# Preparation and Characterization of Liquid Crystal Composite Film Using Photosensitive Hydrophilic Matrix

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## SYNOPSIS

Methoxybenzylidene n-butylaniline (MBBA) and ethoxybenzylidene n-butylaniline (EBBA) liquid crystal were synthesized. To investigate the applications of hydrophilic monomers and polymers on the field of liquid crystal composite film, 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (Aa) were selected as monomers for the polymer matrix. To prepare the liquid crystal composite film, MBBA, EBBA, and commercial liquid crystals ZLI-2444, 2452, 2459, and BDH-E7 were mixed with HEMA, Aa, and photosensitive materials and then irradiated by UV light. The electro-optical behavior and the microstructure of the liquid crystal composite films were investigated by He-Ne laser and scanning electron microscopy, respectively. The effects of UV light irradiation and monomer ratio on the electro-optical behavior of liquid crystal composite films were investigated. The reproducibility and storage stability of the liquid crystal composite films were investigated. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer dispersed liquid crystal (LC) films have considerable potentials for large area displays and light control applications since they can be switched electrically from a light scattering state to a transparent state and do not require polarizers and alignment layers. Two typical aggregation structures of polymer/LC composite systems have been reported: that is, polymer dispersed liquid crystals (PDLC)[1-3] and bicontinuous liquid crystals (BCLC) or self-supported liquid crystals (SSLC).[4-6] The electro-optical effect based on the light scattering-light transmission switching of a polymer dispersed LC film has been investigated for possible application to a large area, flexible display device.[7-9]

A light scattering state in an ac electric field off state depends on optical heterogeneities such as a spatial distortion of nematic directions and/or mismatching in refractive indices of the compounds. Therefore, the light scattering and light switching

properties of the composite film are influenced decisively by the phase separation structure of the composite films. The size of LC domain (channel) can be controlled on the basis of the solvent evaporation rate or the curing rate during the separation of the composite film.

In this paper, we report the preparation of LC composite films using a photosensitive technique. The electro-optical behavior and the microstructure of the LC composite films were investigated by He-Ne laser and scanning electron microscopy (SEM), respectively. Effects of UV light irradiation and monomer ratio on the electro-optical behavior of LC composite films were also investigated in detail.

## EXPERIMENTAL

A He-Ne laser (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 Figure 1. An external ac electric field was applied across the composite film. The transmitted light intensity through the vertical LC cell without any polarizers was measured with a
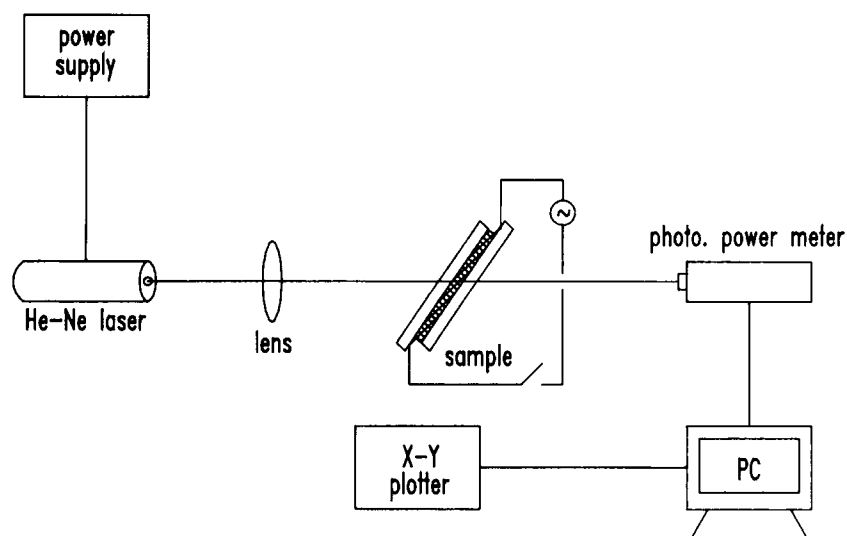
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**Figure 1** Schematic diagram of the experimental setup.

photodiode under the modulation of the applied ac electric field. The intensity of the transmitted light was recorded with a digital storage oscilloscope (Kawasaki KPS-102). Thermal characteristics of the polymer and the LC were evaluated by a Du Pont 2000 thermal analyzer. Elemental analyses were calculated with a Heraeus CHN-O rapid elemental analyzer. The UV and IR spectra of the compounds were investigated by a Jasco-7850 UV/VIS spectrophotometer and a Jasco VALOR III grating FT-IR spectrophotometer, respectively. The microstructure of the LC composite films was studied by using a JEOL JSM-35 scanning microscope.

## MATERIALS

Commercial liquid crystals ZLI-2444, 2452, 2459, and BDH-E7 from Merck Co. were used without any further treatment. Hydrophilic monomers of 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (Aa), hydrophobic monomers of methyl methacrylate (MMA) and styrene (St) were purified by distillation in vacuo under nitrogen. Benzoin methyl ether (BME) from Tokyokasei Co. was used without any purification.

## METHOXYBENZYLIDENE N-BUTYLANILINE (MBBA)

A mixture of methanol (150 mL), n-butylaniline (14.9 g), and p-methoxybenzaldehyde (13.6 g) with

three drops of acetic acid was refluxed at 72°C with stirring for 8 h. After complete, the reaction solvent was removed by using a rotatory evaporator. The crude product was distilled at 217°C in vacuo (4 torr) to yield methoxybenzylidene n-butylaniline. Yield was 95%; C-N (crystal–nematic LC) transition temperature was 20°C; N-I (nematic LC–isotropic liquid) transition temperature was 37°C.

$C_{18}H_{21}ON$ (267): Calc.: C, 80.89; H, 7.85; N, 5.24. Found: C, 81.01; H, 8.06; N, 5.31.

## ETOXYBENZYLIDENE N-BUTYLANILINE (EBBA)

The mixture of n-butylaniline (14.9 g), methanol, and p-ethoxy benzaldehyde (15 g) with 3 drops of actic acid was refluxed at 72°C for 8 h. After the reaction, solvent was removed by using a rotatory evaporator. The pure product of ethoxybenzylidene n-butylaniline was obtained by a distillation of the reaction mixture at 276°C/4 torr. Yield was 87%; C-N (crystal–nematic LC) transition temperature was 37°C; N-I (nematic LC–isotropic liquid) transition temperature was 78°C.

$C_{19}H_{23}ON$ (281) Calc.: C, 81.10; H, 8.12; N, 5.22. Found: C, 81.11; H, 8.25; N, 5.14.

**Table I   Solubility of Liquid Crystals in Monomers**

| | EBBA & MBBA[a] | ZLI-2444 | ZLI-2454 | ZLI-2459 | BDH-E7 |
|---|---|---|---|---|---|
| St | O | O | O | O | O |
| MMA | O | O | O | O | O |
| Aa | O | X | X | X | O |
| HEMA | O | X | X | X | O |

[a] O = soluble; X = insoluble.

## PHOTOPOLYMERIZATION

To evaluate the photopolymerization of monomers, methylmethacrylate, acrylic acid, styrene, and 2-hydroxyethyl methacrylate were added to 1 wt % of 2-methoxy-2-phenylacetophenone (benzoin methyl ether) as a photoinitiator, sandwiched between two glass plates, and then irradiated with UV light (20 mw/cm$^2$) for 10 min. PDLC films were prepared by mixing monomers and liquid crystals, some 11 $\mu$ spacers were added. The mixture was sandwiched between two glass plates, and the plate was then irradiated under UV light. From the thermal stability of the MBBA/EBBA system,[10] a volume ratio of $\frac{2}{3}$ for MBBA/EBBA was selected in this investigation. Liquid crystals used here are MBBA/EBBA ($\frac{2}{3}$ vol %), ZLI-2444, 2452, 2459, and BDH-E7 (from Merck). The results of the photopolymerization are summarized in Table II.

## RESULTS AND DISCUSSION

The solubility of the liquid crystals in monomers was investigated. The results are summarized in Table I. It turns out that the liquid crystals are all soluble in lipophilic monomers. However, only MBBA/EBBA and BDH-E7 can be dissolved in hydrophilic monomers HEMA and Aa. Table II shows the results of the phase separation after the photopolymerization of the monomers. It was found that hydrophilic monomers are suitable for the LC composite systems. A complete phase separation leads the formation of an optical boundary between the LC phase and polymer matrix. To investigate the optical characteristics of the LC composite films, systems of BDH-E7 in HEMA/Aa and MBBA/EBBA in HEMA were chosen in this investigation.

The effect of LC concentration of (BDH-E7) in HEMA/Aa system on the electro-optic response of the LC composite films was investigated. The results are summarized in Figure 2. As can be seen in the figure, the contrast value [transmittance (V > V$_{th}$ = 50 V)/transmittance (V = 0)] increased with an increasing in the LC concentration. The highest contrast value was obtained in the system of 70 wt % of LC concentration. The system of MBBA/EBBA ($\frac{2}{3}$ vol %) in HEMA was also investigated. The transparent state cannot be obtained, however, even if a large voltage of 130 V was applied to the LC composite film. This result suggests that there is too high of an optical boundary between LC phase and polymer matrix. The difference of refractive index between LC and polymer matrix is too large ($\Delta n \cong 0.2$) to cause the forming of the transparent state.

Benzene is a nonsolvent for the polymer matrix and is a good solvent for the liquid crystals. To in-

**Table II   Results of Photopolymerization**

| | EBBA & MBBA[a] | ZLI-2444 | ZLI-2452 | ZLI-2459 | BDH-E7 |
|---|---|---|---|---|---|
| St | X | X | X | X | X |
| MMA | X | X | X | X | X |
| Aa | X | △ | △ | △ | O |
| HEMA | O | △ | △ | △ | O |
| HEMA + Aa | X | △ | △ | △ | O |

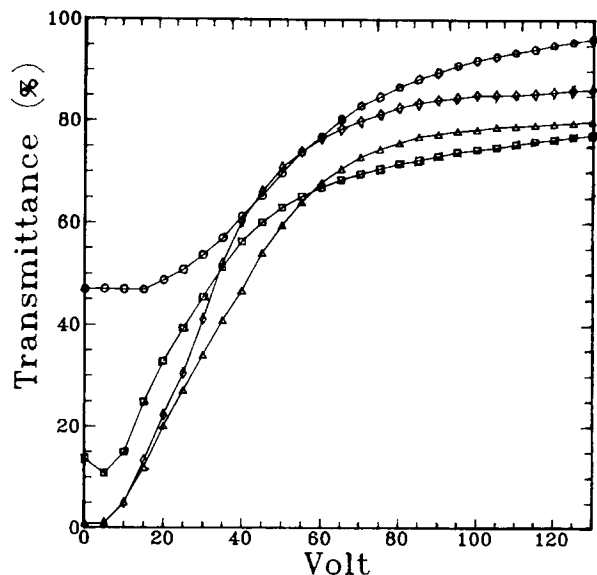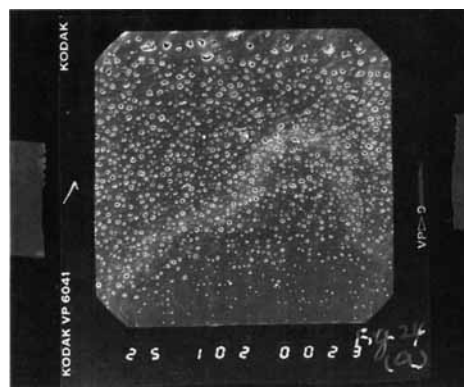[a] O = phase separated completely; △ = phase separated incompletely; X = no phase separation.

**Figure 2** Effect of LC concentration (BDH-E7) in HEMA/Aa on the electro-optic response. LC concentration: ○, 10%; □, 30%; △, 50%; ◇, 70%.

tance for 30 min and then exposed with 10 cm distance for 10 min more.

To study the effect of polymer composition on the electro-optical characteristics of the LC composite film, systems of BDH-E7 LC in HEMA, Aa, and HEMA/Aa were investigated. The results are summarized in Figures 6–11. As can be seen in the figures, the pathway of run 1 and run 2 in every system are different. After run 2, however, the pathway of every running will follow the same pathway of run 2. The result suggests that LC molecules can-

vestigate the distribution of liquid crystals in polymer matrix, LC composite film was extracted with benzene and then studied by using the SEM technique. As shown in Figure 3(a), in the LC composite film containing 10 wt % LC, the LC drops are distributed in the polymer matrix separately. In Figure 3(b), the LC composite film contains 70 wt % of liquid crystal, and it is apparent that the LC material forms a phase-separated continuous phase in the polymer matrix. It seems reasonable from the phase-separated structure as shown in Figure 3 that the polymer/LC composite film can be treated as a binary dielectric composite composed of the two different dielectrics (polymer matrix and LC). These results are consistent with those obtained in Figure 2.

UV strength is proportional to exposure distance square. The effect of exposure distance on the electro-optical response was evaluated. As can be seen in Figure 4, the transmittance of the LC composite film increased with decreasing exposure distance. This result suggests that sufficient UV irradiation is needed to complete the phase separation of the liquid crystals in the polymer matrix. Increase of UV irradiation increases the degree of polymerization and molecular weight of the matrix and decreases the solubility of the matrix in LC phase and, consequently, enforces phase separation. As can be seen in Figure 5, the transmittance increased with a film which was exposed initially with 40 cm distance



(a)

⊢━━━━┥
10 μm



(b)

⊢━━━━┥
10 μm

**Figure 3** (a) Distribution of liquid crystals (BDH-E7, 10 wt %) in poly(HEMA-co-Aa). (b) distribution of liquid crystals (BDH-E7, 70 wt %) in polymer poly(HEMA-co-Aa).
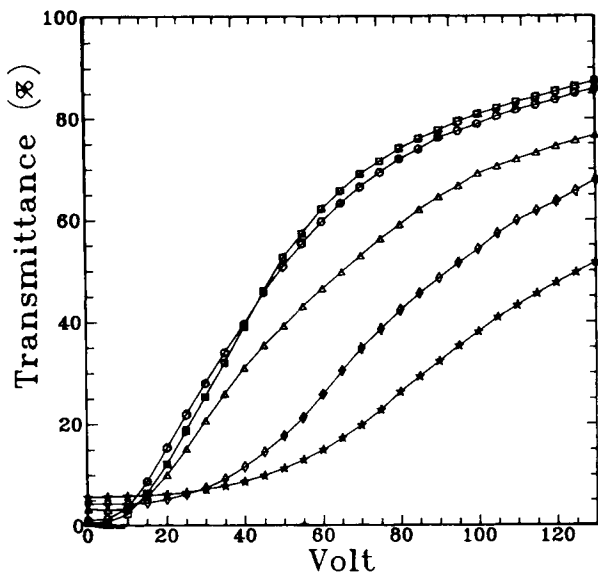
**Figure 4**  Effect of exposed distance on the electro-optic response [BDH-E7 in poly(HEMA-co-Aa)]. Exposed distance: ○, 5 cm; □, 10 cm; △, 20 cm; ◇, 30 cm; ★, 40 cm.



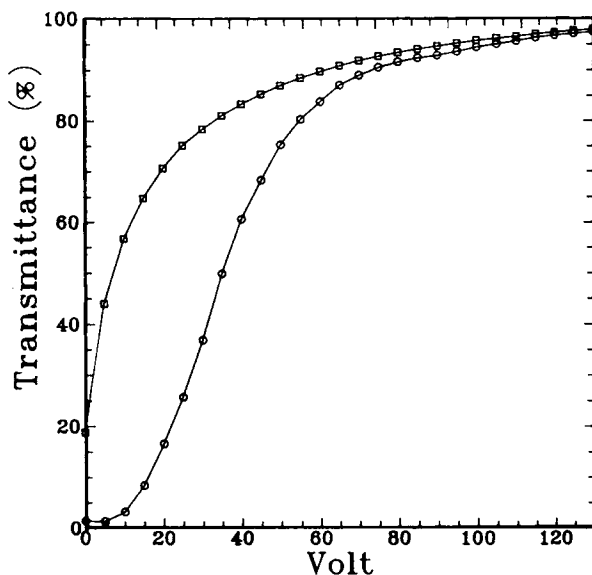**Figure 6**  Transmittance versus applied voltage for PDLC film with 70 wt % LC in poly(HEMA): ○, run 1; □, run 2.

not return to the original position completely after they were applied enough large voltage. Polymer compositions in Figures 7 and 8 seem to be good conditions for the polymer matrix since the transmittance appears to level off at a certain applied

voltage, and relatively high contrast values can be obtained.

The microstructures of the LC composite film with 70 wt % LC in various polymers are shown in Figure 12. As shown in the figure, liquid crystal domains seem to be dispersed in the polymer matrix
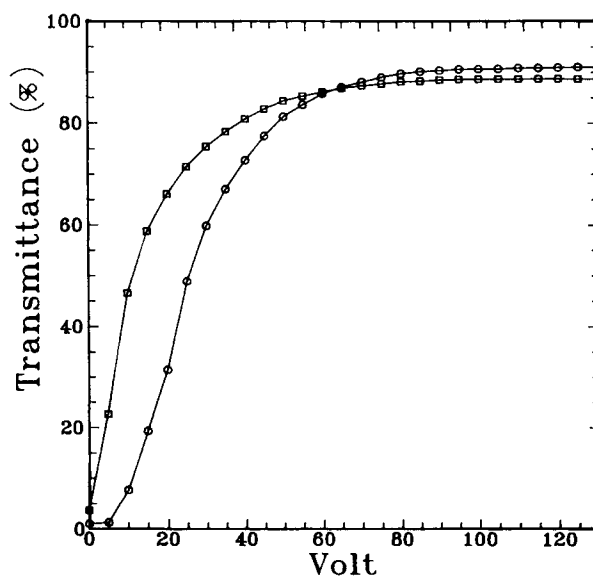


**Figure 5**  Transmittance versus applied voltage for PDLC film [BDH-E7 in poly(HEMA-co-Aa)] with (a) △, 40 cm exposed distance for 30 min and (b) ○, then exposed with 10 cm for a further 10 min.



**Figure 7**  Transmittance versus applied voltage for PDLC film with 70 wt % LC in poly(HEMA-co-Aa), with HEMA/Aa = 4/1 (v/v): ○, run 1; □, run 2.
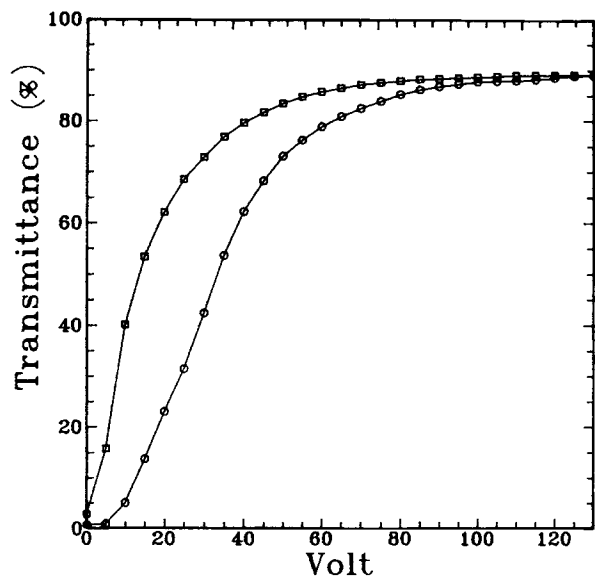
**Figure 8** Transmittance versus applied voltage for PDLC film with 70 wt % LC in poly(HEMA-*co*-Aa), with HEMA/Aa = 3/2 (v/v): O, run 1; □, run 2.
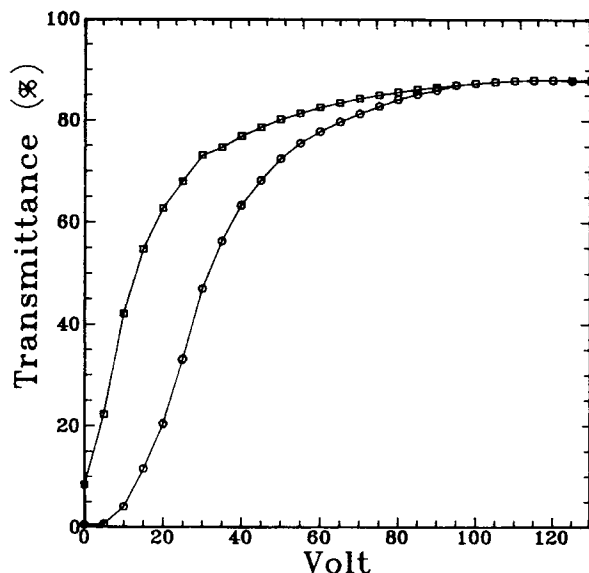


**Figure 10** Transmittance versus applied voltage for PDLC film with 70 wt % LC in poly(HEMA-*co*-Aa), with HEMA/Aa = 1/4 (v/v): O, run 1; □, run 2.

separately in homopolymer systems. A continuous LC channel, however, was found in the poly-(HEMA-*co*-Aa) system. The results of Figures 6–12 indicate that the size and the morphology of LC domains will affect the electro-optical characteristics of the LC composite film. It was found that the electro-optical characteristics of the LC composite film with structure of continuous channel is advanta-

geous compared to that of the film with separated domains. The results suggest that the interaction forces between the polymer surface and the LC molecules existing in separated domains should be larger than those existing in the continuous channel. We believe that the amount of the curved and the nonparallel polymer walls in separated domains are also larger than those in the continuous channel.
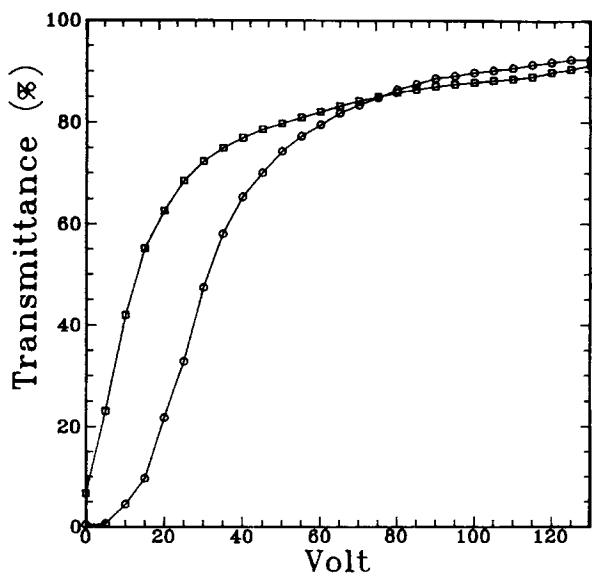


**Figure 9** Transmittance versus applied voltage for PDLC film with 70 wt % LC in poly(HEMA-*co*-Aa), with HEMA/Aa = 2/3 (v/v): O, run 1; □, run 2.
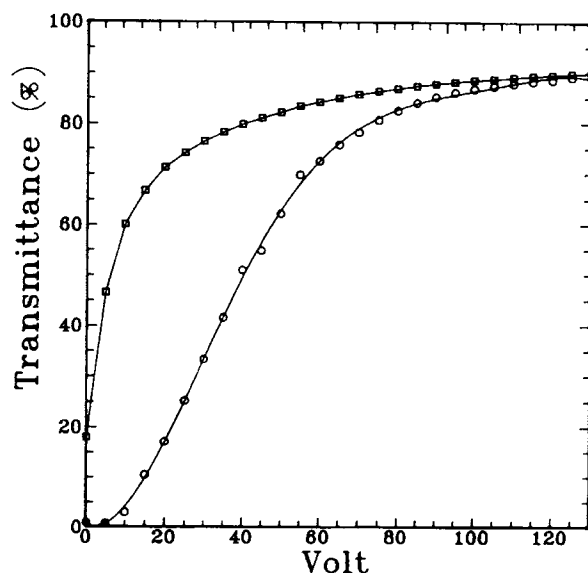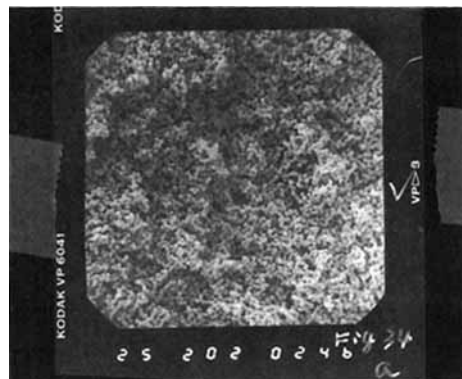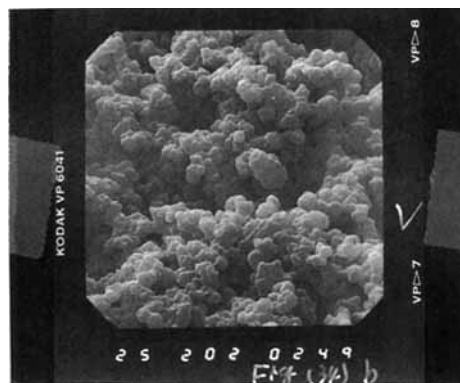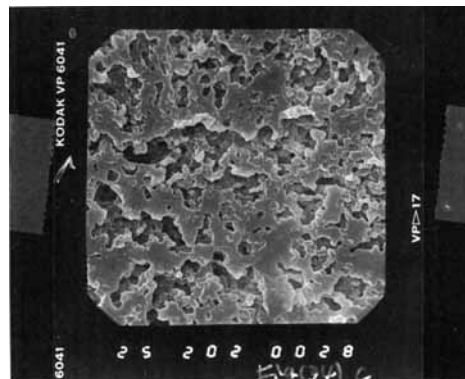


**Figure 11** Transmittance versus applied voltage for PDLC film with 70 wt % LC in poly(Aa): O, run 1; □, run 2.

(a)



(b)



(c)

**Figure 12**  Microstructure of the polymer matrix, 70 wt % of LC (BDH-E7) in (a) poly(HEMA), (b) poly(Aa), (c) poly(HEMA-*co*-Aa), with HEMA/Aa = 3/2 (v/v).

As can be seen in Figure 1, the largest transmittance will be obtained while the LC cell is in a vertical position (angle degree = 0). Positive angle means a right deviation of the LC cell, and negative angle value means a left deviation of the cell. The angle dependent response on copolymer composition for LC composite films with 70 wt % LC was investigated. The results are summarized in Figure 13. As can be seen in the figure, transmittance decreased with increasing angle.

Figure 14 shows the reversible turbid and transparent changes corresponding to the (a) off and (b) on (90 V) ac electric field applied, respectively. With respect to light scattering phenomena of the LC composite film, two origins may be proposed in the case of absence of an electric field: (1) a spatial distortion of nematic directors induced by nonparallel matrix walls, and (2) an optical boundary between the LC phase and polymer matrix. The LC directors in the LC domain are randomly oriented due to strong polymer surface/LC molecule interaction on the curved or nonparallel polymer walls in the case of the absence of an ac electric field.[11] When an ac electric field is applied to the LC composite film, the directors reorient parallel to the direction of an applied field; the refractive index of the LC phase is sufficient close to that of the polymer matrix; the optical boundaries disappear; and,
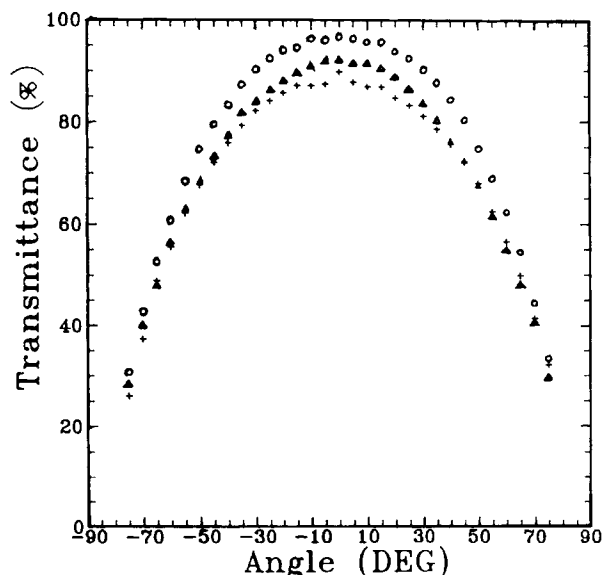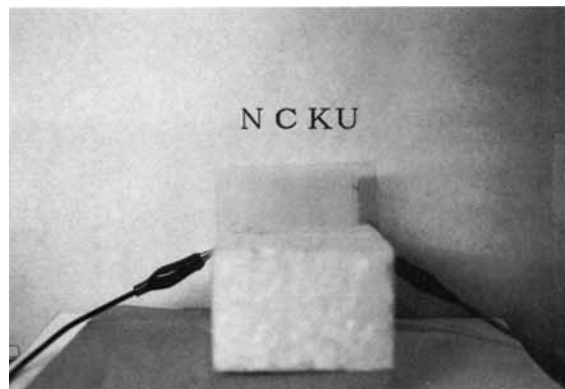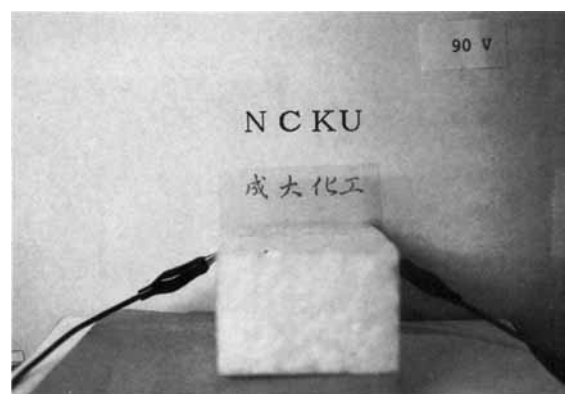


(a)



(b)

**Figure 14** Reversible turbid and transparent changes corresponding to field (a) off, and (b) on (90 V).

consequently, the LC composite film becomes transparent.

## CONCLUSION

Hydrophilic monomers 2-hydroxy ethyl methacrylate and acrylic acid are suitable for the preparation of LC composite films in this investigation. LC composite films can be prepared by using photochemical methods. Amounts of LC materials will affect the microstructure and the electro-optical characteristics of the LC composite films. The electro-optical characteristics of the film with a structure of continuous channel is advantageous compared to that of the film with separated domains.



**Figure 13** Angle dependent response on ratios of monomer components for PDLC films with 70 wt % LC (BDH-E7): (a) ○, poly(HEMA); (b) +, poly(Aa); (c) △, poly(HEMA-co-Aa); HEMA/Aa = 3/2 (v/v).

## REFERENCES

1. T. Kajiyama, A. Miyamoto, H. Kikuchi, and Y. Morimura, *Chem. Lett.,* **89,** 813 (1989).
2. J. L. Fergason, *SID Int. Symp. Dig. Tech.,* **16,** 68 (1985).
3. P. S. Drzaic, *J. Appl. Phys.,* **60,** 2142 (1986).
4. T. Kajiyama, H. Kikuchi, and A. Takahara, *Proc. SPIE,* **1665,** 20 (1992).
5. A. Miyamoto, H. Kikuchi, Y. Morimura, and T. Kajiyama, *New Polym. Mat.,* **2,** 27 (1990).
6. H. G. Craighead, J. Cheng, and S. Hackwood, *Appl. Phys. Lett.,* **40,** 22 (1982).
7. J. W. Doane, N. A. Waz, B. G. Wu, and S. Zumer, *Appl. Phys. Lett.,* **48,** 269 (1986).
8. T. Kajiyama, H. Kikuchi, A. Morimura, and J. C. Hwan, *Chem. Lett.,* **1989,** 817 (1989).
9. T. Kajiyama, S. Washizu, and M. Takayanagi, *J. Appl. Polym. Sci.,* **29,** 3955 (1984).
10. D. L. Fishel and Y. Y. Hsu, *J. Chem. Soc.,* **23,** 1557 (1971).
11. M. Matzumoto and I. Tznoda, *Liquid Crystal Materials and Applications,* (in Japanese), Kogyo Chosakai Press, Tokyo, 1983.