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Liquid Crystals
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Temperature dependent light transmission-light scattering switching of (homeotropic liquid crystalline polymer network/liquid crystals/chiral dopant) composite film

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Online publication date: 06 August 2010

To cite this Article Yang, Huai , Kikuchi, Hirotsugu and Kajiyama, Tisato(2000) 'Temperature dependent light transmission-light scattering switching of (homeotropic liquid crystalline polymer network/liquid crystals/chiral dopant) composite film', Liquid Crystals, 27: 12, 1695 — 1699

To link to this Article: DOI: 10.1080/026782900750037284

URL: http://dx.doi.org/10.1080/026782900750037284

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LIQUID CRYSTALS, 2000, VOL. 27, NO. 12, 1695–1699

Temperature dependent light transmission–light scattering switching of (homeotropic liquid crystalline polymer network/liquid crystals/chiral dopant) composite film

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(*Received 24 April 2000; accepted 27 June 2000*)

A (photo-polymerizable liquid crystal (LC) monomer/LCs/chiral dopant/photoinitiator) mixture with a smectic A (SmA)–chiral nematic (N*) phase transition was sandwiched between two ITO glass substrates which were not subjected to any surface orientation treatment. When an electric field-induced homeotropically oriented SmA phase of the mixture was irradiated with UV light, an oriented liquid crystalline polymer (LCP) network was formed upon photo-polymerization of the LC monomer. Then, a (homeotropically oriented LCP network/LCs/chiral dopant) composite with a SmA–N* phase transition was prepared. A focal-conic texture appeared in the heat-induced N* phase of the composite upon heating from the transparent state of the homeotropically oriented SmA phase; the focal-conic texture exhibited strong light scattering. Upon cooling the composite to the SmA phase, this phase was again homeotropically oriented due to the strong intermolecular interaction between the LC molecules and the homeotropically oriented LCP network. Thus, the transparent state of the SmA phase and the light scattering state of the N* phase occurred reversibly upon cooling and heating, accompanied by the thermal SmA–N* phase transition.

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1. Introduction

An anisotropically oriented liquid crystalline polymer (LCP) network/liquid crystal (LC) composite can be obtained by photo-polymerization of a LC monomer/LC/photoinitiator mixture in a mesogenic state. The LCP network in the composite after photo-polymerization may maintain the molecular orientation of the initial LC mixture. Thus if the initial LC mixture is homeotropically or homogeneously oriented before photo-polymerization, the resultant LCP network may maintain the homeotropic or homogeneous orientation of the LC [1–3]. This type of (LCP network/LC) composite has therefore attracted much interest for display applications [4].

Side chain type liquid crystalline polymer (SCTLCP)/LC composite systems have been studied extensively for their unique characteristics [5–17]. In the case of a SCTLCP/LC/chiral dopant composite system with a SmA–N* phase transition sandwiched between substrates inducing a homeotropic alignment, an extremely sharp change from a transparently homeotropic state of the SmA phase to a strongly light-scattering focal-conic state of the N* phase was observed at the heat-induced SmA → N* phase transition. Upon cooling the composite system slowly from N* to SmA, the SmA phase was again homeotropically oriented. On the other hand, upon cooling the composite system to the SmA phase rapidly, the strong light-scattering state of the N* phase was frozen in. Also, when an a.c. electric field above a threshold value was applied to the light-scattering SmA phase, it was transformed to the homeotropically oriented transparent SmA phase. Based on these results, a thermal-addressing LC display has been developed [14, 15]. Furthermore, since the latent heat of the SmA → N* phase transition is very small (it being a very weak first order or second order transition [16, 17]), the change from transparent SmA to light-scattering N*, corresponding to the SmA → N* phase transition, could be induced by low power laser energy; when a small amount of dichroic dye was doped into the composite system [18, 19].

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010001743

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Recently a novel thermal-addressing LC display was proposed for the helically oriented LCP network/LCs/chiral dopant composite system with SmA–N* phase transition. The LCP network was formed in the planarly oriented N* phase of the photo-polymerizable LC monomer/LCs/chiral dopant/photoinitiator mixture. Since the planar texture of the N* phase was stabilized by the LCP network, the transparent planar texture was maintained in the SmA phase upon cooling the composite from N* to SmA. When an electric field above a threshold value was applied to the composite in the SmA phase, polydomains exhibiting strong light scattering were formed. When the electric field was turned off, the light-scattering state of the SmA phase remained due to its mechanical characteristics. Both the transparent and the light-scattering states of the SmA phase were very stable. Upon heating the composite, a drastic change from light-scattering SmA to transparent N* occurred in a temperature range of about 0.1 K. The transparency of the N* phase was maintained again in the SmA phase upon cooling the composite. Thus, a novel thermal-addressing LC display could be realized with the characteristic that transparent characters may be stored on a light-scattering background, in an opposite fashion to conventional thermal-addressing LC displays which show light-scattering characters on a transparent background. However, this novel thermal-addressing LC display showed a very fast speed for memory switching, sufficient contrast and an endurable memory effect [19].

In this study, thermally sensitive light-transmission/light-scattering switching has been investigated for the LCP network/LCs/chiral dopant composite system prepared by photo-polymerization of a photo-polymerizable LC monomer/LCs/chiral dopant/photoinitiator mixture with homeotropic orientation.

2. Experimental

2.1. *Materials*

A photo-polymerizable LC monomer (MPBAHB), a smectic A LC (S6, Merck Co., Ltd.), a nematic LC (E48, Merck Co., Ltd.), a chiral dopant (ZLI-4572, Merck Co., Ltd.) and a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (TCI Co., Ltd.) were used as the components for the [photo-polymerizable LC monomer/LCs (SmA-LC + N-LC)/chiral dopant/photoinitiator] mixture. The weight ratio of the photo-polymerizable LC monomer to the photoinitiator was 5 : 1. The chemical structure and some physical properties of these materials are shown in figure 1. MPBAHB was synthesized by the method proposed by Broer *et al.* [20]; its purity was measured by NMR, FTIR and elemental analysis. The (MPBAHB/LCs (S6 + E48)/ZLI-4572/photoinitiator) mixture was prepared by a solvent casting method from acetone solution.

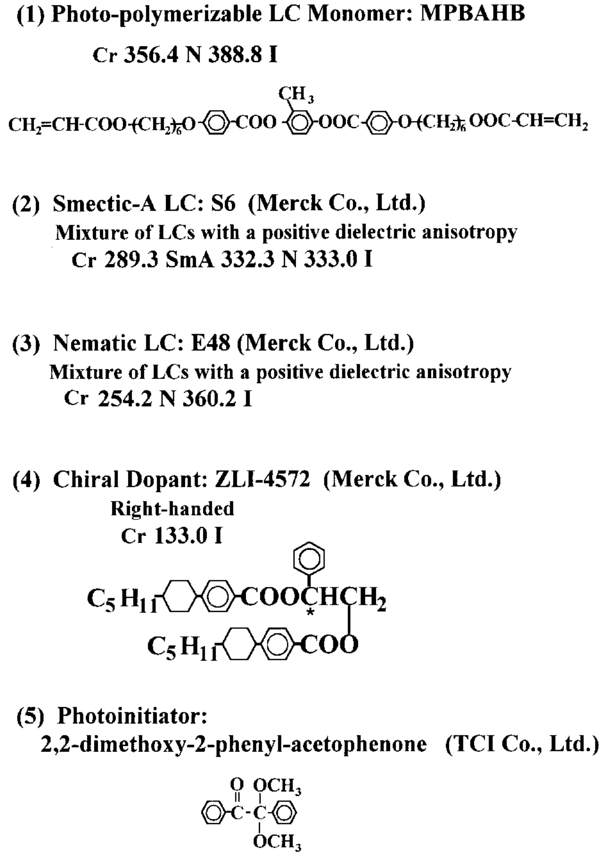

Figure 1. Chemical structure and some physical properties of the materials used.

2.2. *Fabrication of the cell*

A PET 14 µm thick film was used as a cell spacer. The inner surfaces of the cell substrates were not subjected by any surface orientation treatment and the (MPBAHB/LCs (S6 + E48)/ZLI-4572/photoinitiator) mixture was filled into the cell by capillary action in the isotropic phase.

2.3. *UV irradiation-induced photo-polymerization*

Before the photo-polymerization of the (MPBAHB/LCs (S6 + E48)/ZLI-4572/photoinitiator) mixture, the SmA phase was homeotropically oriented by application of an a.c. electric field to the cell due to the positive dielectric anisotropy of the LC molecules. The cell was then irradiated by UV light (4 W, 365 nm) for about 20 min. LCP network was formed in the homeotropically oriented SmA phase upon photo-polymerization of the LC monomer, forming the (LCP network/LCs (S6 + E48)/ZLI-4572) composite. The composition, phase transition temperature, N* pitch length and cell thickness for the (LCP network/LCs (S6 + E48)/ZLI-4572) composite are listed in the table.

Table. Composition, phase transition temperatures, pitch length of the N* phase and cell thickness for the composite.

LCP network/LCs (S6 + E48)/ZLI-4572/wt %	Phase transition temperature/K	Pitch length of N* phase/μm	Thicknes of cell spacer/μm
2.0/92 (80.0 + 12.0)/6.0	Cr 275.0 SmA 322.2 N* 335.1 I	0.5	14.0

2.4. *Measurements*

The phase transition temperatures and the aggregation structure of the (LCP network/LCs (S6 + E48)/ZLI-4572) composite were investigated on the basis of polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and wide angle X-ray diffraction (WAXD) studies. The POM observations were carried out under crossed Nicols using a Nikon polarizing optical microscope equipped with a hot stage calibrated to an accuracy of ± 0.05 K. The DSC thermograms were obtained with a Perkin Elmer Pyris 1 at a heating rate of 5.0 K $\min^{-1}$ under a dry He purge. The WAXD studies were made using Ni filtered CuK_α radiation ($\lambda = 0.15405\,\mathrm{nm}$) from a M18XHF (Macscience Co., Ltd.) X-ray generator.

The (LCP network/LCs (S6 + E48)/ZLI-4572) composite for scanning electron microscopic (SEM, Hitachi S-2150) observation was prepared in the following way. After UV irradiation of the cell for photo-polymerization, the sealant material of the cell was removed to allow diffusion of hexane into the cell. After extracting the LCs and chiral dopant with hexane, the cell was dried *in vacuo* for a few hours. It was then opened with caution and the substrates plus LCP network were coated with a thin gold layer to eliminate any electric charge problem for SEM study. The Cano-wedge technique [21] was used to measure the pitch length of the N* phase for the (LCP network/LCs (S6 + E48)/ZLI-4572) composite.

The thermo-recording characteristics of the (LCP network/LC (S6 + E48)/ZLI-4572) composite were investigated with a home-made instrument schematically shown in figure 2. A He-Ne laser (2 mW, 632.8 nm) provided incident light; the intensity of transmitted light was recorded with a photodiode. The transmittance of the blank cell was normalized as 100%.

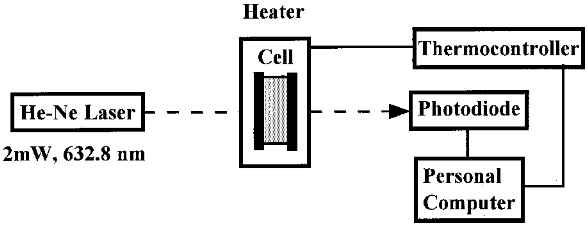

Figure 2. Experimental set-up for measuring the thermo-optical characteristics of the composite.

3. Results and discussion

Figure 3 shows the temperature dependence of transmittance for the (LCP network/LC (S6 + E48)/ZLI-4572) composite. A change from transparent SmA to strongly light-scattering N* occurred in a temperature range of about 0.3 K at the thermal SmA → N* phase transition on heating the composite. The temperature dependence of transmittance was almost independent of the heating rate, 10.0 or 30.0 K $\min^{-1}$, as shown (curves 1 and 2). On cooling the composite at a rate of 1.0 or 5.0 K $\min^{-1}$ (curves 3 and 4), the change from light-scattering N* to transparent SmA also occurred in a temperature range of about 0.3 K at the thermal N* → SmA phase transition. Even if the composite in the N* phase was quenched in water at 298.2 K, the change from light-scattering N* to transparent SmA could also be achieved. Since the LCP network was formed in the homeotropically oriented SmA phase of the (MPBAHB/LCs (S6 + E48)/ZLI-4572/photoinitiator) mixture. It is reasonable to suppose that the LCP network should also be oriented homeotropically in the cell.

Figures 4 (*a*, *b*, *c*) show SEM photographs of the LCP network under varying magnifying power after the LCs and chiral dopant was extracted from the cell with hexane. These photographs were taken while the angle between the observing direction and the normal of the cell substrate was about 53°. The pictures apparently

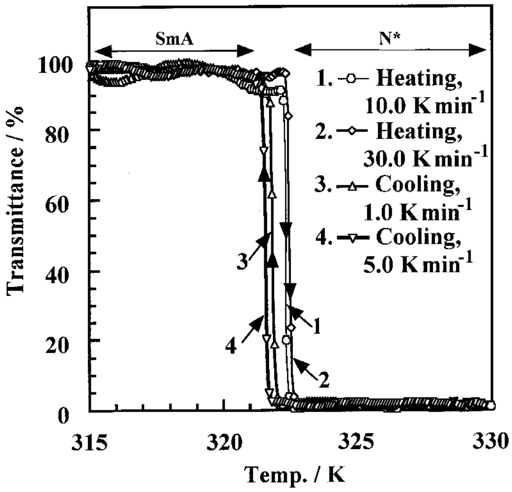

Figure 3. Plot of temperature versus transmittance for the composite.

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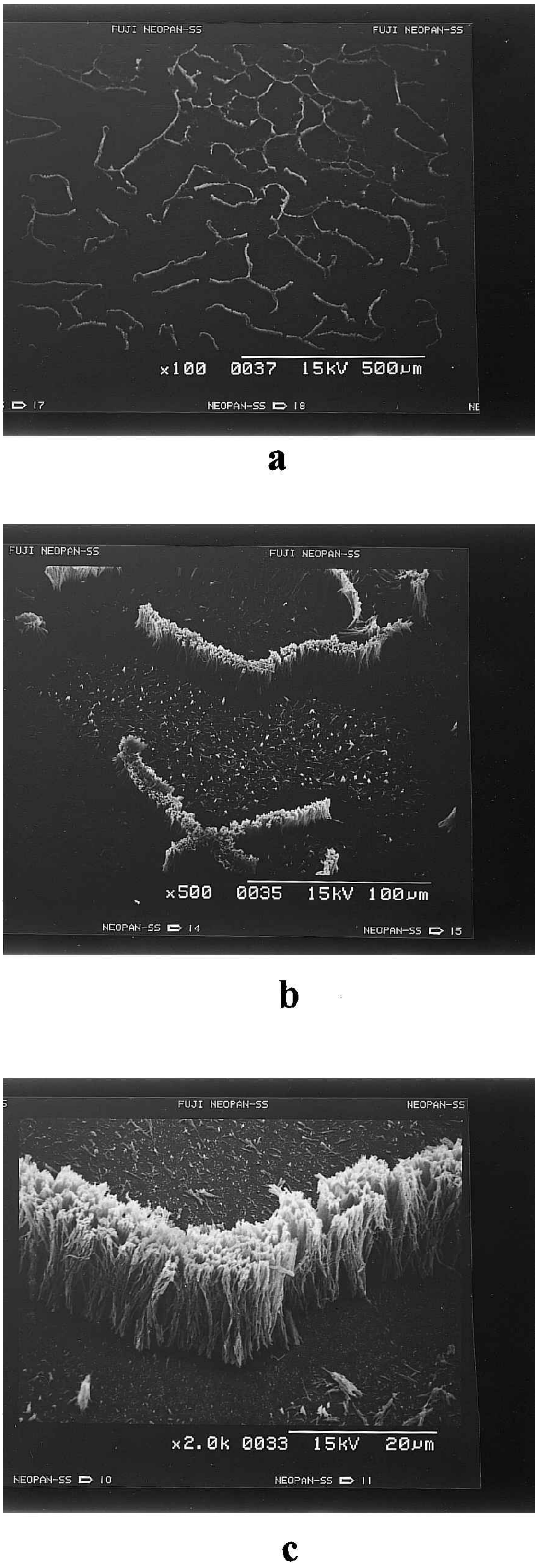

Figure 4. SEM photographs of the homeotropically oriented LCP network in the composite after the molecules of the LCs and the chiral dopant were extracted with hexane.

indicate that the LCP network really was homeotropically oriented to the substrate in the cell. Thus, the homeotropically oriented SmA phase may have remained stable in the cell due to (i) the mechanical stability of the LCP network since the LCP network is stable below 420–470 K [22–24], and (ii) the intermolecular interaction between the LCP network and the LC molecules, resulting in the transparent state in the temperature range of the SmA phase upon heating. Moreover, due to this intermolecular interaction, the direction of the helical axes of the small domains in the heat-induced N* phase should tend to be parallel to the cell surfaces, forming a focal-conic texture in the heat-induced N* phase. Therefore, the composite showed strong light scattering in the temperature range of the heat-induced N* phase. On cooling from N* to SmA, the SmA phase was homeotropically rearranged due to the intermolecular interaction between the LCP network and the LC molecules. Thus, the transparent SmA and the light-scattering N* phases occurred reversibly upon cooling and heating, being accompanied by the thermal SmA–N* phase transition.

4. Conclusion

A (homeotropically oriented LCP network/LCs (S6 + E48)/chiral dopant (ZLI-4572)) composite with the SmA–N* phase transition was prepared. The transparent state of the homeotropic SmA phase and the light-scattering state of the N* phase occurred reversibly, accompanied by the thermal SmA–N* phase transition due to intermolecular interaction between the LCP network and the LC molecules. The temperature range for light transmission → light scattering switching upon heating, and that for light scattering → light transmission switching upon cooling, were as narrow as about 0.3 K.

The effect of the composition of the composite on the light transmission–light scattering switching will be discussed in a future communication.

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