Photorefractivity of Mixtures of a Ferroelectric Liquid Crystal and Photoconductive Polymers

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The photorefractive properties of mixtures of a ferroelectric liquid crystal and photoconductive polymers were investigated by two-beam coupling experiments. A photorefractive effect based on reorientation of spontaneous polarization was induced in these mixtures. Asymmetric energy exchange was observed in the Bragg diffraction condition and gain coefficients of 10–15 cm^{-1} were obtained. It was found that the internal electric field was efficiently formed in polymer/FLC mixtures.

The photorefractive effect of organic materials has been attracting great interest recently.[1–10] The photorefractive effect is an optical modulation of the refractive index of a material resulting from a number of processes.[1–3] This phenomenon enables us to obtain a dynamic volume hologram that is one of key technologies for the optical signal processing. Materials that exhibit photorefractive effect are comprised of three components: a photoconductive chromophore, an electron trap reagent, and a component that exhibits an electrooptic effect. The interference of two laser beams in a photorefractive material gives rise to a refractive index grating, shifted in phase from the interference pattern by $\pi/2$. The interference induces a charge separation within the material between the light and dark areas of the interference pattern, producing a corresponding space-charge field (internal electric field). This space-charge field in turn leads to a change in the refractive index through an electrooptic effect, producing the refractive index grating.[1–3] The laser beams are themselves diffracted by the induced grating, which results in a change in the intensities of the transmitted beams, the intensity of one beam increases while that of the other decreases —a phenomenon known as asymmetric energy exchange in photorefractive two-beam coupling.

Recently, we have reported the photorefractivity of ferroelectric liquid crystals (FLCs) doped with a small amount of a low-molecular-weight photoconductive compound.[11–13] In FLCs, spontaneous polarization responds to the internal electric field and exhibit very fast photorefractive response. In order to achieve higher photorefractivity, improvement of the charge separation efficiency is necessary. One feasible approach is a incorporation of photoconductive polymers. Ono et al.[14–16] and Golemme et al.[17] have reported the photorefractivity of nematic LC/polymer composites and found that the photorefractivity was greatly enhanced in these composites. In the current study, a two-beam coupling experiment has been carried out on surface-stabilized ferroelectric liquid crystals (SS-FLCs) mixed with photoconductive polymers. Two types of polymers were incorporated and the photorefractivities of those polymer/FLC mixtures were compared. In a polymer/FLC mixture the local concentration of photoconductive chromophore is higher than in monomeric compound/FLC mixtures and is expected to lead to a higher photorefractivity.

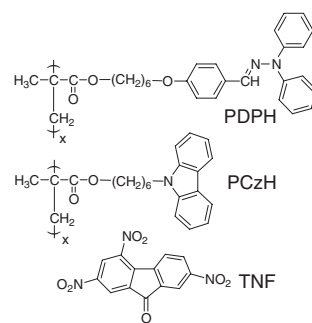The structures of the photoconductive polymers used in this

Figure 1. Structures of compounds used in this study.

Table 1. Properties of polymers used in this study

	M_n	M_w	M_w/M_n	T_g
PCzH	42600	67800	1.59	75.3 °C
PDPH	40300	65100	1.61	75.8 °C

study are shown in Figure 1. The molecular weights and the glass transition temperatures of these polymers are listed in Table 1. TNF (0.1 wt %) was used as a sensitizer/electron trap reagent. The FLC used in this study was FELIX-017/100 (Clariant Co., Sc* → 73 °C → S$_A$ → 77 °C → N* → 87 °C → I, Ps = 47 nC/cm^2). The FLC, polymer and TNF were dissolved in dichloroethane and the solvent was evaporated. The mixture was then dried in a vacuum at room temperature for one week. The samples were injected into a 10-μm-gap glass cell equipped with 1-cm^2 ITO electrodes and a polyimide alignment layer. The photoconductivity was measured using a R8340 ultra high resistance meter (Advantest) and an Ar$^+$ laser (Laser Graphics 165LGS-S, 488 nm, continuous wave, 5 mW). Figure 2 shows the photoconductivity of polymer films and polymer/FLC mixtures. PDPH polymer film doped with 1 wt % of TNF exhibited a large photoconductivity. On the other hand, PCzH film exhibited a low photoconductivity. The difference comes from the π–π stacking of carbazole moieties in the PCzH film. When these polymers are mixed with FLC at the polymer concentration of 0.5 wt %, there was no difference in the photoconductivity between PDPH and PCzH. This indicates that the carbazole moieties of PCzH are well dispersed in the FLC medium at this concentration.

The two-beam coupling experiment was performed with a *p*-polarized Ar$^+$ laser. The beam was divided into two by a beam splitter and interfered in the sample film. Each beam had an intensity of 2.4 mW and a diameter of 1 mm. The angle between the two incident beams was set to 20° (the two beams impinging on the sample at angles of inclination of 40 and 60°), producing a grating spacing (Λ) of 1.9 μm inside the material ($n = 1.65$). An external electric field of 0.2 V/μm was applied to the sample. The measurement condition was in the Bragg regime.[2] The gain coefficients were calculated from the change in transmittance of laser beams in the two-beam coupling experiment.[12] The gain
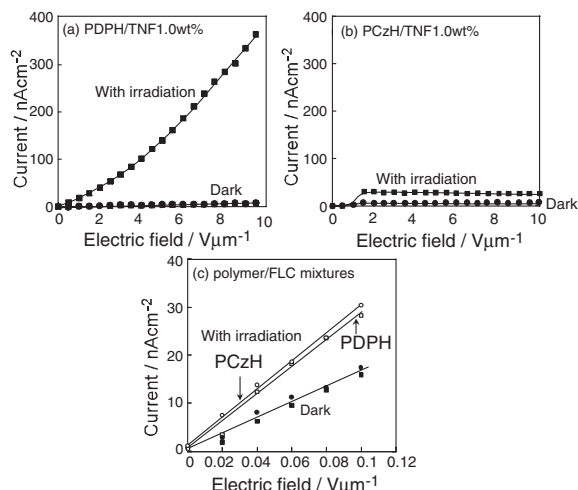
Figure 2. Photoconductivities of the polymers used in this study. (a), (b) Photocurrent of polymer films doped with 1.0 wt % of TNF. The thickness of the films was 100 μm. (c) Photocurrents of polymer/FLC/TNF mixtures in 10-μm-gap cell. The concentration of the polymers were 0.5 wt % and TNF was 0.1 wt %.
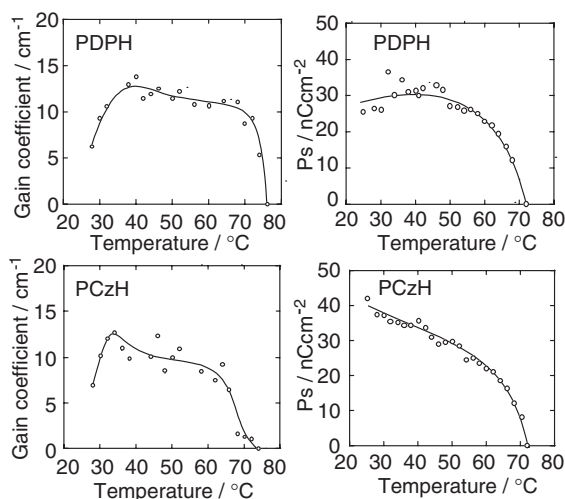

Figure 3. Temperature dependences of gain coefficients and spontaneous polarizations of polymer/FLC/TNF mixtures. Spontaneous polarizations were measured by triangular voltage method.

coefficients and the spontaneous polarizations of polymer/FLC/ TNF mixtures are plotted as a function of temperature in Figure 3. They exhibited photorefractivity only at temperatures where the samples exhibited the ferroelectricity. The results indicate that the photorefractivity of these sample comes from the response of the spontaneous polarization to the photoinduced internal electric field. Decrease in gain coefficient at lower temperatures may be due to an increase in viscosity of the FLC. No difference was observed in the diffraction efficiency between PCzH and PDPH sample. That is consistent with the photoconductivity of those mixtures. The gain coefficient of ca. 14 cm^{-1} for poly-

mer/FLC at the polymer concentration of 0.5 wt % is comparable to that of FLC doped with 2 wt % of low-molecular-weight photoconductive compound (CDH) reported previously (15–30 cm^{-1}).[13] Although the concentration of photoconductive chromophore in polymer/FLC mixture was 1/4 of that of CDH/FLC mixture, the gain coefficient of polymer/FLC mixture was almost the same as that of CDH/FLC mixtures. The higher photoconductivity compensates the low concentration of the polymer. The performance of photorefractive FLC is dominated mainly by the photoconductivity and the homogeneity of the SS-state. Kobayashi et al. have reported the fabrication of polymer stabilized FLC panels.[18] They photopolymerized acrylate monomers in FLC medium and obtained highly homogeneous SS-FLCs. Thus, both high photoconductivity and high homogeneity of SS-state can be achieved by polymerization of photoconductive monomers in a FLC medium.

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