Preparation and Electrooptical Properties of Liquid Crystal Dispersed Film by Electron-Beam Irradiation

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ABSTRACT: Polymer films consisting of nematic liquid crystal (LC) droplets and polymer networks were prepared by using a low-energy electron beam to irradiate a homogeneous mixture of nematic LC and bifunctional methacrylate monomer. Influences of such polymerization conditions as polymerization temperature, monomer concentration, and radiation energy on electrooptical properties of the compound films were examined. The polymer yield, affecting to a large extent the film properties, depended on the monomer concentration and the radiation energy. Compound films, which have a switching function from the scattering state to transparency by applying approximately $20-30$ V between the two sides of the film, were obtained. In addition, it was found that a compound film with excellent electrooptical properties was prepared by changing impure LC in the droplets into pure LC. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1675–1681, 1997

Key words: electron beam; liquid crystal–polymer film; electrooptical property; compound film

INTRODUCTION

A polymer film consisting of submicrometer-sized liquid crystal (LC) droplets and polymer matrix, which exhibited permeability to water and gases, was first reported by Kajiyama and colleagues.[1] Since Fergason revealed that such film has a capability to switch from a light-scattering film to a transparent film by an electric field[2] the switching property of the film has been extensively studied, because the film has such wide potential applications as a very large display and a bright flexible display without a polarizer. So far, there are three methods for preparation of the film. The first method is to fill micropores in the solid matrix polymer with nematic LC.[3] The second is an emulsification method in which nematic LC is emulsified into an aqueous solution containing a film-forming polymer.[2] The third is an application of phase separation of nematic LC after polymerization of a homogeneous solution of nematic LC and matrix material.[4]

The phase-separation method which uses ultraviolet (UV) irradiation to polymerize a homogeneous mixture of nematic LC and reactive material was extensively studied.[5] However, the UV polymerization method had several disadvantages. UV-polymerizable materials need a photoinitiator to initiate the polymerization, and UV light can not penetrate into opaque films and colored films. On the other hand, the polymerization by electron beam (EB) irradiation did not have such disadvantages, though little work has been done on the preparation of the film[6] or porous film[7] using EB.

Previously, we reported on the solid-state polymerization of liquid-crystalline and non-liquid-crystalline (meth)acrylate monomers by EB.[8] In
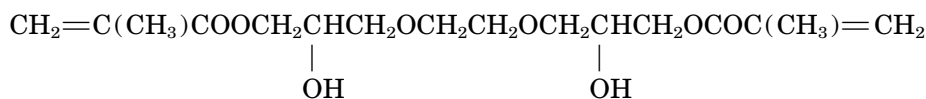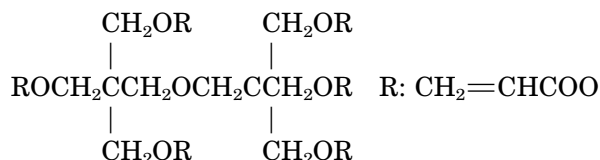
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addition, effects of the addition of nonpolymerizable liquid-crystalline compounds to compatible methacrylate monomers on the polymerization behaviors were investigated.[9–12] In mixtures containing a non-liquid-crystalline methacrylate and a liquid-crystalline compound, such phenomena as increases in the polymer yield and in the molecular weight were observed, suggesting that monomer orientation favorable for polymerization took place in such solid mixtures.

There will be wide applications for a film which has durability and can change transmittance by applying the electric field of 20 to 50 V.

In this article we report that a film containing LC droplets in the polymer matrix was prepared by polymerization of a liquid mixture of nematic LC and (meth)acrylate monomer by means of EB irradiation. The transmittance of the film can be changed by the application of a low electric field. In addition, the electrooptical properties of the EB-prepared compound film were compared with that of a UV-polymerized one.

EXPERIMENTAL

A bifunctional monomer, epoxyester 40EM (Kyoeisha Chemical Co., Ltd.), was used as an EB-curable monomer without purification.

$$CH_2{=}C(CH_3)COOCH_2\underset{\overset{|}{OH}}{CH}CH_2OCH_2CH_2OCH_2\underset{\overset{|}{OH}}{CH}CH_2OCOC(CH_3){=}CH_2$$

A hexafunctional monomer, Kayarad DPHA (Nippon Kayaku Co., Ltd.), was used as a crosslinking material without purification.

$$ROCH_2\underset{\overset{|}{CH_2OR}}{\overset{\overset{CH_2OR}{|}}{C}}CH_2OCH_2\underset{\overset{|}{CH_2OR}}{\overset{\overset{CH_2OR}{|}}{C}}CH_2OR \quad R: CH_2{=}CHCOO$$

A commercial nematic liquid crystal mixture E-44 (Merck Ltd.) was used as LC.

Preparation of Film

A compound film was prepared as follows. Different proportions of mixtures containing monomer and LC were melted at 130°C. The obtained homogeneous mixture was then cast on indium tin oxide (ITO-) coated glass, and sandwiched by covering with ITO-coated poly(ethylene terephthalate) (PET) film (125 μm) with a 10-μm spacer. Then the sandwiched samples were irradiated by EB or UV from the PET-surface side to produce a compound film inserted between the ITO-coated glass and the ITO-coated PET film.

Measurements

Electrooptical properties of the compound films were recorded on an LCD-5000 LC display evaluation system (Otsuka Electronics Co., Ltd.) using a halogen lamp and a detector with an acceptance angle of 5 degrees. The AC electric field was applied to the sandwiched sample by applying a 1-kHz-square wave voltage. The zero and 100% transmittances were arbitrarily assigned to the numerical values at extinction of light and at perfect transmittance without the ITO-coated glass and the ITO-coated PET film.

The determination of polymer yield was carried out as follows. A homogeneous mixture of LC and monomer was cast on slide glass and irradiated by EB or UV at 100°C. Then extractable compounds were removed from the compound film by extracting with hot ethanol for 4 h and drying under vacuum. The polymer yield was calculated on the basis of the quantity of starting monomer.

EB irradiation was performed with an EBC-200-AA2 low-energy electron beam accelerator (Nissin-High Voltage Co., Ltd.) under nitrogen atmosphere. The acceleration voltage was 180 kV and the irradiation dose was 5–20 Mrad. UV irradiation was carried out using a F 450 UV lamp (Fusion UV Systems, Inc.) under nitrogen atmosphere. The photoinitiator was Irgacure 184 (Ciba-Specialty-Chemicals, Inc.).

The nature of mesophase was examined using a polarizing microscope equipped with a Mettler FP-82HT hot stage with a FP-80HT central processor. The phase diagram of the mixture was observed at a cooling rate of 5°/min in the first cooling.

A fracture section of the film after extraction with hot ethanol coated with gold was observed using a JEOL JSM-5400 scanning electron microscope.
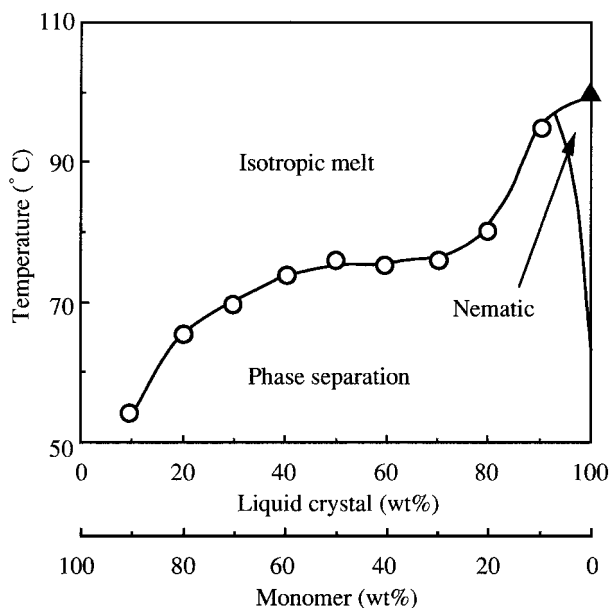
Figure 1 Phase diagram of binary mixture of LC and monomer.

A BET surface area of the film on PET film (50 μm) after extraction with hot ethanol was observed by a Quantasorb surface-area measuring apparatus (Quantachrome Corp.) using nitrogen as absorbant. Since the BET surface area of the PET film was below 1 m^2/g, it was negligibly small.

RESULTS AND DISCUSSION

A film composed of LC droplets and polymer matrix was prepared by polymerizing a binary liquid mixture of the LC and a non-liquid-crystalline (meth)acrylate monomer with EB irradiation. The LC mixture E-44 showed nematic mesophase from −6 to 100°C. The binary mixture of the LC and a bifunctional monomer gave rise to phase separation at temperatures lower than 55 to 95°C, depending on the composition, whereas all mixtures gave homogeneous isotropic melt at temperatures higher than 100°C. Figure 1 shows the relationship between the composition of mixtures and the melting (isotropic) temperature.

Since the polymerization must be conducted so as to produce LC droplets dispersed in polymer matrix by phase separation during polymerization, a polymerization temperature sufficiently higher than the melting temperature was chosen.

The EB was used to irradiate the mixture of LC and monomer through the covering PET film to polymerize the monomer. Results of polymerization of the bifunctional monomer are shown in Table I. Because the radiation dose and the LC-to-monomer ratio are major factors affecting the conversion of monomer and the degree of cross-linking in the polymer yield, these variables were examined. It has been known that in this kind of a compound film the ratio of LC to matrix polymer has an influence on the morphology and thereby the electrooptical property of the film.[13,14] In general, there is a tendency that a larger proportion of the LC produces bigger LC droplets which can be regulated by a lower applied electric field. Thus mixtures containing 40−80 wt % of the LC and 60−20 wt % of the bifunctional methacrylate were irradiated by EB. When a mixture with the LC-to-monomer (LC/M) ratio of 6/4 was irradiated at 10 Mrad, yield of the polymer was not high (60%, Film B).

Although in the ratio of 4/6 the polymer yield increased to a satisfactorily high value of 95%, the proportion of LC was too little for an electrooptical film. In both the cases of a low dose of 5 Mrad and of too high an LC ratio of 80%, low polymer yields of 30−40% were obtained (Films C and D). When UV of 170 mJ/cm^2 was used for irradiation once or twice instead of EB irradiation, the polymer yield was not high (50% and 65%, respectively, for Films G and H). Accordingly, the EB and UV polymerization of the bifunctional monomer alone did not provide sufficiently high monomer conversions.

Thus the cause for the low monomer conversion was examined. When the polymerization proceeded to a certain conversion, LC droplets were formed, with solid polymer matrix surrounding them. As a result, unreacted monomer was included in both droplets and matrix.

It is noteworthy that when a mixture of more reactive hexafunctional monomer and LC in the ratio of 6/4 was irradiated at 10 Mrad, an almost quantitative polymer yield of 105% was attained.

Next, mixtures of the bifunctional monomer and the hexafunctional monomer in the ratios of 3/1, 1/1, and 1/3 were used as the monomer mixture. Polymerizations of mixtures of 60% LC and 40% monomer were carried out by irradiating with 10 Mrad EB at 100°C. The results of polymerizations are summarized in Table II. The polymer yield increased from 70 to 100% with increasing proportion of the hexafunctional monomer, and at the monomer ratio of 1 : 1 the yield was a satisfactory 90%.

Table I   Polymerization Conditions and Polymer Conversion in EB and UV Polymerizations of Mixtures of Monomer and LC[a]

Film Designation	EB Dose (Mrad)	UV Exposure[b] (mJ/cm^2)	LC/Monomer Ratio (wt/wt)	Polymer Conversion (%)
Bifunctional monomer				
A	10		4/6	95
B	10		6/4	60
C	10		8/2	30
D	5		6/4	40
E	20		6/4	75
F	10 × 2		6/4	85
G		170	6/4	50
H		170 × 2	6/4	65
Hexafunctional monomer				
I	10		6/4	105

[a] Irradiation temperature: 100°C.
[b] Photoinitiator: 5 wt %.

Electrooptical Properties of the Film

Electrooptical properties of the films were examined by measuring transmittance of the light with or without applied electric field. The results are depicted in Figure 2.

Transmittance without applied field (off-transmittance) of Film A having the LC/M ratio of 4/6 was quite high (36%), and the transmittance increased with increasing the applied field to reach 75% at 30 V. The same tendency was seen for the Films C and D, which had both higher LC/M ratios and low polymer yields. On the other hand, for Films B, E, and F, which had the ratio of 6/4 and a polymer yield of more than 60%, the off-transmittance was low (10%) and the transmittance reached 62–67% at the applied field of 30 V. Thus the difference in the transmittance was desirably larger in the latter films (B, E, F) than in the former (A, C, D). The low off-transmittance suggests that the film contains a large

Table II   Films Obtained Using a Mixture of Bifunctional and Hexafunctional Monomers as the Monomer[a]

Film Designation	Bifunctional/ hexafunctional Ratio (wt/wt)	Polymer Conversion (%)
J	3/1	75
K	1/1	90
L	1/3	100

[a] Electron beam irradiation dose: 10 Mrad; irradiation temperature: 100°C. LC-to-monomer ratio: 6/4.

amount of liquid crystals randomly orienting in the droplets.

Although Film I, prepared by polymerizing the mixture of LC and hexafunctional monomer, exhibited considerably high off-transmittance, the transmittance did not change with application of an electric field. Therefore it is assumed that the LC molecule did not have mobility in this film, probably because the degree of crosslinking in the polymer matrix was too dense. The same tendency was observed for Films G and H, in which the bifunctional monomer was polymerized by UV irradiation (data not shown). Therefore UV was
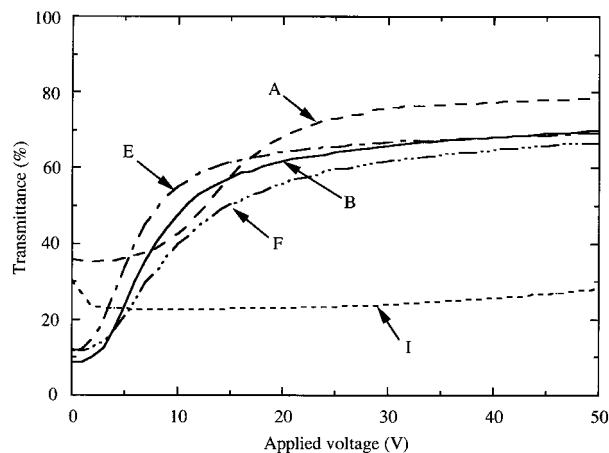

Figure 2   Effects of the LC-to-monomer ratio, irradiation dose, and monomer structure on the electrooptical property. A: LC bifunctional monomer = 4/6; B: 6/4; E: 6/4 under 20 Mrad irradiation; F: 6/4 under 10 Mrad, twice; I: LC hexafunctional monomer = 6/4 under 10 Mrad.
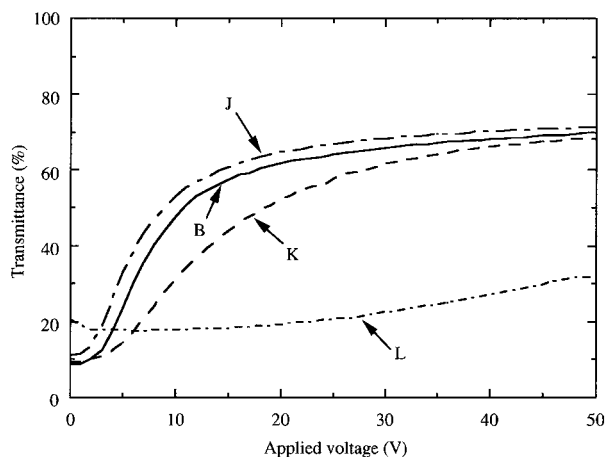
Figure 3 Effects of mixture of bifunctional and hexafunctional monomer on the electrooptical property. B: bifunctional monomer only; J: bifunctional monomer/ hexafunctional monomer ratio = 3/1; K: 1/1; L: 1/3. Irradiation dose: 10 Mrad. LC monomer ratio = 6/4.

not suitable for the preparation of this kind of compound film.

Subsequently, the electrooptical property of compound films which were prepared by polymerizing the three-component mixtures consisting of LC and the bifunctional and hexafunctional monomers, was determined (Fig. 3). Although Film L, having too high a content of hexafunctional monomeric units, exhibited no difference in the transmittance, Films J and K had about 10% off-transmittance and 60–70% transmittance by 30 V application. Film J, especially, having a large difference in the transmittance, is a desirable film near the target.

For Films B and J, effects of the standing time on the electrooptical property were examined. The result is shown in Figure 4. Although the off-transmittance of Films B and J did not depend on the time of standing, the 5-day-old films showed lower transmittance by low applied electric fields than the corresponding fresh films. It is assumed that this phenomenon was caused by monomer transfer from the polymer matrix to the LC droplet.

It has been reported that electrical hysteresis was influenced by the glass temperature of the matrix polymer.[15] The matrix polymer obtained by polymerizing a mixture of bifunctional and hexafunctional monomers must have higher glass temperature than the polymer produced from a bifunctional monomer. Accordingly, the excellent properties of Film J might be partially ascribable to higher glass temperature.

Morphology of the LC–Polymer Compound Film

Scanning electron microscopic (SEM) observation was carried out for the fracture surface of the remaining films from which the LC had been extracted. All extracted films except A, I, and L had so-called polymer-ball network structure, in which polymer granules were connected to form networks. SEM microphotographs of the fracture surface of Films B and I are shown in Figure 5. Films A, I, and L showed similar morphology. The vacant space appearing in the microphotograph must have been occupied by an LC droplet. In addition, for the films having low polymer yields (such as C, D, and G), the polymer balls were smaller than those of the films having high polymer yields (B, E, F, H, J, and K). On the contrary, there was no vacant space inside Films A, I, and L.

So far, it has been reported that the LC-containing polymer film which was produced by polymerizing a mixture of oligomer and liquid crystal by UV irradiation had so-called "swiss cheese" morphology.[16,17] For such films, dependence of the electrooptical property on the droplet size was revealed.

It has also been demonstrated that for the LC–polymer compound film containing a high proportion of polymer walls, application of high electric fields was necessary for changing the opaque film into transparent film. Therefore, because in such films the polymer wall has interfacial interactions with liquid crystal molecules, too-high proportions of the polymer network or too-small LC droplets may prevent the LC molecules from orienting with the applied electric field.[18,19]

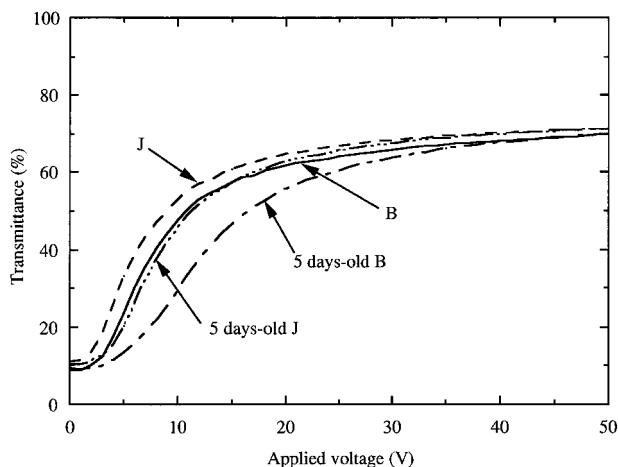Next, for the films remaining on the PET films

Figure 4 Dependence of the time of standing B and J: the first day of preparation; 5-day-old B and J films.
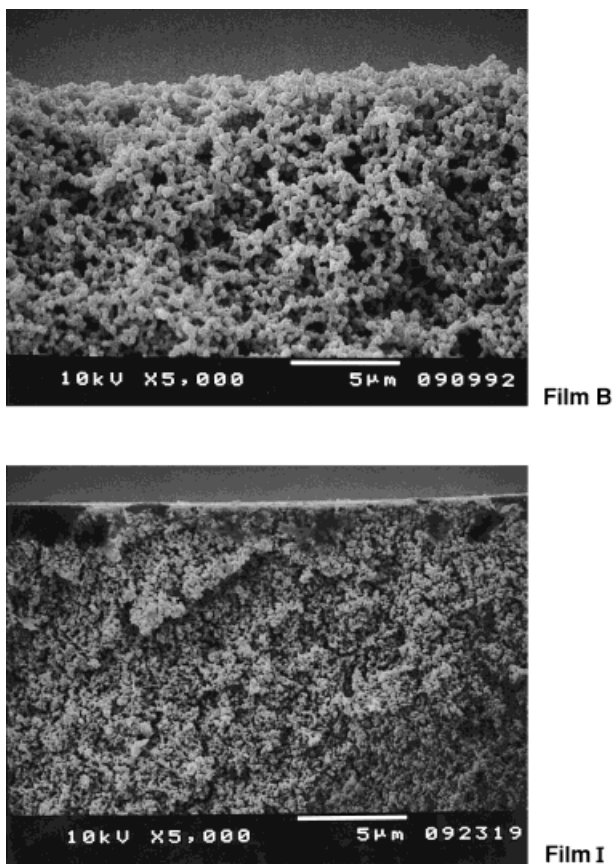
Figure 5 SEM microphotographs of the fracture surface of the films. B: 4/6 LC/bifunctional monomer) at 10 Mrad; I: 4/6 LC/hexafunctional monomer) at 10 Mrad.
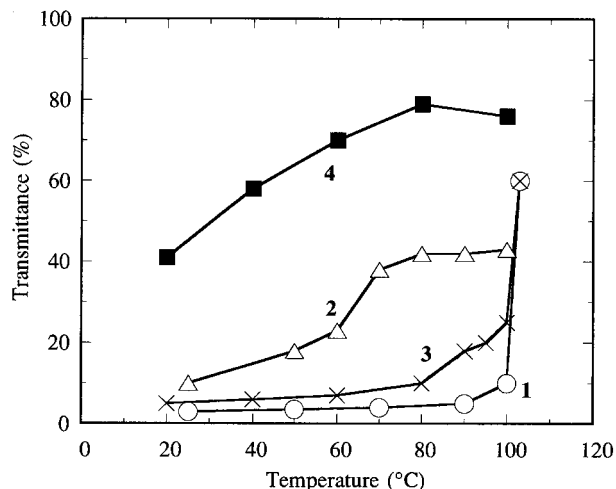

Figure 6 Temperature dependence of the off-transmittance for the compound films. 1: A compound film prepared from mixing LC and polyvinyl alcohol. 2: The EB-polymerized film B. 3: The pure LC-reinjected Film B after extraction. 4: The LC and monomer (6/4)-reinjected Film B after extraction.

after extraction, the BET surface area was determined by the nitrogen adsorption method. The results, summarized in Table III, reveal that the films containing very high surface areas (such as I and L) had no electric-field dependence of the transmittance. It is noteworthy that the BET surface area of the film prepared by polymerizing

three-component mixtures containing LC increased with increasing content of the hexafunctional monomer, and, a 25% content of the hexafunctional monomer was suitable.

An alternate method of preparing a compound film exhibiting excellent electrooptical properties was found. Since contamination of the LC droplet with unreacted monomer was assumed to be one of the factors in decreasing the electrooptical properties, the impure LC was exchanged with pure LC by extracting it from the compound film, followed by recharging the pure one.

The electrooptical property of the recharged film was determined in terms of the temperature dependence of the off-transmittance, because the temperature dependence of the off-transmittance corresponds to its dependence on the applied volt-

Table III   BET Surface Area of the Film After Extraction with Hot Ethanol

Film Designation	Ratio of Bifunctional to Hexafunctional Monomer	BET Surface Area (m^2/g)
A	1/0	13
B	1/0	7
E	1/0	13
F	1/0	6
I	0/1	210
J	3/1	10
K	1/1	23
L	1/3	74

age. As shown in Figure 6, the film recharged with pure LC (curve **3**) had a tendency for the transmittance to sharply increase near the LC melting temperature (100°C). This important tendency is very similar to that of an excellent compound film composed of the LC and poly(vinyl alcohol)(curve **1**). On the other hand, both original Film B (curve **2**) and film recharged with a mixture of the LC and the monomer (curve **4**) demonstrated a gradual increase in off-transmittance as the temperature increased.

In conclusion, an LC-containing compound film having excellent electrooptical properties was obtained by polymerizing a mixture of LC and monomer (6/4), followed by exchanging the included LC droplet into pure LC.

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