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## Liquid Crystals

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**To cite this Article** Nakazawa, Yukihito and Sasaki, Takeo(2006) 'Photorefractive effect in composites of ferroelectric liquid crystal and photoconductive polymer', *Liquid Crystals*, 33: 2, 159 – 165

**To link to this Article:** DOI: 10.1080/02678290500450857

**URL:** <http://dx.doi.org/10.1080/02678290500450857>

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# Photorefractive effect in composites of ferroelectric liquid crystal and photoconductive polymer

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(Received 16 June 2005; in final form 27 September 2005; accepted 4 October 2005)

The photorefractive effect in composites of a ferroelectric liquid crystal (FLC) and several photoconductive polymers was investigated. The photorefractivity of mixtures of photoconductive polymers and an FLC (polymer/FLC), as well as that of photoconductive-polymer-stabilized ferroelectric liquid crystals (PPS-FLCs) was examined. The polymer/FLC samples exhibited two-beam coupling gain coefficients of about  $6\text{--}12\text{ cm}^{-1}$  in a  $5\text{ }\mu\text{m}$  gap cell. The photopolymerization of a methacrylate monomer in the FLC medium established a polymer-stabilized state in which the alignment of FLC molecules was mechanically stabilized. The noise in a two-beam coupling signal was reduced significantly in the PPS-FLC samples.

## 1. Introduction

The photorefractive effect is defined as the optical modulation of the index of refraction due to a charge redistribution [1–3]. An organic photorefractive material is typically composed of several compounds. The components necessary for the photorefractive effect are a photoconductive compound, an electron-trap reagent and a material that exhibits an electro-optic effect. The interference of two laser beams in a photorefractive material induces charge generation at the light positions of the interference fringes. In common organic compounds, the mobility of electrons is much smaller than that of holes. While the electrons stay in the light areas, photo-generated holes are dispersed through diffusion or drift to positions throughout the material. Consequently, the light positions of the fringes are charged negatively while the dark positions are charged positively. An internal electric field is thus formed at the areas between the light and the dark positions. An electro-optic effect is induced by this internal electric field, and the refractive index of the areas between the light and the dark positions is altered. Thus, a refractive index grating is formed along the interference fringes.

A characteristic of the photorefractive effect is that the phase of the refractive index grating is shifted from the interference fringes. The phase-shifted refractive index grating affects the propagation of interfering laser

beams, and the intensity of one beam increases while that of the other beam decreases. This phenomenon is known as asymmetric energy exchange in photorefractive two-beam coupling. The photorefractive effect in organic materials has been studied extensively since 1990 [4]. The photorefractivities of glassy polymers [5–8], low-molecular mass LCs [9–17], polymer LCs [18–20], and amorphous compounds [21, 22] have been previously examined and reported.

In earlier studies, the photorefractive effect in FLCs mixed with low-molecular-mass photoconductive compounds was investigated [23–25]. FLCs exhibit spontaneous polarization and are known to be sensitive to electric fields. When laser beams interfere in an FLC mixed with a photoconductive compound, the direction of spontaneous polarization is governed by the internal electric field. A refractive index grating is formed through an orientation change of the FLC molecules according to the direction of spontaneous polarization. The FLCs exhibit photorefractivity only at the temperature at which the materials exhibit a ferroelectric phase (SmC\*).

In this study, we investigated the photorefractivity of FLC/photoconductive polymer composites. Two types of composites, (1) an FLC simply mixed with photoconductive polymers (polymer/FLC), and (2) a polymer-stabilized FLC (PPS-FLC) in which a photoconductive monomer is photopolymerized, were examined. The two types are shown in figure 1. The magnitude of the two-beam coupling gain coefficients

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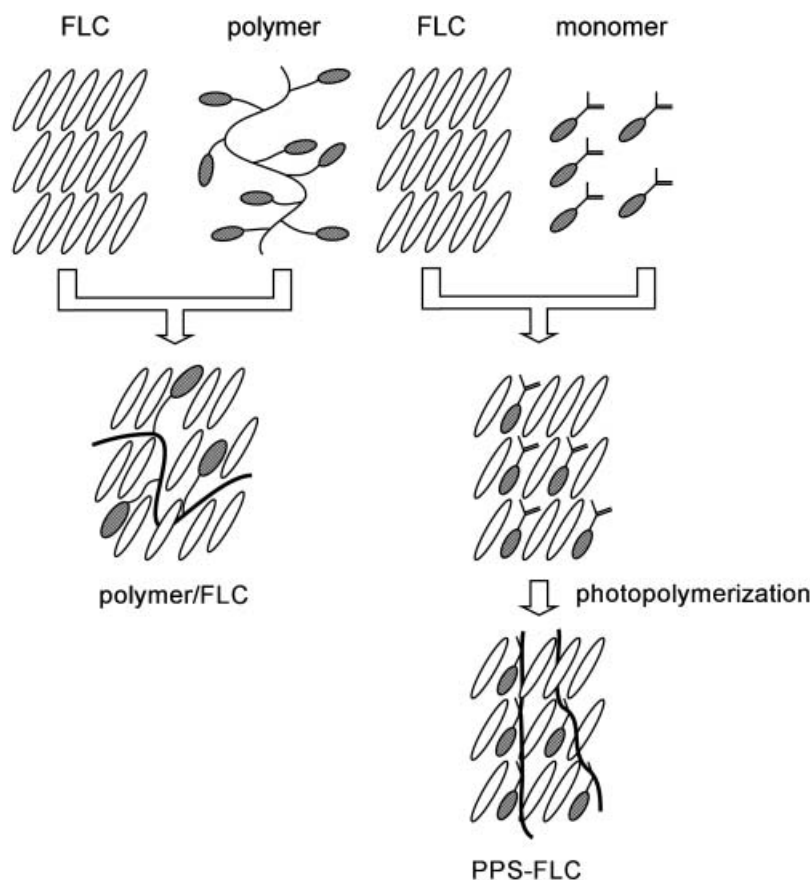


Figure 1. Illustration of the polymer/FLC and the PPS-FLC.

are discussed with reference to the morphology of the composites.

## 2. Experimental

### 2.1. Samples

A commercially available FLC, FELIX-M4851/050 (Clariant Co.,  $P_s = -14 \text{ nC cm}^{-2}$ , SmC\* 65 SmA 70 N\* 73 I, °C) was used in this study. Figure 2 shows the structures of the photoconductive side chain polymers and the monomer used. The molecular masses and glass transition temperatures of the polymers are listed in table 1. The polymer-stabilized FLC samples were prepared as follows. Mixtures of FLC, a photoconductive monomer (5.0 wt%), a sensitizer (TNF, 0.1 wt%) and a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (Sigma-Aldrich Inc., 0.05 wt%) were injected into glass cells equipped with  $1 \text{ cm}^2$  ITO electrodes and a polyimide alignment layer (cell gap: 5 and  $10 \mu\text{m}$ ). In order to obtain a highly ordered SS-state, the samples were heated to the isotropic phase, and then deliberately cooled to ambient temperature. After the thermal treatment, the samples were photocured using a

500 mW high pressure mercury lamp at 365 nm for 300 s.

### 2.2. Measurements

The textures of SS-states and the switching angles of the samples were observed using a polarizing optical microscope (Olympus BX-50, Mettler FP-80 and FP-82, Kenwood PW36-1). The two-beam coupling experiment was performed using a p-polarized  $\text{Ar}^+$  laser (Laser Graphics, 165LGS-S, 488 nm, continuous wave). The intensity of the laser was 2.5 mW for each beam (1 mm diameter). A schematic illustration of the experimental set-up is shown in figure 3. The beam was divided into two by a beam splitter and the beams were then allowed to interfere in the sample film. The transmitted intensities of the two beams were measured by photo-detectors. The angle between the two incident beams was set to  $20^\circ$  producing an interference fringe interval ( $A$ ) of  $1.87 \mu\text{m}$  ( $n=1.65$ ). In order to increase the efficiency of charge separation, an external d.c. electric field of  $3.0 \text{ V } \mu\text{m}^{-1}$  was applied to the sample.

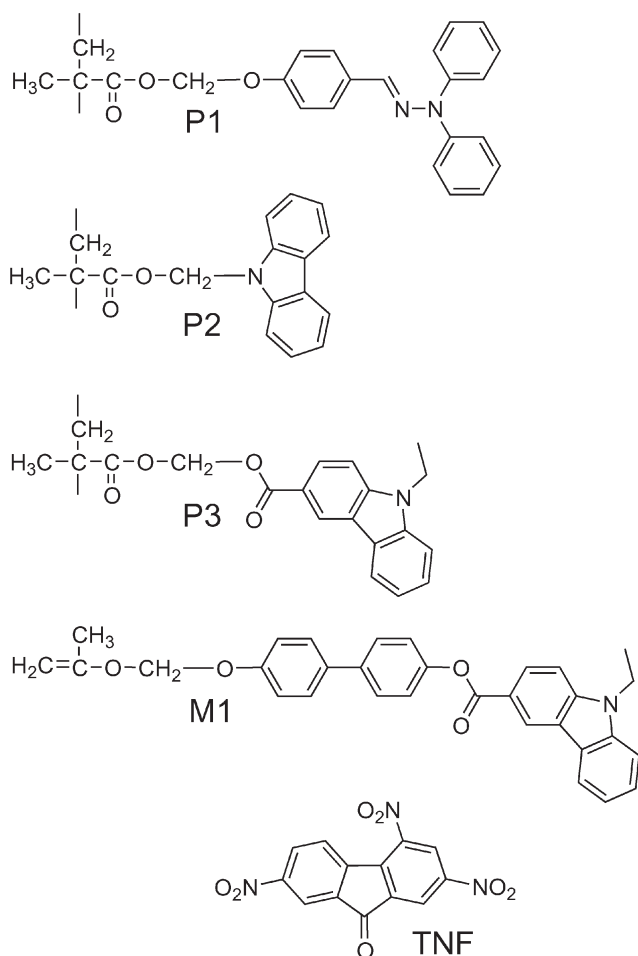


Figure 2. Molecular structures of the photoconductive polymers (P1, P2, P3), a photoconductive monomer (M1) and a sensitizer (TNF).

### 3. Results and discussion

#### 3.1. Photorefractive effect in polymer/FLC samples

A typical example of the two-beam coupling signal observed for a P2/FLC sample is shown in figure 4. The interference of the laser beams in the sample resulted in increased transmitted intensity for one of the beams and decreased transmitted intensity for the other. An asymmetric energy exchange was observed only when an external electric field was applied, indicating that beam coupling was not caused by a thermal grating. As  $Q=2\pi\lambda L/nA^2=3\sim 6$  ( $\lambda$ , wave length;  $L$ , interaction path

Table 1. Properties of the three polymers used in this study.

Polymer	$M_n$	$M_w$	$M_w/M_n$	$T_g/^\circ\text{C}$
P1	20400	62600	3.08	75
P2	15300	28500	1.86	75
P3	20100	62000	3.08	78

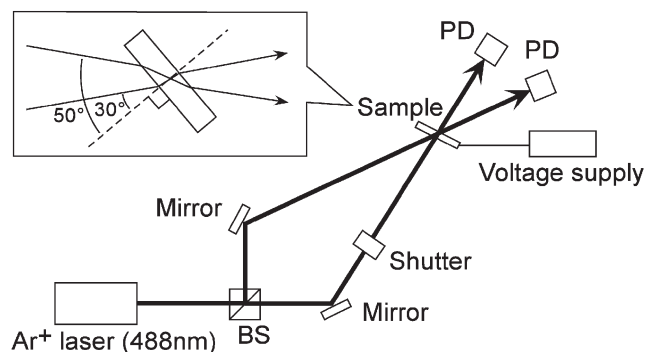


Figure 3. Schematic illustration of the set-up for the two-beam coupling experiment.

length;  $n$ , refractive index;  $A$ , grating spacing), the diffraction observed in this experiment was in the Bragg regime [1]. The energy exchange between the two beams is characterized by the two-beam coupling gain coefficient,  $\Gamma$ , which is calculated according to:

$$\Gamma = \frac{1}{D} \ln \left( \frac{gm}{1+m-g} \right) \quad (1)$$

where  $D=L/\cos\theta$  is the interaction path length for the signal beam ( $L$ =sample thickness,  $\theta$ =propagation angle of the signal beam in the sample),  $g$  is the ratio of intensities of the signal beam behind the sample with and without a pump beam, and  $m$  is the ratio of the beam intensities (pump/signal) in front of the sample.

Figure 5 shows the polarizing optical microscopy (POM) photomicrographs of the polymer/FLC samples. The polymer/FLC in a  $10\mu\text{m}$  gap cell did not form an

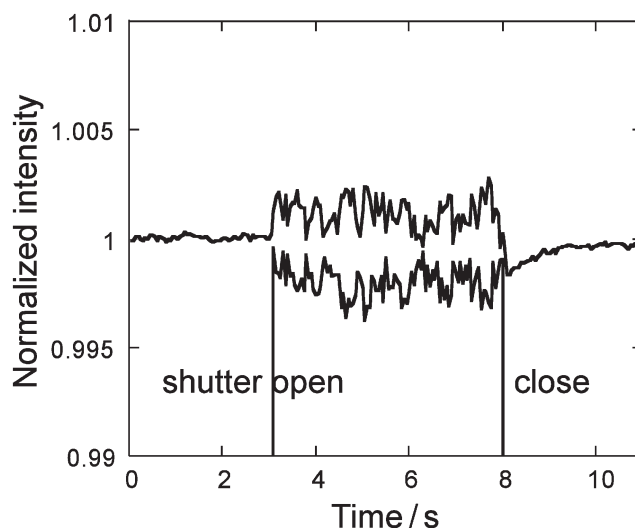


Figure 4. Typical example of the asymmetric energy exchange observed in the FLC mixed with P2 (0.5 wt%) and TNF (0.1 wt%). The sample temperature was  $52^\circ\text{C}$  and an electric field of  $0.2\text{ V}\mu\text{m}^{-1}$  was applied.



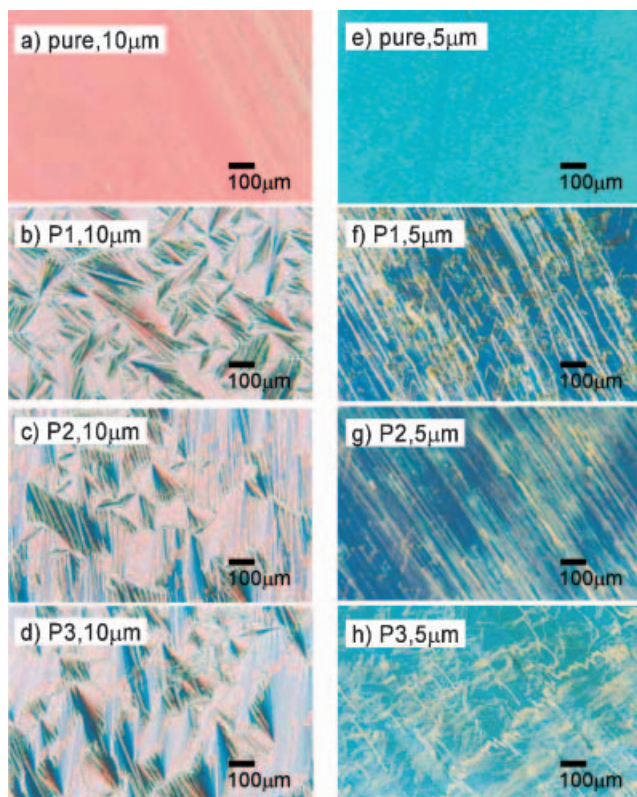


Figure 5. POM photomicrographs of mixtures of the photoconductive polymer (0.5 wt%), TNF (0.1 wt%) and FLC (FELIX-M4851/050) in a 10  $\mu\text{m}$  gap cell (*a-d*) and a 5  $\mu\text{m}$  gap cell (*e-h*). (*a, e*): Pure FLC; (*b, f*): P1-mixture; (*c, g*): P2-mixture; (*d, h*): P3-mixture.

SS-state, and fan-shaped textures were observed. Light scattering was very severe in this 10  $\mu\text{m}$  sample and it was impossible to measure the photorefractivity. On the other hand, the polymer/FLC in a 5  $\mu\text{m}$  gap cell did form an SS-state. As shown in figure 6, the switching angles of the FLC molecules of the polymer/FLC were found to be almost the same as that for the pure FLC.

Figure 7 shows the temperature dependence of spontaneous polarization ( $P_s$ ) of the polymer/FLC samples. The magnitudes of the  $P_s$  of the polymer/FLC samples were smaller than that for the pure FLC. The  $P_s$  in polymer/FLC vanished at 64°C. This temperature was almost the same as that for pure FLC indicating that the polymers are not miscible with the FLC at the molecular level.

Figure 8 shows the gain coefficients of the polymer/FLC samples. The gain coefficients of the FLC mixed with P1, P2 and P3 were measured to be about 12, 7 and 6  $\text{cm}^{-1}$ , respectively. The difference in gain coefficients between P1, P2 and P3 is probably due to the differences in the photoconductive chromophores. The gain coefficients were almost the same in P2/FLC and

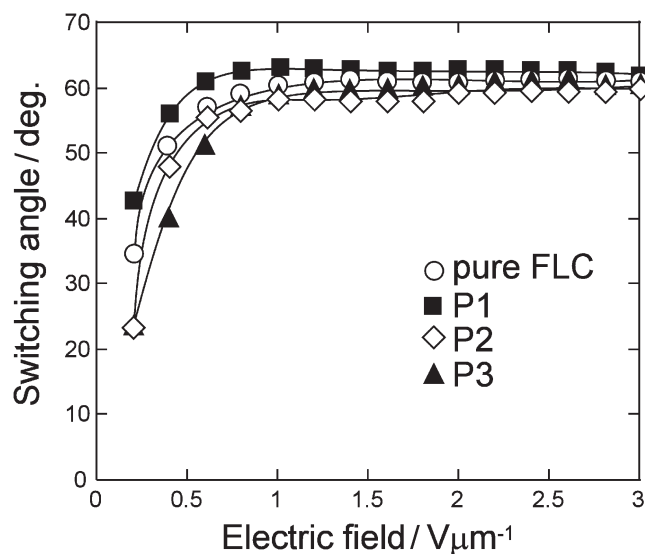


Figure 6. Electric field dependence of the switching angles for the polymer/FLC samples and pure FLC.

P3/FLC. The FLC sample mixed with a 0.5 wt% low-molar-mass photoconductive material (CDH) exhibited a gain coefficient of 4  $\text{cm}^{-1}$  in the 10  $\mu\text{m}$  gap cell. Although the introduction of a polymer into an FLC results in a large number of defects in the SS-state, the magnitude of the gain coefficient was almost comparable to that for the CDH/FLC samples. It is likely that a larger photoconductivity of the polymer compensates for the low homogeneity of the SS-state.

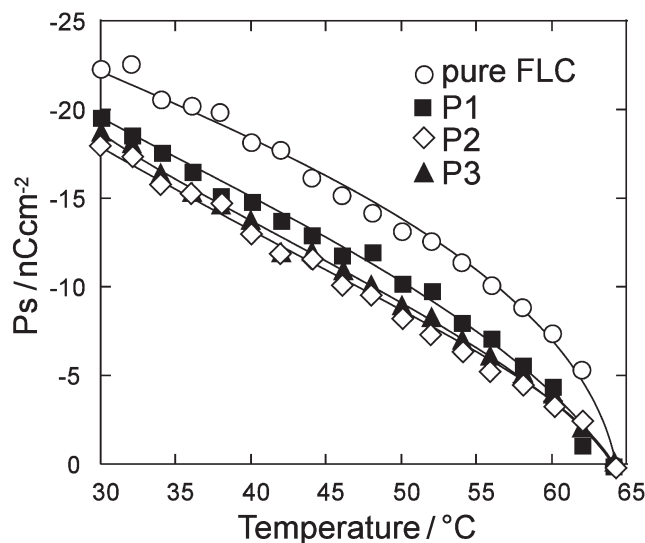


Figure 7. Temperature dependence of the spontaneous polarization of pure FLC and polymer/FLC samples.

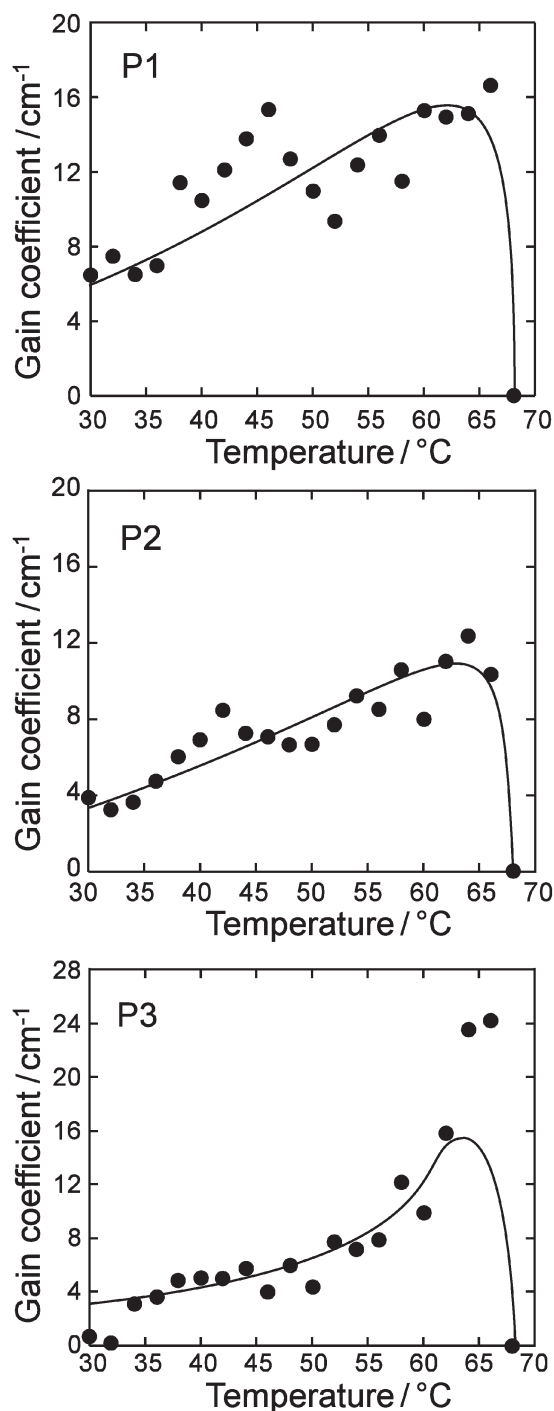


Figure 8. Temperature dependence of the gain coefficients of mixtures of photoconductive polymer (P1–P3), TNF and FLC. The concentration of polymers was 0.5 wt%, and that of TNF was 0.1 wt%. An external electric field of  $0.2 \text{ V } \mu\text{m}^{-1}$  was applied.

### 3.2. Photorefractive effect in PPS-FLC samples

The gain coefficient of an FLC is reduced by the presence of defects in the SS-state because of light

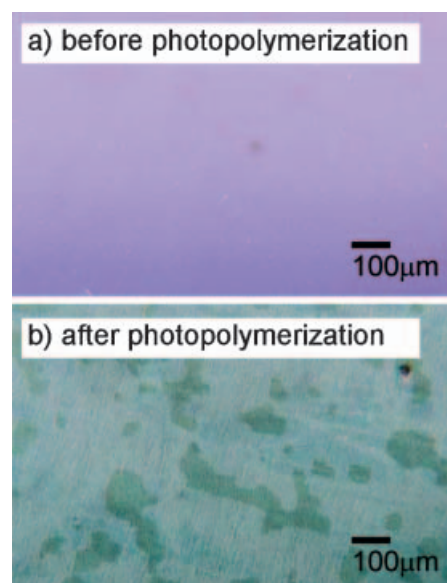


Figure 9. Textures of the photoconductive monomer (5.0 wt%) containing a photoinitiator (0.1 wt%) and TNF (0.1 wt%) mixture before and after photopolymerization.

scattering. Defect-free SS-FLC materials are desirable for a photorefractive material. It has been reported that a defect-free SS-state can be obtained using a polymer-stabilized FLC [26, 27]. The PS-FLC is formed through the photopolymerization of mesogenic acrylate monomer in an SS-state of a FLC in a  $2 \mu\text{m}$  gap cell.

POM photomicrographs of the textures of the FLC mixed with photoconductive monomer M1 before and after ultra violet light irradiation are shown in figure 9.

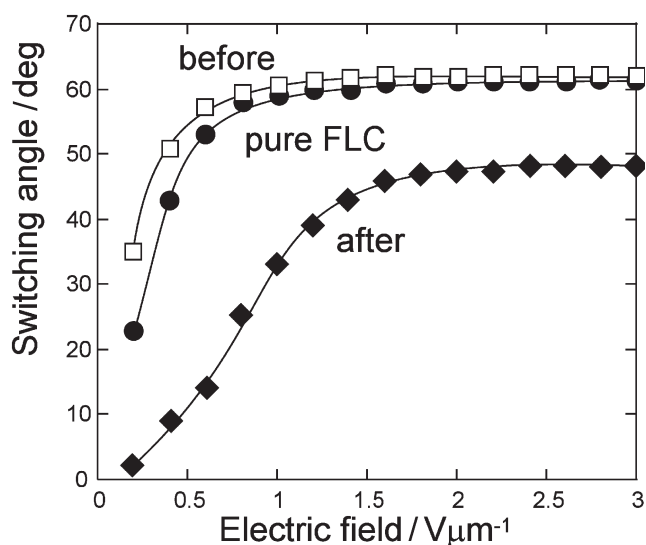


Figure 10. Electric field dependence of switching angles before and after the photopolymerization of the materials, and pure FLC.

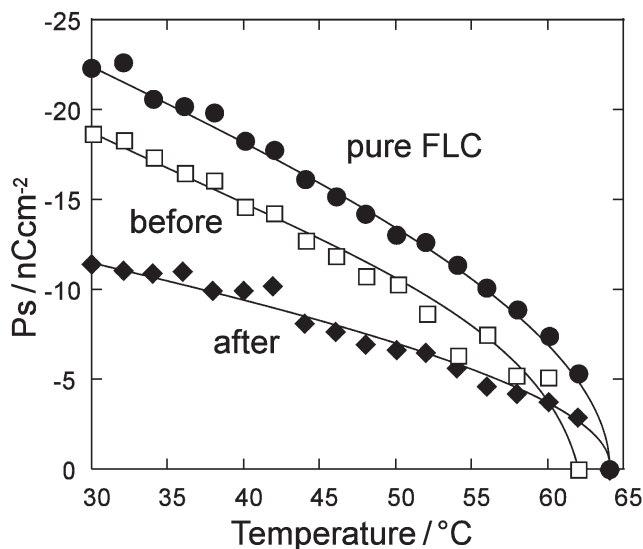


Figure 11. Temperature dependence of the spontaneous polarizations of monomer/FLC mixture before and after photopolymerization, and that of pure FLC.

The SS-state of the monomer/FLC mixture was almost a monodomain, and a highly homogeneous SS-state was retained after irradiation. After the irradiation, a striped texture appeared along the rubbing direction, as a result of the photopolymerization of the photoconductive monomer along the rubbing direction.

The electric field dependence of the switching angle of the PPS-FLC sample is shown in figure 10. A decrease in the switching angle in the FLC was observed after the photopolymerization. The spontaneous polarization of the PPS-FLC material is shown in figure 11. The  $P_s$  of the monomer/FLC mixture vanished at temperatures lower than that of pure FLC; however, the  $P_s$  of pure FLC and PPS-FLC vanished at the same temperature. The difference in the phase transition temperature before and after irradiation indicates that the product polymers aggregate and are excluded from the FLC medium; the  $P_s$  was reduced by photopolymerization. The polymer network formed in the FLC clearly affected the physical properties of the host FLC.

Figure 12 shows typical examples of the asymmetric energy exchange observed in the M1 monomer/FLC mixture before and after UV irradiation. The noise in a two-beam coupling signal was significantly reduced in the PPS-FLC (after photopolymerization) when compared with the monomer-doped FLC (before irradiation). The noise in a two-beam coupling signal is caused by the thermal fluctuation of defects in the SS-state. The fluctuation of defects is considered to be suppressed in a polymer-stabilized FLC. The PPS-FLC material thus exhibited the photorefractive effect even at an applied electric field of  $3.0 \text{ V} \mu\text{m}^{-1}$ , while the

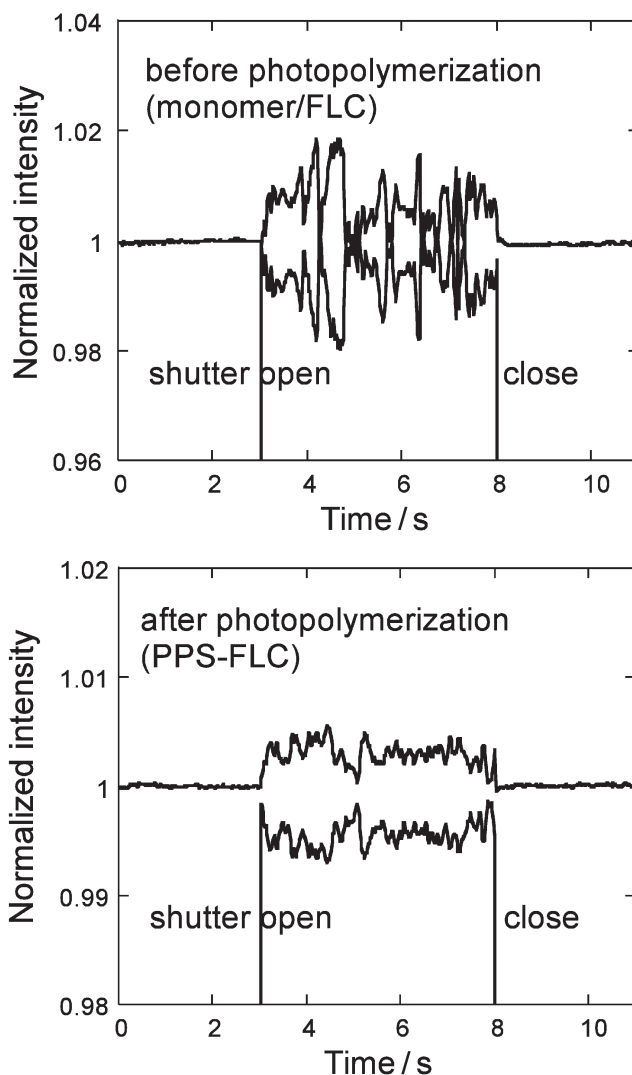


Figure 12. Typical examples of asymmetric energy exchange before and after photopolymerization of the samples. The sample temperature was  $30^\circ\text{C}$  and the applied electric field was  $1.0 \text{ V} \mu\text{m}^{-1}$ .

non-photopolymerized monomer/FLC material did not exhibit clear two-beam coupling at such a high electric field.

#### 4. Conclusions

The photorefractivity of FLC mixed with photoconductive polymers, and that of a PPS-FLC, were investigated using two-beam coupling experiments. The gain coefficients of the polymer/FLC materials were found to be  $6\text{--}12 \text{ cm}^{-1}$  in a  $5 \mu\text{m}$  gap cell. The PPS-FLC material showed a highly homogeneous SS-state and exhibited a two-beam coupling signal with low noise. The PPS-FLC material fabricated by

photopolymerization of a photoconductive monomer in FLC showed tolerance of an external electric field.

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