

Effect of Fluorine Group on Electro-optical Properties of PDLC Films Prepared with Water-soluble Polymers

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Polymer-dispersed liquid crystals (PDLCs) have been extensively studied for use in new electro-optical applications, such as optical switches, smart windows, light shutters, and holographic films because PDLC films are easy to prepare for a large area displays, and their light transmittance is much higher than conventional liquid crystal (LC) displays.¹⁻⁴ PDLCs are dispersed micro-sized LC droplets in a continuous polymer matrix. It is generally known that the electro-optical properties of PDLC films are significantly affected by a number of parameters including the size and morphological shape of the LC domains, the kind of polymer matrix, and the anchoring properties.⁴⁻⁷ Therefore, the properties of the polymer matrix, including the polymer structure, the molecular weight, and others, play important roles in governing the electro-optical properties of PDLC films.

Ryu *et al.* have studied the influence of stearyl methacrylate (SMA) content on the electro-optical properties of PDLCs prepared with monodispersed poly(methyl methacrylate) (PMMA)/LC microcapsules. They concluded that the threshold and driving voltages were improved when the SMA content increased.⁴ Kim *et al.* investigated the effect of prepolymer structure and oligomeric surface modifying agent (OSMA) on the electro-optical properties of PDLCs.^{8,9} The polypropylene glycol- and polytetramethyl ether glycol-based polyurethane acrylates showed lower threshold operating voltages. Also, the contact angle of the resin surface with an LC drop increased, and domain size decreased significantly, with the addition of OSMA. Pogue *et al.* reported the monomer functionality effects in the anisotropic phase-separation of LCs. They found that lowering monomer functionality reduced the volume fraction of phase-separated domains in floodlit samples.¹⁰ Pan *et al.* revealed the effect of matrix composition on the electro-optical properties of PDLC. They found that the long-chain alkyl and mesogenic groups in methacrylate monomers greatly affected the saturation and threshold voltages as well as response time.¹¹ Kundu *et al.* evaluated the dispersion of LC in the polymer matrix as well as the light transmission of PDLC governed, as governed by the nature of the polymer, its molecular weight, and the applied voltage.¹² Schulte *et al.* reported the presence of fluorine atoms at the polymer/LC interface of homographic PDLC gratings can reduce the anchoring strength and the switching voltage.¹³

In previous work, we synthesized acrylamide-based poly-

mers, that is, poly(acrylamide-styrene) and poly(acrylamide-methyl methacrylate), in the preparation of PDLC films.^{14,15} In this paper, we report the introduction of a fluorine group into acrylamide-based polymer chains, having investigated the effect of this functional group on the electro-optical properties of the PDLC films prepared from the polymers.

Experimental Section

Materials. The LC used in this study was 4-pentyl-4'-cyanobiphenyl (BL087), supplied by Merck. BL087 is a rod-shaped polar molecule and shows nematic LC phase in the temperature range from 24 °C to 35 °C. Acrylamide (AAM), styrene (St), 4-fluorostyrene (St-F), and dioxane were obtained from Aldrich Chem. *N,N'*-Azobisisobutyronitrile (AIBN) was purchased from Junsei Chem. of Japan, was selected as an initiator. All chemicals were used as received, without further purification. The chemical structure of the liquid crystal is shown in Figure 1.

Synthesis of Polymers. To synthesize poly(acrylamide) (polyAAM), a solution of AAM (20 g), AIBN (0.5 g), and dioxane (105 mL) was placed in a 500 mL four-neck round flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. The mixtures were reacted at 60 °C for 30 min under a nitrogen atmosphere. After the reaction was completed, the crude product was washed with acetone several times, and finally was dried in a vacuum oven at 30 °C for 24 h.

Product characterization. white powder; yield 89%; FTIR (KBr) peaks at 3198 (N-H stretch), 2930 (C-H stretch), 1664 (C=O stretch), 1451 (CH₂ deformation); ¹H NMR (D₂O) peaks at δ 1.40-1.67 (d, 4H, -CH₂-CH-), 2.06-2.22 (d, 2H, -CH₂-CH-), 4.67 (m, 2H, -NH₂); Elementary analysis: C, 44.69%; H, 7.07%; N, 17.30%.

Poly(acrylamide-styrene) [poly(AAM-St)] was synthesized from AAM (17.06 g, 0.24 mol), St (2.50 g, 0.024 mol), AIBN (0.49 g), and dioxane (105 mL) in a manner similar to the synthesis of polyAAM.

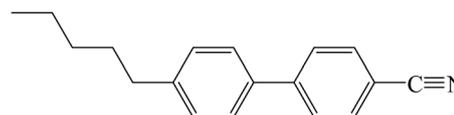


Figure 1. Molecular structure of BL087.

Product characterization: white powder; yield 92%; FTIR peaks at 3197 (N-H stretch), 2931 (C-H stretch), 1663 (C=O stretch), 1450 (CH₂ deformation); ¹H NMR (D₂O) peaks at δ 1.50-1.63 (d, 4H, -CH₂-CH-), 2.04-2.19 (d, 2H, -CH₂-CH-), 4.65 (m, 2H, -NH₂), 7.09-7.24 (m, 5H, aromatic protons); Elementary analysis: C, 51.40%; H, 7.27%; N, 16.60%.

Poly(acrylamide-4-fluorostyrene) [poly(AAm-St-F)] was synthesized from AAm (17.06 g, 0.24 mol), St-F (2.93 g, 0.024 mol), AIBN (0.5 g), and dioxane (105 mL) in a manner similar to the synthesis of polyAAm.

Product characterization: white powder; yield 90%; FTIR peaks at 3198 (N-H stretch), 2932 (C-H stretch), 1664 (C=O stretch), 1450 (CH₂ deformation); ¹H NMR (D₂O) peaks at δ 1.48-1.58 (4H, -CH₂-CH-), 2.02-2.34 (2H, -CH₂-CH-), 4.62 (2H, -NH₂), 7.09-7.24 (m, 4H, aromatic protons); ¹⁹F NMR (D₂O) peak at δ -115.5 ppm (s, 1F, -benzene-F); Elementary analysis: C, 51.70%; H, 6.97%; N, 16.14%.

Characterization. Fourier transform infrared (FT-IR) spectroscopy was performed on KBr pellets with a Bio-Rad Co. digilab FTS-165. ¹H NMR and ¹⁹F NMR spectra were determined using a Bruker Co. DRX300 spectrometer operating at 500 MHz with D₂O as the solvent. An elemental analyzer (CE EA-1110) was used in the elemental (C, H, N) analyses of the polymers.

Polymer films were prepared by placing a 5 wt% aqueous solution of the polymer onto slide glass and by allowing it to dry at room temperature. The contact angle between the polymer film and the dropped LC was measured at a temperature of 20 ± 1 °C using the sessile drop method with a Surface & Electro-Optic Co. SEO 300A. For each sample, every calculated contact angle was an average of 10 measurements with a standard deviation below 1°.

The ratio of polymer to LC was fixed at 100:65 (w/w). Polymer (4.5 g) was dissolved in water (25.5 g) to prepare an aqueous solution of polymer, and then LC was added to the solution. The LC-in-polymer solution was mixed at 3000 rpm for 5 min and then stored for 24 h to degas. The solution was cast onto indium tin oxide (ITO) glass, and then allowed to dry at room temperature for 24 h. The thickness of final film was maintained within 10 mm using an applicator. The electro-optical properties of the PDLC films were investigated using an LCMS-100 (Sesim Photonics Technology of Korea).

The PDLC film was fractured in liquid nitrogen, and then the LC was extracted with hexane at room temperature over

Table 1. Elementary analysis of polymers

Polymer	Calculated (%)			Found (%)		
	C	H	N	C	H	N
PolyAAm	50.73	7.04	19.72	44.69	7.07	17.30
Poly(AAm-St)	56.52	7.13	16.96	51.40	7.27	16.60
Poly(AAm-St-F)	54.80	6.85	16.83	51.70	6.97	16.14

the course of 3 h. The fracture surface of the PDLC films was examined using a scanning electron microscope (SEM, JEOL JXA 840A).

Results and Discussion

Acrylamide-based polymers containing various hydrophobic moieties, that is, polyAAm, poly(AAm-St), and poly(AAm-St-F), were synthesized by polymerization of acrylamide or acrylamide with styrene or 4-fluorostyrene in the presence of an AIBN initiator. The synthetic mechanism of the polymers is shown in Scheme 1. All of the synthesized polymers in this work were soluble in water. The chemical structure of the resulting polymers was characterized by FT-IR, ¹H NMR, ¹⁹F NMR spectroscopy, and elementary analysis. The results of the elementary analysis are shown in Table 1. The actual carbon content of the polymers was found to be lower than that indicated by the calculated data.

Figure 2 shows the FT-IR spectra of polyAAm and poly(AAm-St-F). Both spectra exhibited intense IR signals

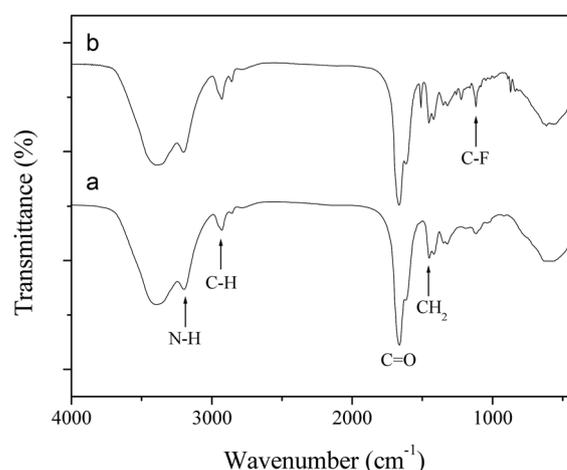
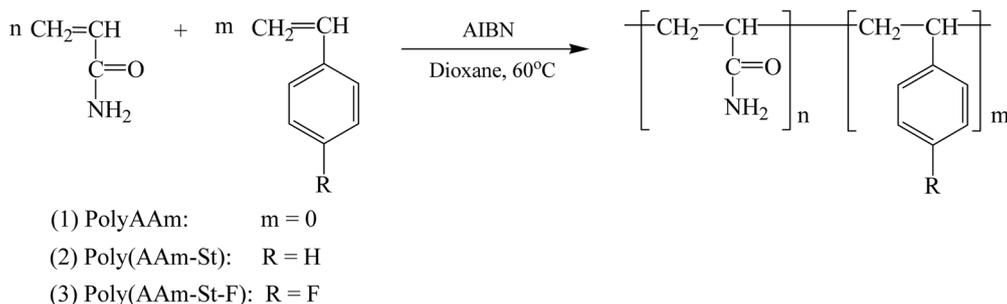


Figure 2. FT-IR spectra of (a) polyAAm and (b) poly(AAm-St-F).



Scheme 1. Synthetic mechanism of acrylamide-based polymers.

at 3198 and 1663 cm^{-1} , easily attributed to the N-H and C=O stretch of the amide. The absorption bands at 2932 and 1450 cm^{-1} can be ascribed to the C-H stretch and CH_2 deformation. In the poly(AAm-St-F) spectra, the characteristic band at 1118 cm^{-1} is the evidence of the C-F stretch.¹⁶

Regarding the ^1H NMR spectra (D_2O), the chemical shifts at 1.48-1.582 and 2.02-2.34 belong to the CH_2 and CH protons, respectively. The chemical shifts at 4.62 and 6.92-7.03 can be attributed to the NH_2 protons and the aromatic ring, respectively. Concerning the ^{19}F NMR spectra (D_2O), the chemical shift at -115.5 ppm corresponds to the C-F group. The structural characterization of FT-IR, ^1H NMR, ^{19}F NMR, and EA confirmed the chemical structure of the polymers studied in the present work.

The contact angle value presents the compatibility of the polymer with the LC. The partial compatibility between the polymers and the LC was studied by means of contact angle measurements. In the result, the contact angles of the polyAAm, poly(AAm-St), and poly(AAm-St-F) were 31, 22, and 25°, respectively. It was clear that the partial compatibility of the polymers with the LC was significantly increased by the addition of hydrophobic moieties. This result indicates that LC molecules are oriented with their nonpolar groups toward the hydrocarbon segment of the polymer chains.¹⁵ The presence of hydrophobic moieties in polymer chains can cause various intra- and intermolecular interactions. The contact angle of poly(AAm-St-F) is higher than that of poly(AAm-St), due to the lower surface energy of the fluorine atoms in poly(AAm-St-F).⁹ Upon addition of a fluorine functional group to the polymer chains, the affinity between the polymer chains and the LC decreases. This decreased affinity plays an important role in the electro-optical properties of PDLC films.

In the present study, PDLC films were manufactured with various polymer/LC mixtures, and the effect of the fluorine group on the electro-optical properties of the films was investigated.

Figure 3 shows the electro-optical properties of the PDLC films as a function of applied voltage measured at ambient

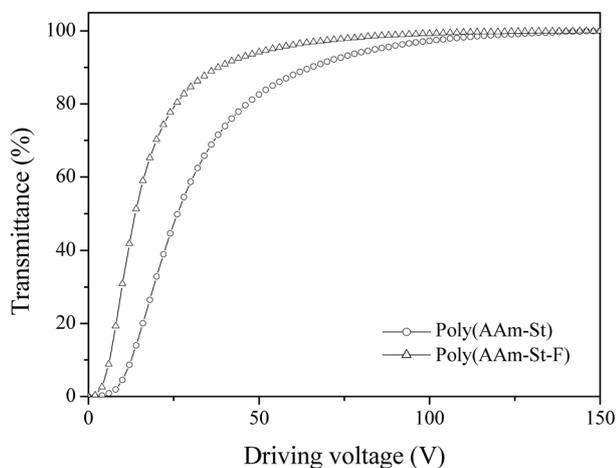


Figure 3. Transmittance of PDLC films as a function of applied voltage.

Table 2. Electro-optical properties of PDLC films

Polymer	T10 (V)	T50 (V)	T90 (V)
Poly(AAm-St)	12.5	26.1	65.3
Poly(AAm-St-F)	6.2	13.7	38.0

temperature. The transmittance of the PDLC films dramatically increased with increasing applied voltage. The electro-optical properties, such as the applied voltages for 10, 50, and 90% transmittance, are summarized in Table 2. The applied voltages for 10, 50, and 90% transmittance of poly(AAm-St-F) film are significantly lower than those of poly(AAm-St) film. The results can be explained by reference to anchoring energy.

The anchoring energy at the polymer-LC interface can be determined according to the contact angle, as follows.^{4,17}

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta \quad (1)$$

$$W_A = \gamma_S + \gamma_L - \gamma_{SL} \quad (2)$$

$$= \gamma_L (1 + \cos \theta) \quad (3)$$

where γ_S , γ_L , and γ_{SL} are the surface tension for a solid, that for a liquid, and the interfacial tension between a liquid and a solid, respectively. W_A is the anchoring energy between the polymer and the LC, and θ is the contact angle.

$$\frac{W_{A2}}{W_{A1}} = \frac{1 + \cos \theta_2}{1 + \cos \theta_1} = \frac{1 + \cos 25^\circ}{1 + \cos 22^\circ} = 0.98 \quad (4)$$

where W_{A1} and W_{A2} are the anchoring energy between the poly(AAm-St) or poly(AAm-St-F) and the LC, respectively. θ_1 and θ_2 are the contact angle of poly(AAm-St) and poly-

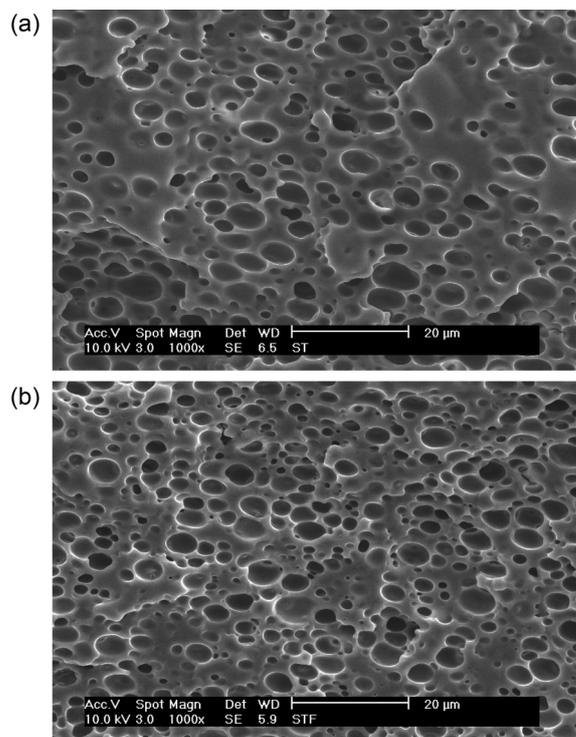


Figure 4. SEM photographs of polymer/LC films after extraction of LC with *n*-hexane: (a) poly(AAm-St) and (b) poly(AAm-St-F).

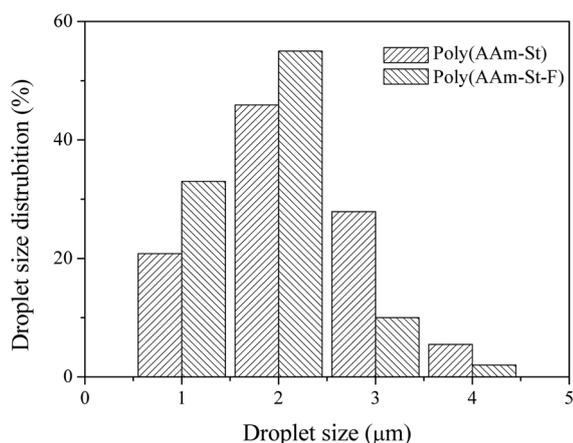


Figure 5. LC droplet size distribution of polymer/LC films after extraction of LC with *n*-hexane.

(AAm-St-F).

According to the result of calculation, the poly(AAm-St-F) film showed a lower anchoring energy at the polymer-LC interface than did the poly(AAm-St) film. This was probably due to introduction of the fluorine group into the polymer chains, which thereby reduced the anchoring energy and the domain size, resulting in an enhancement of the electro-optical properties in the poly(AAm-St-F) film.^{9,18}

To further investigate the effect of the fluorine group on the electro-optical properties, the morphology of the PDLC films, after removal of the LC by extraction with *n*-hexane, was examined by SEM method. The SEM micrographs of the PDLC films are shown in Figure 4. Figure 5 presents the LC droplet size distribution of polymer/LC films. It can be seen that the size of the LC droplet in the polymer matrix can depend markedly on the films made with the polymers. In PDLC films, LC size and shape are the most important factors determining the electro-optical performance of the films. In poly(AAm-St) film, the LC droplets are irregular in shape and irregularly dispersed in the polymer matrix, as shown in Figures 4(a) and 5. However, as shown in micrograph of poly(AAm-St-F) [Figures 4(b) and 5], the LC droplets are spherical and dispersed uniformly in the polymer matrix. The introduction of a fluorine group into

polymer chains leads to a decrease of the surface free energy of the polymer, resulting in increased interfaces between the polymer and the LC molecules.⁹

In conclusion, the partial compatibility of the acrylamide-based polymers with the LC was significantly increased by the addition of hydrophobic moieties. The presence of a fluorine functional group in the polymer structure led to a significant improvement in the electro-optical properties of the PDLC film. The SEM results indicated that poly(AAm-St-F)-based PDLC film has a reduced LC droplet size and thereby improved electro-optic properties in comparison with those of poly(AAm-St).

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