Synthesis of Poly(benzylmethacrylate-co-perfluorooctylethylmethacrylate) and Electrooptical Properties of the Resultant Polymer/Liquid Crystal Composite Films

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SYNOPSIS

Methacrylate copolymers of benzylmethacylate (BMA) and perfluorooctylethylmethacrylate (FMA) were synthesized and applied to the polymer/liquid crystal (LC) composite films. The copolymers were prepared by a radical solution polymerization. The high composition of FMA resulted in a precipitation during the polymerization. The contact angle of the LC on the copolymer films decreased with increasing FMA composition. Due to a small interaction between the LC and the copolymers, the copolymer/LC composite films showed low driving voltage in the range of 18–25 V_{rms}, corresponding to about $\frac{1}{3}$ the value of the poly(methyl methacrylate) (PMMA)/LC composite film. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The polymer/liquid crystal (LC) composite and/or polymer dispersed liquid crystal (PDLC) films have been intensively studied because of the great potential for applications of large-scale, low-cost, flexible devices and improved brightness owing to the absence of polarizers.[1–6] They can be electrically switched between an opaque scattering state and a transparent state. Several methods to disperse the LC droplets in the polymer matrix were reported with regard to methods of a solvent-induced phase separation (SIPS),[2,3] a photopolymerization-induced phase separation (PPIPS),[4] and an LC emulsion in aqueous polymer solution.[5]

These polymer/LC composite films have been developed on the basis of the same and simple operating principle: The composite film is opaque in the absence of an electric field because of the refractive index mismatching between the polymer and the randomly aligned LC. When the electric field is applied to the film, the nematic director of LC should be aligned along the electric field to make the film transparent as a result of the index matching between the aligned LC and the polymer matrix.

One of the problems of the polymer/LC composite film is that the driving voltage is relatively higher than that of the conventional LC display that does not contain a polymer matrix. It has been known that an interaction at the interface between the polymer matrix and the LC plays an important role for the alignment of LC molecules. In general, the low boundary interaction between the polymer and the LC can align the LC molecules easily under the electric field. Therefore, the characteristics of the polymer matrix is an important factor as well as are the LC and the shape of LC domain.[7]

This article describes the synthesis and characterization of methacrylate copolymers for the polymer/LC composite films and electrooptical properties of the polymer/LC composite films fabricated by the SIPS method. To reduce the interaction between the polymer and the LC and to suite the refractive index of the polymer with the LC, perfluorooctylethylmethacrylate (FMA) and benzylmethacrylate (BMA) were selected and copolymerized with various copolymerization ratios. The solubilities and contact angle of the copolymers were measured. The dependence of the copolymer composi-

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tion and molecular weight on the electrooptical properties of the copolymer/LC composite film was also investigated.

EXPERIMENTAL

Materials

FMA (Hoechst Japan Co., Ltd.) and BMA (Wako Pure Chemical Co.) were purified by column chromatography to remove an inhibitor before polymerization. 2,2'-Azobis(2-methylpropionitrile) (AIBN) (Tokyo Kasei Co.) was recrystallized from the ethanol solution and stored at $0°C$. Poly(methylmethacrylate) (PMMA) is commercially available (Aldrich, $M_n = 5920$, $M_w = 12,300$) and was used as received. This work adopted a mixture of nematic LC consisting of 4-alkyl (or alkyloxy)-4'-cyanobiphenyl and 4-alkyl-4'-cyanotripheyl named E7 (BDH-Merck, Japan, $N_o = 1.521$, $N_e = 1.746$, $T_{NI} = 61°C$). All other solvents and chemicals were used as received.

Polymer Synthesis

The copolymers were synthesized by a free-radical solution polymerization in toluene with AIBN as the initiator. The concentration of monomers was about 9.1% (w/v). The monomer feed ratio and the synthesized copolymer composition are summarized in Table I. As an example of the general copolymerization procedure, the synthesis of copolymer **1f** is described as follows:

Copolymer **1f:** 2.5 g (4.7 mmol) of FMA, 2.5 g (14.2 mmol) of BMA, and 150 mg of AIBN were dissolved in 50 mL of toluene. The reaction mixture was treated with a gentle stream of nitrogen. After sealing, the mixture was heated to $60°C$ for 6 h. The resulting homogeneous viscous solution was cooled and added dropwise into 500 mL of methanol to precipitate the polymer. After two additional precipitations from the dichloromethane solution into methanol, the copolymer was dried at $30°C$ in vacuum for 48 h. Yield: 2.5 g (50 wt %). ^{1}H-NMR (CDCl$_3$): δ (ppm) = 0.75 (brs), 0.92 (brs), 1.2–1.4 (m), 1.6–1.9 (m), 2.35 (brs, OCH$_2$C$\underline{H}_2$C$_8$F$_{17}$), 4.15 (brs, OC$\underline{H}_2$CH$_2$C$_8$F$_{17}$), 4.90 (brs, OC$\underline{H}_2$Ph), 7.29 (s, OCH$_2$C$_6$$\underline{H}_5$). IR (film on NaCl): 1730 (C=O), 1587 (Ph), 1454, 698 (Ph), 656 (C—F) cm^{-1}.

Copolymer **1g** was found to be insoluble in the reaction medium and precipitated during the reaction. This copolymer was purified by washing with methanol and extraction with hot methanol for a few days. The yields of the isolated polymers were in the following range: **1a** (34%), **1b** (49%), **1c** (53%), **1d** (47%), **1e** (51%), **1f** (50%), and **1g** (40%).

Characterization

Differential scanning calorimetry data were obtained with a Mettler TA-4000 heating at a rate of $10°C$/min. The molecular weight and molecular weight distributions were measured in the THF eluent with a Waters 150C GPC system equipped with a UV detector. The columns (Shodex) were calibrated with polystyrene standards of known molecular weight. FTIR spectra were recorded with a JEOL JIR-5500. ^{1}H-NMR spectra were measured with a JEOL JXR NMR instrument operating at 270 MHz. The copolymer composition was determined by ^{1}H-NMR or IR spectroscopy using separated signals of each

Table I   Monomer Feed Ratio and Copolymer Composition

| | Feed Ratio | | [Monomer] | Composition[a] | |
| | BMA : FMA | | | BMA : FMA | |
Polymer	Wt : Wt	Mol : Mol	[AIBN]	Wt : Wt	Mol : Mol
1a	100 : 0	100 : 0	31.1	100 : 0	100 : 0
1b	90 : 10	96.5 : 3.5	31.8	92.3 : 7.7	97.3 : 2.7
1c	80 : 20	92.4 : 7.6	30.2	84.1 : 15.9	94.1 : 5.9
1d	70 : 30	87.6 : 12.4	24.9	75.9 : 25.1	90.1 : 9.9
1e	70 : 30	87.6 : 12.4	1.7	72.8 : 27.2	89.0 : 11.0
1f	50 : 50	75.1 : 24.9	20.7	52.6 : 47.4	77.0 : 23.0
1g	20 : 80	43.0 : 57.0	14.5	38.5 : 61.5	65.4 : 34.6[b]

[a] Determined by NMR.
[b] Determined by FTIR.

monomer. Refractive indices were measured by an Abbe's refractometer using casted copolymer films.

Solubility tests of copolymers were conducted with a copolymer concentration of 10% (w/w). The solubility behavior of the copolymer/LC mixture in chloroform with the concentration of 35, 40, and 45% (w/w) were examined with regard to the LC concentration range between 50 and 80% in the mixture at 23°C. Contact angle measurements were made on film surfaces at 23°C with a Kyowa CA-DT contact angle meter. Film thickness of the copolymer/LC composite films was measured by a Rank-Tayler Hobson Talystep on the basis of a stylus contact method. A polarization microscope was used to observe the LC droplets of the polymer/LC composite film. The transmittance change of the composite film was measured with a Hitachi U-4000 UV-vis spectrometer.

Preparation of the Polymer/LC Composite Film

A polymer/LC composite film in this study was prepared by the SIPS method using a chloroform solution at a ratio of the copolymer and the LC of 40 : 60.[2,3] The concentration of the copolymer/LC mixture in the solution was adjusted to 30–50 wt % to obtain a composite film with similar thickness. The solution was first filtered through a 0.5 μm Teflon filter and spin-coated on an indium–tin–oxide (ITO)-coated glass substrate at 500–1000 rpm for 10 s and then at 1500 rpm for 70 s at 23°C, forming a 17 ± 1 μm-thick film. For the measurements of electrooptical properties, the resultant film sample was sandwiched with an another ITO glass substrate.

Transmittance of the composite films fabricated from copolymers 1a and 1b changed after repeating the voltage impression several times, so that the electrooptical properties were measured on the composite films fabricated from the copolymers 1c–1f. Morphology of the composite films showed a slight change over a period of measurements.

Electrooptical Properties

Electrooptic measurements were carried out by measuring transmission of a He—Ne laser beam (632.8 nm) through the polymer/LC composite film with increasing and decreasing the impressed voltage between 0 and 80 V_{rms} at a rate of 0.89 V_{rms}/s. The incident angle of the laser beam was perpendicular to the film. The intensity of transmitted light was measured by an optical multimeter (Advantest TQ8215), setting the distance between the cell and

the photodiode (7 × 7 mm) at 300 mm and recorded on a digital storage oscilloscope (Kikusui COM7101A). The switching behavior of the film was also measured with an applied voltage of 80 V_{rms}. All measurements were performed using a 1 kHz square wave at 23°C.

RESULTS AND DISCUSSION

Polymer Synthesis

The copolymers were synthesized by a free-radical polymerization using AIBN as an initiator. The results of GPC and DSC measurements and refractive index of copolymers 1a–1g are summarized in Table II. In the case of the synthesis of 1f and 1g, FMA tended to separate from the solution when the monomers and toluene were mixed, but it became soluble above 40°C. Copolymer 1g was found to be insoluble in the reaction medium and precipitated as a viscous swelled polymer during the reaction. This means that the copolymer with high composition of FMA is insoluble in toluene. Copolymers 1a–1f were completely soluble. The results of the GPC measurement showed that all copolymers distributed monomodally. All copolymers were amorphous. The number-average molecular weight was in the order of 10,700–22,600 g/mol, and the weight-average molecular weight, in the order of 20,900–45,100 g/mol, except for 1e. The molecular weight of 1e was higher than that of the other copolymers because of the low concentration of AIBN. Because 1g was precipitated during the polymerization, the molecular weight of the soluble portion of 1g was low compared to that of 1a–1d and 1f. The glass

Table II   Results of GPC, DSC, and Refractive Index Investigations

| Polymer | Molecular Weight[a] | | | Tg (°C)[b] | Refractive Index[c] |
	M_n	M_w	M_w/M_n		
1a	22,600	45,100	2.00	66.8	1.568
1b	17,370	40,370	2.32	62.6	1.554
1c	17,500	40,100	2.29	62.4	1.536
1d	19,100	36,800	1.93	61.4	1.515
1e	55,900	170,000	3.00	62.0	1.510
1f	18,100	34,200	1.89	56.5	1.449
1g	10,720[e]	20,900[d]	1.95	55.0	1.403

[a] Determined by GPC, polystylene standards, UV detection.
[b] Determined by DSC, heating rate: 10°C/min, first heating.
[c] n_D.
[d] Soluble portion in THF.

transition temperatures (T_g) and the refractive index of the copolymers varied with the copolymer composition. The T_g decreased with increasing the composition of FMA. The refractive index also decreased with increasing the composition of FMA because of the low refractive indices of fluorine-containing materials.

Solubility

The solubility behavior of the copolymers was influenced by the FMA composition. Table III summarizes the results of solubility tests at 23°C, fixing the concentration at 10 wt %. Copolymers 1a–1e could be dissolved in all tested solvents, whereas copolymers 1f and 1g showed low solubilities. Copolymer 1f was insoluble in DMF, and 1g, insoluble in both DMF and toluene, but partially soluble in chloroform and THF, suggesting a low solubility of FMA in the tested solvents.

The solubility behavior of the copolymer/LC mixtures in chloroform was affected by not only the composition of FMA in the copolymer but also by the concentration of the copolymer/LC mixtures. Table IV lists the results for copolymers 1d and 1f at 23°C. The mixture of 1d and the LC was dissolved at all tested conditions. Copolymers 1a–1c and 1e showed the same results as those of 1d. On the other hand, the solubility of the mixture of 1f and the LC was affected by the LC content in the polymer/LC mixture as well as by the concentration of the mixture in the solution. A phase separation between the LC and the copolymer solution occurred when the LC content in the mixture was high and both the LC and the copolymer precipitated at the mixture concentration of 45 wt %, as shown in Table IV. However copolymer 1f and the LC in a pure state were each soluble at more than 50 wt % in chloro-

Table IV   Solubility Behavior of Copolymer/LC Mixtures

Polymer	Concn[a]	LC Concentration (Wt %)[b]			
		50	60	70	80
1d	35	+	+	+	+
	40	+	+	+	+
	45	+	+	+	+
1f	35	+	+	+	−[c]
	40	+	+	−[c]	−[d]
	45	−[d]	−[d]	−[d]	−[d]

[a] Mixture concentration in $CHCl_3$ solution, wt %.
[b] Wt % in LC/copolymer mixture.
[c] LC was separated from the solution.
[d] Both LC and copolymer separated from the solution.

form. It can be seen from these results that the solubility of the LC in the copolymer solution decreases with increasing the composition of FMA and the interaction between 1f and the LC was lower than between 1d and the LC.

Contact Angle

The boundary interaction between a copolymer and the LC can be estimated from a contact angle of the polymer film with the LC. A transparent polymer film without the LC was prepared by a casting method from methylene chloride or THF solutions. Figure 1 shows the variation of contact angle of the copolymer films with the LC, H_2O, ethylene glycol (EG), and hexane. In all cases, the contact angle became larger with increasing the composition of FMA in the copolymer. The contact angle values on
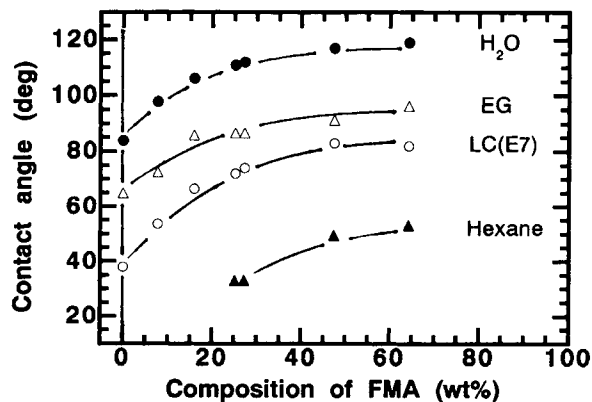
Table III   Solubility of Copolymers 1a–1g

Polymer	Solubility[a]			
	$CHCl_3$	Toluene	THF	DMF
1a	+	+	+	+
1b	+	+	+	+
1c	+	+	+	+
1d	+	+	+	+
1e	+	+	+	+
1f	+	+	+	±
1g	±[b]	−	±[b]	−

[a] Determined for a 10% (w/v) solution.
[b] Pertially soluble, swelled.

Figure 1   Contact angle dependence on composition of FMA.

(a)

(b)

(c)

(d)

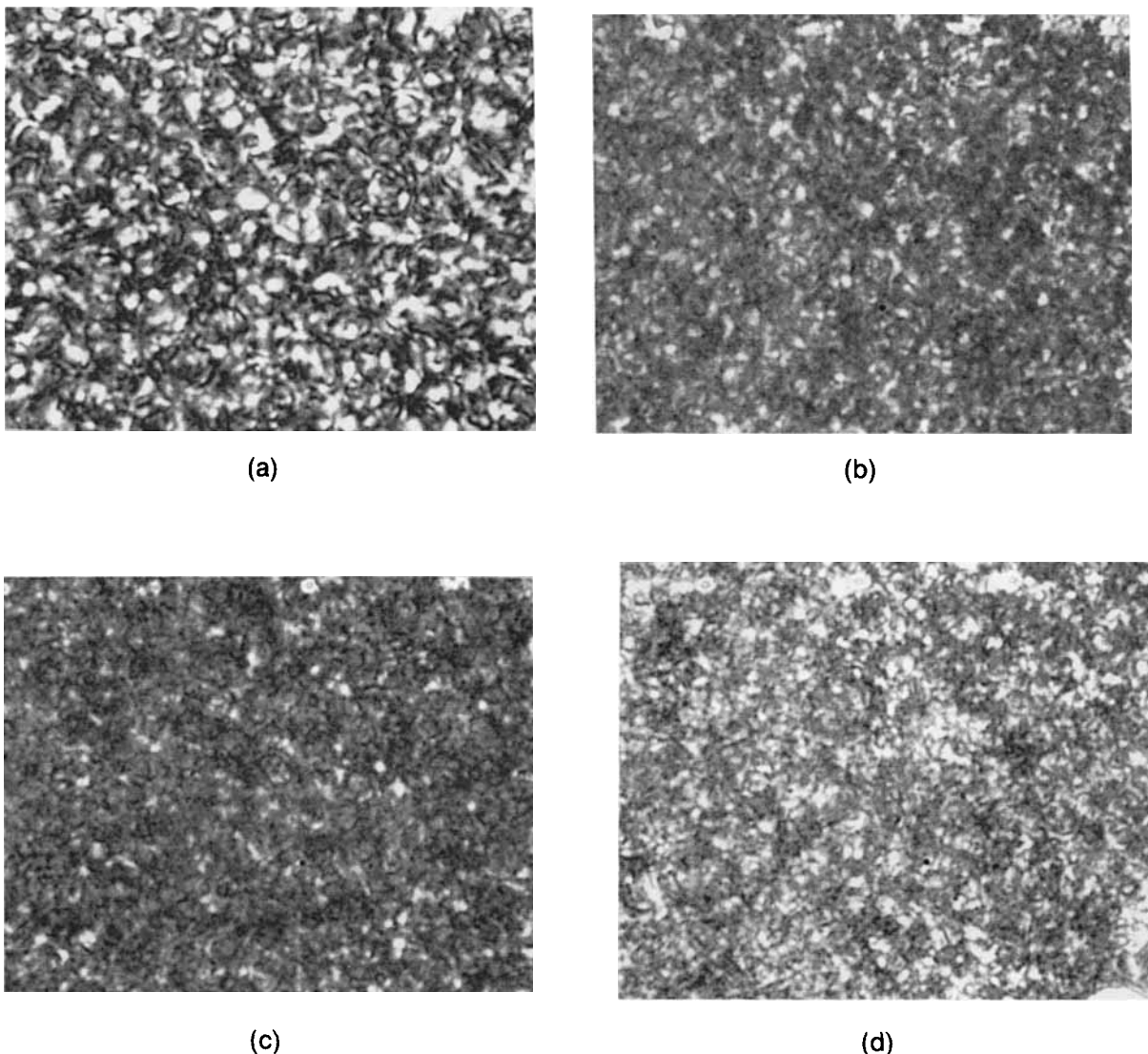**Figure 2** Polarized microscope observation of the composite films: (a) 1c/LC; (b) 1d/ LC; (c) 1e/LC; (d) PMMA/LC composite films.

the copolymers were 82°–117° for H_2O and 37°–83° for the LC. On the other hand, the contact angle on the PMMA with H_2O was 62° and that with the LC could not be measured since the LC spread out on the PMMA film. These results also show that the interaction between the copolymer and the LC decreased with increasing the composition of FMA and was lower than that between PMMA and the LC.

Morphology of the Copolymer/LC Composite Film

The morphology of the composite film is usually observed by a scanning electron microscope (SEM) after extracting the LC with a solvent that does not dissolve the polymer matrix.[2] Unfortunately, extraction of the LC by methanol was not effective for the present composite films despite the fact that methanol could not dissolve the copolymers. The extracted LC domains in the composite films were destroyed to become transparent except in the case of the PMMA/LC composite film. For this reason, we used a polarization microscope that was also useful for observing the film morphology. Figure 2 shows photographs of 1c–1e and PMMA with 60 wt % of the LC composite film without extracting the LC. It can be seen from the photographs that the 1d/ LC, 1e/LC, and PMMA/LC composite films were similar in morphology to one another and that the 1c/LC was slightly larger in the LC domain size
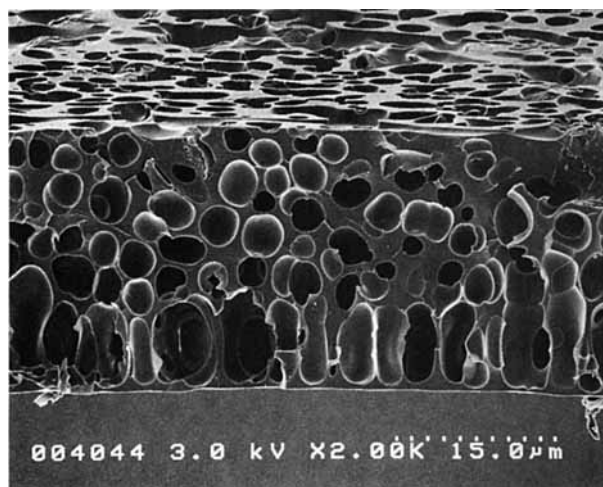
Figure 3 SEM photograph of the PMMA/LC composite film after extracting the LC with methanol.

than were the others. SEM observation of the PMMA/LC composite film showed that the size of the LC droplet was between 3 and 10 μm, as shown in Figure 3.

The **1a**/LC and **1b**/LC composite films slowly increased in transmittance even when they were stored at 23°C and became transparent after storing for 1 month, suggesting that the LC domain became large. This tendency was also observed for the other copolymers, but the growing speed was much slower than for **1a** and **1b**. Figure 4 shows the change in the transmittance of light at the wavelength of 500 nm for the composite films stored at 23°C. The PMMA/LC composite film showed no change in transmittance. The high composition of BMA might cause a fast change of the transmittance. The higher molecular weight of the polymer could contribute to maintain the morphology because the **1e**/LC com-
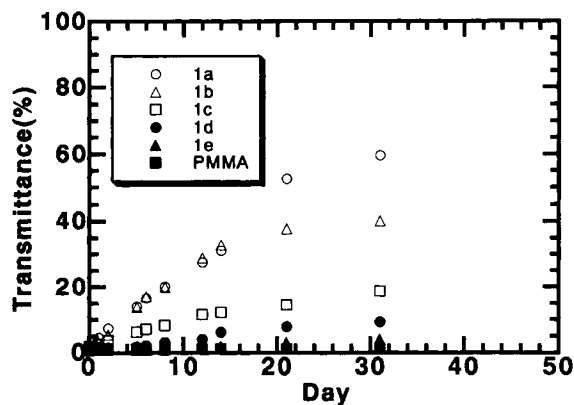
posite film was stabler in transmittance than was the **1d**/LC composite film, as shown in Figure 4.

Electrooptical Properties

Measurement of the electrooptical properties of each copolymer/LC composite film was carried out on the film sandwiched between the ITO glasses just after the sample preparation, so that the LC droplet in each sample remained a similar size. The light transmittance was measured on the composite films prepared from **1c–1f** and PMMA except those from **1a** and **1b** since the latter one changed in the transmittance with repeating the electric field impression. Table V lists the results of maximum transmittance (T_{max}), threshold voltage (V_{90}: a voltage at which the transmittance reached 90% of T_{max}), hysteresis (voltage difference between up and down processes reached to the half of T_{max} to T_{min} [minimum transmittance]), and response time.

Driving Voltage of the Composite Film

Figure 5 shows the transmittance as a function of applied voltage at 1 kHz with a sweep rate of 0.89 V_{rms}/s for the composite films prepared from **1d**, **1f**, and PMMA. It can be seen that V_{90} and T_{max} varied with the copolymer composition. As shown in Table V and Figure 5, V_{90} of the **1c–1f**/LC composite films was much lower than that of the PMMA/LC, resulting from a small interaction between the copolymers and the LC compared to the interaction between PMMA and the LC.

The **1f**/LC composite film was slightly lower in V_{90} than were the **1d**/ and **1e**/LC composite films because of a higher content of FMA. In addition, the lower V_{90} of the **1c**/LC composite film than that

Figure 4 Change of transmittance of the copolymer/LC composite films (film was stored at 23°C and measured at 500 nm).

Table V Electrooptical Properties of the Copolymer/LC Composite Films

	Polymer				
	1c	**1d**	**1e**	**1f**	PMMA
T_{max} (%)[a]	77	83	81	72	82
V_{90} (V_{rms})[b]	18	24	25	21	57
Hys. (V_{rms})[c]	5.0	5.5	2.5	7.5	24
τ_{on} (ms)[d]	< 1	2	2.5	1.5	9
τ_{off} (ms)[e]	> 100	> 100	14	30	> 100

[a] Maximum transmittance.
[b] Voltage at which the transmittance reached 90% of T_{max}.
[c] Hysteresis.
[d] Time for a transmittance change from minimum to 90% of T_{max}.
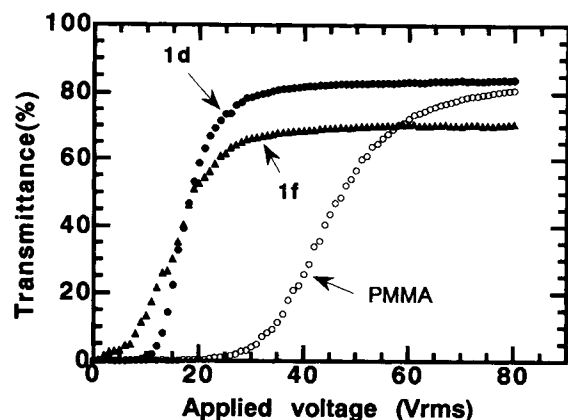[e] Time for a transmittance change from T_{max} to 10% of T_{max}.

Figure 5 Transmittance vs. applied voltage curves for a copolymer/LC composite film.

of the other films might be caused by a larger droplet size compared to that of the others, as shown in Figure 2.

Maximum Transmittance (T_{max})

T_{max} was affected by the refractive index of the copolymer. T_{max} of the composite films was between 72 and 83%. Because of the large index mismatching between the aligned LC ($N_o = 1.523$) and the copolymer **1f** ($N = 1.449$), the maximum transmittance of the **1f**/LC composite film was 72% and lower than that of the films prepared from **1c** ($N = 1.536$, T_{max} was 77%), **1d** ($N = 1.515$, 83%), **1e** ($N = 1.510$, 81%), and PMMA ($N = 1.490$, 82%).

Hysteresis

Hysteresis of each film was between 2.5 and 7.5 V_{rms} for the copolymers **1c–1f** and 24 V_{rms} for PMMA. The composite films prepared from the copolymers **1c–1f** were lower in hysteresis than was the composite film prepared from PMMA. It is known that a fluorine-containing monomer could decrease the hysteresis.[8] It is interesting that the hysteresis of **1e**/LC was 2.5 V, whereas **1d**/LC showed a higher hysteresis value of 5.5 V. The morphology of the LC domain of each film was almost invariable concerning the microscope observation, as shown in Figure 2. The molecular weight of the copolymer could play an important role in this phenomenon and the hysteresis might have a relation to the switching behavior as described below.

Switching Behavior

The experimental values of response time of the composite films are also listed in Table V, where τ_{on} is defined as the time for a transmittance change

from T_{min} to 90% of the ($T_{max} - T_{min}$) upon turning the electricity on, and τ_{off} is measured as the time for a transmittance change from T_{max} to 10% of the ($T_{max} - T_{min}$) upon turning the electricity off. The τ_{on} value was around a few milliseconds except in the case of the PMMA/LC composite film, where τ_{on} was 9 ms. The **1c**/LC composite film was faster in τ_{on} than were other composite films because of the large droplet size.[2] On the other hand, the composite films were very slow in τ_{off} except the composite films prepared from **1e** and **1f**. Figure 6 shows the switching behavior of composite films of **1d**/LC and **1e**/LC upon the applied voltage on and off. These copolymers had a similar copolymer composition and the morphology of the composite films were almost invariable, as shown in Figure 2. These composite films agreed in τ_{on} with each other, but their τ_{off} was completely different. In the case of the **1d**/LC composite film, both a fast and a slow decay were present, taking more than 100 ms to return the original scattering state, whereas τ_{off} of the **1e**/LC composite film was 14 ms. The slow decay was also observed in the **1c**/LC and PMMA/LC composite films. It can be assumed that the slow decay was caused by a local molecular motion of the matrix polymer upon the applied electricity off. If the molecular weight of the matrix copolymer was high, the local molecular motion would be suppressed as a result of the absence of slow decay. The suppressed molecular motion could also cause the lower hysteresis of the **1e**/LC composite film. In addition, τ_{off} of the **1f**/LC composite film was about 30 ms in spite of the low molecular weight of **1f** that was similar to **1c** or PMMA. The high content of FMA, which reduced the interaction between the polymer and the LC, might be also concerned with a fast response.
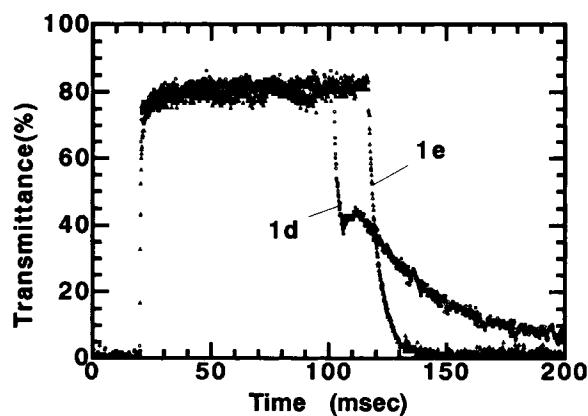

Figure 6 Switching behavior of the composite films: Applied voltage was 80 V_{rms}, 1 kHz square wave.

CONCLUSIONS

To apply the polymer/LC composite films that had a small boundary interaction between the polymer and the LC, methacrylate copolymers comprising the perfluorooctylethyl side group and the benzyl side group were synthesized by the radical solution polymerization. The copolymer was precipitated during the polymerization if the content of FMA was high. The solubility of the copolymers in organic solvents decreased with increasing the composition of FMA. The contact angle of the copolymers with various liquids was larger than that of PMMA and increased with increasing the FMA composition in the copolymer. These were the consequences of lower interaction between the LC and the copolymer than that of PMMA.

The copolymer/LC composite films were prepared by the SIPS method from a chloroform solution. Due to the low interaction between the copolymer and the LC, the threshold voltage of the copolymer/LC composite films was in a range 18–25 V_{rms}, which was much lower than that of the PMMA/LC composite film. The hysteresis was also smaller than for the composite film using PMMA. The τ_{on} was less than 10 ms for all copolymers, but τ_{off} varied with the copolymers and the molecular weight of them. Suppressed local molecular motion of the matrix polymer upon the electricity off and the low interaction between the matrix polymer and the LC might be effective to obtain the small τ_{off} of the composite film. The τ_{off} of the composite film with the low molecular weight polymer matrix behaved in two decay ways according to the local molecular motion of the matrix polymer upon the electricity off.

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