibrium value of the twist per unit length in the absence of smectic-like short-

Figure 4 The phase diagram of the ternary composite system (in which the CB-15 ratio is fixed as 4.8 wt %): (I) isotropic; (N^*) chiral nematic; (N_S^*) smectic-like short-range ordering; (S_A) smectic-A; (K) crystalline; (M) mesophase; (G) glassy.

Table I   The Ratios (wt %) of PS (4BC/DM)–E7/CB-15 of the Samples A–E and the Thickness (μm) of the Spacers of the Corresponding Cells Sandwiching These Samples

Sample	A	B	C	D	E
Ratios	23.8/71.4/4.8	28.6/66.6/4.8	33.3/61.9/4.8	38.1/57.1/4.8	42.9/52.3/4.8
Thickness	23	20	18	17	16

range ordering and q is the actual value. Minimizing with respect to q, then

$$q = \frac{q_0 k_{22}^0}{k_{22}^0 + \delta k_{22}}$$

which indicates that q decreases rapidly as temperature drops to the $N^* \to S_A$ transition point or, in other words, the pitch $P = 2\pi/q$ increases rapidly. Qualitatively, this effect can be explained as follows. Due to the relative high rigidity, it is difficult for the layer structure of a S_ALC to buckle in order to twist. On cooling from the N^* to S_A phase and near the phase transition temperature, the molecules start to form the smectic-like short-range ordering at some degree, and some groups of molecules begin to show some fleeting layer structure. As the temperature drops closer to the transition, the size of the groups of the molecules gets larger, and smectic-like short-range ordering increases. This results in the increase in the twisting elastic constant k_{22} and the untwisting of the helix. Since all this can only take place near the transition temperature, the pitch change happens within a tiny temperature range just above the transition. This drastic change in pitch also exists in this studied ternary composite system, as shown in Figure 6, which illustrates the temperature dependence of the pitch lengths of the N^* phase of samples A–E (details will be discussed in the near future). Of course, on heating, a drastic decrease in the pitch length should occur. In the present studied composite system, there exist backbones of PS(4BC/DM). However, considering the structures of S_A and N^* phases, the formation of helix doesn't require a rearrangement of the polymer backbones because of the very small change of the twist angles of the mesogenic molecules. So the phenomenon of the drastic change in the pitch length still exists in each studied sample. It is a natural result that a sharp change in transmittance from a transparent to a light scattering state occurs, accompanied by the drastic change in pitch for a cell with a homeotropic boundary condition since S_A and N^* phases are

clear and light scattering in this kind of orientation, respectively. Table II lists the times necessary for the drastic change of the transmittances of these samples on going from 10 to 90% response, respectively. It can be seen that the response time decreases with the heating rate increasing and the PS(4BC/DM) ratio decreasing. The former is a natural result, and the latter is obviously resulted from the decrease in viscosity with the PS(4BC/DM) ratio decreasing.

It can be observed from Figure 5(a)–(e) that the N^* phases just above the $S_A \to N^*$ phase transitions show strong light scattering. However, the intensities of the light scattering of the N^* phases of the samples A and B obviously decrease with an increase in temperature; this tendency decreases with an increasing PS(4BC/DM) ratio, and the light scattering state is already rather stable when the PS(4BC/DM) ratio amounts to 33.3 wt %, as shown in Figure 5(c). This fact demonstrates that the conformation of the backbones of PS(4BC/DM) has an obvious effect on the orientation of the mesogenic molecules of the N^* phases. In the homeotropically aligned S_A of each sample, the planes containing the backbones tend to be parallel to the substrate surfaces. Thus, when a studied sample with a homeotropic boundary condition changes from a S_A into a N^* phase, the plane must tend to continue to be parallel to the surfaces in the initial stage of the formation of the N^* phase due to the memory effect. This results in that the directions of the helices of the small domains tend to be parallel to the substrate surfaces in the initial stage of the formation of the N^* phase too, so focal conic textures form in the N^* phases of these studied samples, and the N^* phases show strong light scattering just above the $S_A \to N^*$ phase transitions. In addition, smectic-like short-range ordering exists in the initial stage of the formation of the N^* phase in each sample. This should also be helpful in the formation of a focal conic texture.[10,11] With the temperature increasing, the backbones of PS(4BC/DM) tend to adopt a random statistical conformation, the smectic-like short-range ordering disappears,

Figure 5 (a) The dependence of the transmittance of the cell sandwiching sample A on temperature at a heating rate of (A) 10.0 and (B) 30.0 K min^{-1} and at a cooling rate of (C) 1.0 and (D) 5.0 K min^{-1}. (b) The same as in (a) but for sample B. (c) The same as in (a) but for sample C. (d) The same as in (a) but for sample D. (e) The same as (a) but for sample E.

and the motion of the mesogenic molecules aggravates gradually. This should result in that the directions of the helices of some small domains tend to rotate to be perpendicular to the substrate surfaces in order to be in a lower energy state with an increasing temperature, except those of the domains near the surfaces, for example, a scroll texture tends to form in the N^* phase of

each sample with an increasing temperature.[12,13] Because the helical axis is also the optical axis, this should result in the increase in the component of the optical axis in the direction perpendicular to the substrate surfaces. Thus, with the temperature increasing, the transmittance of the N^* phases of samples A and B obviously increase. However, since the backbones of PS(4BC/DM)

Figure 5 (*Continued from the previous page*)

tend to adopt a random statistical conformation in a N^* phase, the directions of the helices of the small domains tend to distribute randomly in all the temperature range of the N^* phase if the PS(4BC/DM) ratio is higher enough in a sample. Then the rotation of the directions of the helices of some small domains from the direction parallel to the surfaces to that normal to the surfaces is restricted. Thus, the dependence of the light scattering intensity of a N^* phase decreasing with an increasing temperature decreases with the PS(4BC/DM) ratio increasing and the N^* phases of samples C–E show strong light scattering, as shown in Figures 5(c)–(e), respectively.

Table III lists the transmittances of the resulting S_A phases of these samples cooling from the temperatures above the $S_A \rightarrow N^*$ phase transition temperatures at different cooling rates. From this table and from Figures 5(a)–(e), it can be known that the initial transparent S_A phase of each sample can be obtained again on cooling at a rate of 0.5 K min^{-1}, and strong light scattering can be obtained on cooling at rate of 10.0 K min^{-1} for the samples. On cooling at an intermediate rate between 0.5–10.0 K min^{-1}, the transmittance of the resulting S_A phase of each sample decreases with increasing PS(4BC/DM) ratio and the cooling rate. It has been known that untwisting of a helix will occur when cooling from a N^* phase to a S_A phase since the twisting elastic k_{22} will tend to become infinite near the $N^* \rightarrow S_A$

transition temperature. However, this is a course of dynamics and is necessary for a certain time. If the cooling is slow enough, there is enough time for the untwisting of the helix, and the resulting S_A phase orients in a single crystal manner affected by the anchoring effect of the surfacial orientation agent. If the cooling is too fast, the helix will have not enough time to untwist completely, and the incompletely untwisting helical structure will be frozen in the S_A phase. Then the S_A phase will have a certain intensity of light scattering determined by the degree of the untwisting of the helix. Obviously, the greater the PS(4BC/DM) ratio, the greater the viscosity of the sample becomes and the longer time that the untwisting of the helix is necessary. Thus, the transmittance of the resulting S_A phase decreases with increasing PS(4BC/DM) ratio and cooling rate, and strong light scattering state can be obtained when the cooling rate is fast enough, even though smectic-like short-range ordering exists in a certain temperature range just above the $S_A \rightarrow N^*$ phase transition. The light scattering textures frozen in the S_A phases in these samples have been observed to be stable with the increasing PS(4BC/DM) ratio. Little change in transmittance has been observed for about half a year for the sample with 33.3 wt % PS(4BC/DM) and for about one year and a half for the samples with the ratio over 38.1 wt %.

If an alternating current (a.c.) electric field is applied on the light scattering texture frozen in

Figure 6 The temperature dependence of the pitch lengths of the N^* phases of the samples A–E.

Table III   The Transmittances (%) of the Resulting S_A Phases of These Samples at Different Cooling Rates (K min^{-1})

	Samples				
Cooling Rate	A	B	C	D	E
Transmittance					
0.5	98.0	97.0	97.6	97.1	94.0
1	95.7	96.8	96.0	96.5	72.7
5	52.0	29.0	2.6	1.0	0.8
10	12.8	5.6	1.2	0.8	0.7

field is 1.0 kHz) measured at different temperatures. It can be seen that the threshold voltage for each sample decreases with an increase in temperature. The meaning that the threshold voltage of each sample is zero when measured at the temperature very near the $S_A \rightarrow N^*$ phase transition temperature is that, by the anchoring effect of the orientation agent coated onto the substrate surfaces only, the homeotropic orientation of the S_A phase of each sample is obtainable at the temperature.

CONCLUSION

A drastic change in transmittance from a transparent state to a light scattering one in a cell with the S_A phase of a sample formed by cooling the cell rapidly from N^* phase, the light scattering texture will be changed into the transparently homeotropic S_A phase again because of the positive dielectric anisotropy. Figure 7 shows that the threshold voltages necessary for the focal–conic textures of the S_A phases of samples B–E changed into the homeotropic ones on application of an a.c. electric field (the frequency of the applied electric

Table II   The Response Times Necessary for Drastic Change in the Transmittances of Samples A–E on Going from 10 to 90% Response at Different Cooling Rates (K min^{-1})

	Samples				
Heating Rate	A	B	C	D	E
Time					
10	2.1	3.0	3.9	5.0	7.5
30	0.9	1.2	1.8	2.6	4.0

Figure 7 The dependence of the threshold voltages, V_{th}s, of samples B–E necessary for the focal conic textures of the S_A phases being changed into the homeotropic ones on temperature.

a homeotropic boundary condition sandwiching PS(4BC/DM)−E7−CB-15 ternary composite system has been realized based on the $S_A \rightarrow N^*$ phase transition. The response time of the change increases with the increasing PS(4BC/DM) ratio. A strong light scattering state is obtained in all the temperature range of the N^* phase when PS(4BC/DM) ratio is over 33.3 wt %. If the cell is quenched, the light scattering texture will be frozen in the S_A phase, and, if cooled slowly enough, the transparent S_A phase oriented in a single crystal manner will be obtained again. Moreover, the PS(4BC/DM) ratio and the cooling rate have a remarkable effect on the transmittance of the resulting S_A phase. The frozen light scattering texture of the S_A phase of a sample with a higher PS(4BC/DM) ratio has a greater memory effect, and the light scattering texture can also be erased easily by the application of an a.c. electric field. Based on these characteristics, it is very possible that this ternary composite system will be able to be used as a thermal addressed LCD material since the change from the transparent state to a light scattering ones is based on the very sharp $S_A \rightarrow N^*$ phase transition, and not based on $S_A \rightarrow N(N^*) \rightarrow I \rightarrow N(N^*) \rightarrow S_A$ phase transitions, as the conventional thermal addressed LCD materials behave. This composite display material is most possibly has a faster response time compared with the conventional ones, besides a very high contrast and a very stable memory effect.

Some of explanations are somewhat speculative. Further study and the investigation of comparison between the electrothermo-optical characteristics of this composite system and those of low-molecular-weight S_ALCs and those of the low-molecular-weight S_ALC−NLC−chiral dopant composite system will be carried out to demonstrate that the former is the better candidate for the thermal addressed LCD material than the latter two, which will be discussed in the near future.

REFERENCES

1. Hareng, M.; LeBerre, S.; Hehien, R.; Perbet, J. N. SID International Symposium Digest of Technical Papers 1982, p. 106.
2. Cladis, P. E.; Torza, S. J Appl Phys 1975, 46, 584.
3. Hatoh, H. Mol Cryst Liq Cryst 1994, 250, 1.
4. Finkelmann, H.; Kiechle, U.; Rehage, G. Mol Cryst Liq Cryst 1983, 94, 343.
5. Mittal, K. L. Surface Contamination Plenum: New York, 1979.
6. Kahn, F. J Appl Phys Lett 1973, 22, 386.
7. Cano, R. Bull Soc Fr Min 1968, 91, 20.
8. Yang, H.; Kikuchi, H.; Yamane, H.; Chen, X. F.; Kajiyama, T. Chem Res Chin Univ submitted.
9. Lubensky, T. C. J Phys (Paris), 1975, 36, C1−151.
10. Harada, T.; Crooker, P. Mol Cryst Liq Cryst 1975, 30, 79.
11. Freidzon, Ya; Boiko, N.; Shibaev, V.; Plate, N. Eur Polym J 1986, 22, 13.
12. Kashnow, R. A.; Bigelow, J. E.; Cole, H. S.; Stein, C. R. Liquid Crystal and Orderd Fluids, Vol. 2, Johnson J. F.; Porter, R. S., Eds.; Plenum Press: New York, 1974; p. 483.
13. Cladis, P. E.; Kleman, M. Mol Cryst Liq Cryst 1972, 16, 1.