

Note

PREPARATION OF POLYMER DISPERSED LIQUID CRYSTALS USING PHOTOPOLYMERIZATION

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Abstract 2-Hydroxyethyl methacrylate (HEMA) and styrene copolymers are prepared by photopolymerization. The electro-optical behavior and microstructure of the polymer dispersed liquid crystal films are investigated by using He-Ne laser and scanning electron microscopy, respectively. With increasing E7 content in the copolymer, droplet size increased, threshold voltage decreased.

Keywords Electro-optical properties, Phase separation, Polymer dispersed liquid crystal

INTRODUCTION

In recent years, material scientists have devoted substantial effort to the development of new materials for advanced optical device applications. Polymer dispersed liquid crystal (PDLC) films represent an important new class of materials for such applications^[1-3]. In their most common form, PDLC films consist of micron-sized droplets of low molecular mass liquid crystal (LC) dispersed in a solid polymer matrix^[4-6]. By applying an external electric field, PDLC films can be switched electrically from a light scattering "off-state" to a highly transparent "on-state". These new materials are of considerable interest for large area display applications and light control devices such as optical shutters^[7-9]. From a more fundamental point of view, PDLC films are interesting because they exhibit a behavior, which is unique to systems that consist of mesophases in a confined environment. Depending on the chemical nature of the polymer and the LC, and the preparation techniques, the interface of the LC and polymer will experience different constraints with different effects on the molecular orientation of the LC films inside the droplet. Therefore, the light scattering and light switching properties of the composite film are influenced decisively by the phase separation structure of the composite films.

In this paper, we report the preparation of LC composite films using photopolymerization. The electro-optical behavior and the microstructure of the PDLC films were investigated by using He-Ne laser and scanning electron microscopy (SEM), respectively.

OPERATING PRINCIPLES

The principle of operation of PDLC films is based on the electric field-controlled transmission properties of the composite materials sandwiched between two transparent conducting electrodes^[10, 11]. Light is efficiently

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scattered in initial off-state, depending on the refractive indices of both the LC and the polymer matrix. The nematic LCs used in the experiments exhibit positive dielectric anisotropy at low frequencies and therefore align with their optical axis parallel to an externally applied electrical field. Fig. 1 presents a pictorial model of PDLC films and display devices; namely, that of the nematic-like “bipolar” configuration. As shown in Fig. 1, in the off-state, the polymer-liquid crystal interaction at each microdroplet boundary determines the configuration of the liquid crystal direction within the droplet. In general, this configuration is not uniform within each droplet or from droplet to droplet. As a result, light rays incident on the droplet probe a range of refractive index values between n_o (refractive index in horizontal direction) and n_e (refractive index in vertical direction). Since $n_o \neq n_e$, these indices cannot all be equal to the polymer refractive index n_p and incoming light is scattered by the microdroplets. Since the diameters of the liquid crystal microdroplets are small compared with the film thickness (typically $\sim 30\ \mu\text{m}$), a light ray will be scattered many times before emerging from the film. Because of this strong multiple scattering, the film appears milky white in the off-state. The degree of off-state scattering will depend on the size, number and density of the liquid crystalline microdroplets. Upon application of an electric field of sufficient magnitude to overcome the interactions at the droplet boundaries, the liquid crystal directors within each droplet become uniformly oriented along the direction of the applied field. Under these conditions, normally incident light probes essentially the ordinary refractive index of the liquid crystal alone. If $n_o \approx n_p$, the film will be essentially transparent. Removal of the applied electric field makes the film revert to its off-state described above. Clearly, in order to achieve high on-state transmittance at all operating temperature, one has to ensure that $n_o \approx n_p$ over the entire operating temperature range. Proper choice of both the liquid crystal and the polymer matrix material plays a crucial role in the indices matching problem.

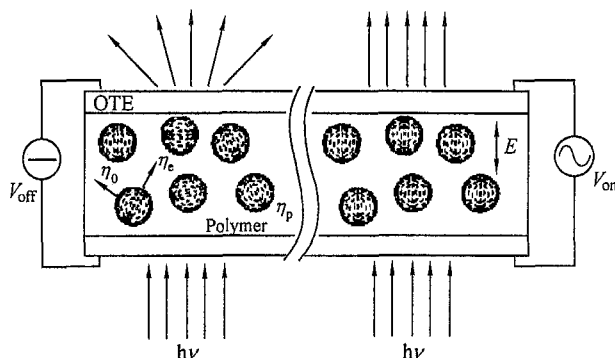


Fig. 1 Cross-sectional view of a generalized PDLC thin film

EXPERIMENTAL

Materials

The LC mixture E7 (Merck Ltd, GB) was used without any further treatment. E7 consists of K15 (47 wt%, 4-*n*-pentyl-4'-cyanobiphenyl), K21 (25 wt%, 4-*n*-heptyl-4'-cyanobiphenyl), M24 (18 wt%, 4-*n*-octoxy-4'-cyanobiphenyl) and T15 (10 wt%, 4-*n*-pentyl-4'-cyano-*p*-terphenyl). It exhibits a nematic phase at room temperature, which easily forms a glassy nematic upon cooling, and crystallization does not readily occur upon rewarming. The nematic-isotropic transition of E7 occurs at $T_{\text{NI}} = 59^\circ\text{C}$. E7 is characterized by the following refractive indices at $T = 20^\circ\text{C}$: $n_o = 1.5183$ and $n_e = 1.7378$ ($\lambda = 632.8$). 2-Hydroxyethyl methacrylate (HEMA) and styrene were purified by distillation in vacuum under nitrogen. Benzoin methyl ether (BME, photoinitiator) obtained from Tokyokasei Co. was used without any purification.

Preparation of PDLC Films

PDLC films are prepared by mixing the total monomer (30 wt%–90 wt%), a photoinitiator (BME) and the liquid crystals (5 wt%–70 wt%). The mixture was sandwiched between two glass plates, and the plate was then irradiated under UV light ($30\ \text{mW}/\text{cm}^2$) for 10 min.

SEM Measurement

Scanning electron microscopy (SEM) is potentially the most powerful technique for studying the structure of PDLC films. Analysis was performed with the electron beam accelerated by 5 keV, and was performed on the sample surface. After removing one of the two glasses, samples were placed under vacuum for several hours; then they were coated with a thin film of gold (thickness of about 10 nm) using a sputter coater.

Electro-Optical Measurement

A He-Ne laser with wavelength of 632.8 nm was used as incident light, irradiating normal to the film surface. The schematic diagram of the experimental setup is shown in Fig. 2. The sample was composed of a PDLC film sandwiched between two flat glass plates which had previously been coated with a thin transparent layer of conducting indium-tin-oxide (ITO). Film thickness, typically 27–30 μm , was controlled by glass microsphere spacers. Portions of the ITO layers which was intentionally not covered during sample preparation served as electrode contacts for applying voltage across the PDLC films. An external a.c. electric field was applied across the composite film. The transmitted light intensity passed through the vertical LC cell without any polarizers was measured with a photodiode under the modulation of the applied ac electric field. The intensity of the transmitted light was recorded with a digital storage oscilloscope.

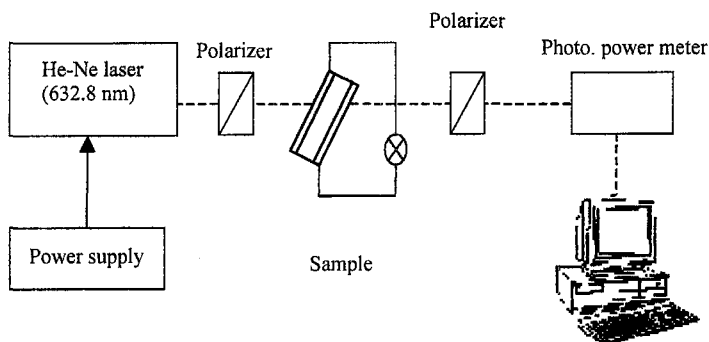


Fig. 2 Experimental setups of electro-optical measurements

Table 1. Characteristics of the copolymers

Copolymers ^a	M_n^b	M_w/M_n	n_p^c	St (%)
PHEMA	2600	1.9	1.4852	0
PHEMA-St-1	1600	1.9	1.4950	10
PHEMA-St-2	1610	1.8	1.5108	20
PHEMA-St-3	1595	1.8	1.5288	30

^a Polymerization condition: photoinitiator BME, 0.8 mol % to total monomer; Solvent, benzene (5 mL)

^b Estimated by GPC (standard; PSt)

^c Determined by refractive index measurements (Abbe refractometer, 20°C)

RESULT AND DISCUSSION

Synthesis of PHEMA-St

In this study, poly(2-hydroxyethyl methacrylate-St) (PHEMA-St) was synthesized. The results of the photopolymerization are summarized in Table 1. As can be seen from Table 1, among the four types of copolymers synthesized, n_p varies from 1.4852 to 1.5288. The refractive index of the copolymer monotonically increases with styrene content. PHEMA and PHEMA-St-1 have lower, and PHEMA-St-3 have higher value of n_p than n_o . PHEMA-St-2 is nearly matched to n_o ($= 1.5183$). It is possible, therefore, to control the value of n_p as desired.

Film Structure

Figure 3 shows the SEM photographs of the phase separation after the photopolymerization of the monomer. As shown in Fig. 3 (a), in the PDLC film containing 10 wt% E7, the LC drops are distributed in the polymer matrix

separately. In Fig. 3(b), the PDLC film contains 60 wt% of E7, and it is apparent that the E7 forms a phase-separated continuous phase in the polymer matrix; in this case the composite is sometime called polymer-network liquid crystal. Figure 4 shows the effect of the copolymer content in the PDLC film on the phase-separation. As can be seen in Fig. 4, the higher the polymer content, the smaller the liquid crystal droplets.

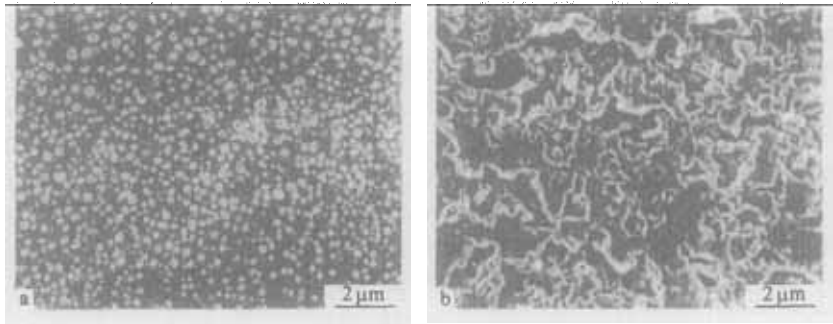


Fig. 3 SEM photographs of E7 dispersed in PHEMA-Sts-2 films
a) E7: 10 wt%; b) E7: 60 wt%

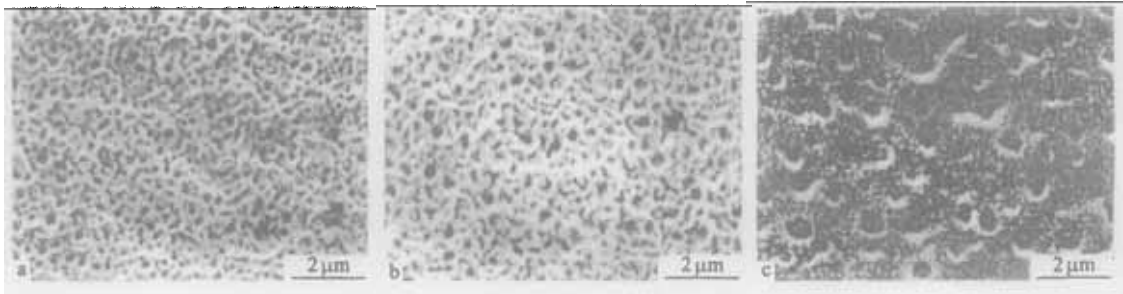


Fig. 4 SEM photographs of E7 dispersed in PHEMA-Sts-2 films
a) E7: 20 wt%; b) E7: 30 wt%; c) E7: 40 wt%

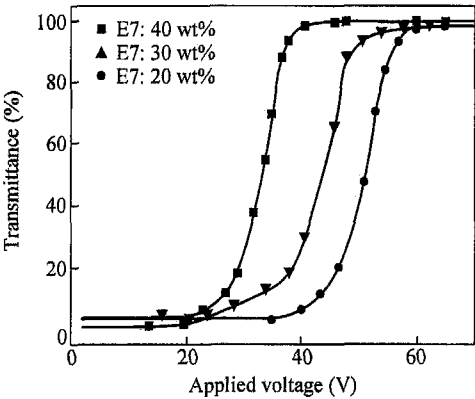


Fig. 5 Transmittance versus applied voltage of E7/PHEMA-St-2 at 1 kHz and 30°C

Electro-Optical Properties

The effect of the content of E7 in PHEMA-St on the electro-optical response of the PDLC films was investigated using the experimental setup shown in Fig. 2. Figure 5 shows the experimental results of diffraction transmittance

versus applied voltage. The transmittance increases with increasing E7 content. On the other hand, with increasing E7 content, the threshold voltage (V_{th}) as well as the saturation voltage (V_{sat}) significantly decreases. Therefore, PDLC films may expect to have valuable applications as tunable optical filters and other optical devices.

REFERENCES

- 1 Choi, C.H., Kim, B.K. and Kajiyama, T., *Mol. Cryst. Liq.*, 1994, 247: 303
- 2 Lovinger, A. J., Amundso, R.A. and Davis, D.D., *Polymer*, 1998, 19: 4489
- 3 Serbutoviez, C., Kloosterboer, J.G., Boots, H.M.J. and Touwslager, F.J., *Macromolecules*, 1996, 29: 7683
- 4 Serbutoviez, C., Kloosterboer, J.G., Boots, H.M.J. and Touwslager, F.J., *Macromolecules*, 1996, 29: 7690
- 5 Serbutoviez, C., Kloosterboer, J.G., Boots, H.M.J., Paulissen, F.A.M.A. and Touwslager, F.J., *Liq. Cryst.*, 1997, 22: 145
- 6 Coates, D., *J. Mater. Chem.*, 1995, 5: 2063
- 7 Mertelj, A. and Copic, M., *Mol. Cryst. Liq. Cryst. Sci. Technol. A*, 1998, 320: 287
- 8 Coles, M.J., Carboni, C. and Coler, H.J., *Liq. Cryst.*, 1999, 26: 679
- 9 Aphonin, O.A., *Liq. Cryst.*, 1995, 19: 469
- 10 Cox, S.J., Reshetnyak, V.Y. and Sluckin, T.J., *Mol. Cryst. Liq. Cryst. Sci. Technol. A*, 1998, 320: 301
- 11 Dinesu, L. and Lemieu, R.P., *Adv. Mater.*, 1999, 1: 42
- 12 Chung, D.B., Tsuda, H., Chida, H. and Mochizuki, A., *Mol. Cryst. Liq. Cryst. Sci. Technol. A*, 1997, 304: 81