

Spontaneous Polarization Vector Reorientation Photorefractivity in Mixtures of Photoconductive Polymer and Ferroelectric Liquid Crystal

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ABSTRACT: The photorefractive properties of mixtures of a ferroelectric liquid crystal and a photoconductive polymer were investigated by two-beam coupling experiments. A photorefractive effect based on reorientation of spontaneous polarization vector was induced in these mixtures. Asymmetric energy exchange was observed, and gain coefficients of 20–50 cm⁻¹ were obtained. The dependences of the gain coefficient on temperature and external electric field were examined.

Introduction

The photorefractive effect is an optical modulation of the refractive index of a material resulting from a number of processes.^{1–3} Materials that exhibit a 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 modulation, referred to as 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), which in turn leads to a change in the refractive index through an electrooptic effect (the Pockels 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. It has been found that the photorefractivity of organic materials is greater than that of inorganic materials. This is due to a higher Pockels constant in organic materials and a greater ability of the component chromophores to reorientate in the internal electric field.^{4,5} A photorefractive effect induced primarily by chromophoric reorientation is known as the orientational photorefractive effect. Several reports on the photorefractivity of nematic liquid crystals show a high-efficiency orientational photorefractive effect in these materials.^{6–12} Ono et al.¹¹ and Golemme et al.¹² have reported the photorefractivity of nematic LC/Polymer composites and found that the photorefractivity was greatly enhanced in these composites, and a memory effect of the index grating was observed.

Recently, the photorefractive effect of ferroelectric liquid crystals (FLCs) has been reported.¹³ An asymmetric energy exchange of gain coefficient 34–52 cm⁻¹

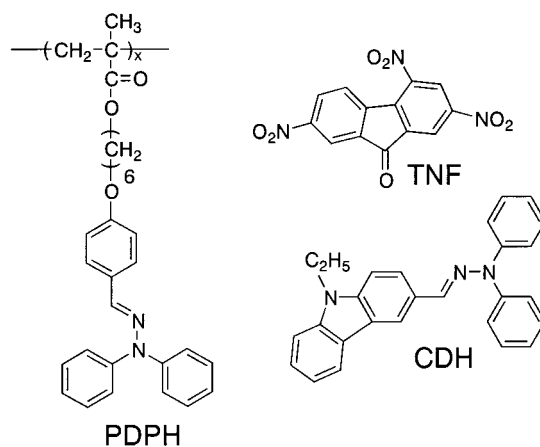


Figure 1. Structures of photoconductive compounds, PDPH and CDH, and electron trap reagent TNF.

was observed when Ar⁺ laser beams (488 nm) were caused to interfere under the application of a 0.1 V/ μ m external electric field in FLCs doped with a small amount of a photoconductive compound (CDH, see Figure 1).^{13c} The photorefractivity of FLCs was observed only at temperatures at which the sample exhibits ferroelectricity. The formation time of the refractive index at 30 °C with the application of 0.3 V/ μ m external electric field was measured to be \sim 30 ms, which is shorter than those measured for nematic LCs. Figure 2 shows a schematic illustration of a proposed mechanism of the photorefractive effect in FLCs. In this proposed scheme the internal electric field alters the direction of the spontaneous polarization in the area between the bright and the dark positions of the interference pattern, and this induces a periodic change in the orientations of FLC molecules. This is a different process than occurs in other photorefractive materials in that the bulk polarization, rather than the molecular dipole, responds to the internal electric field.

In the current study, a two-beam coupling experiment has been carried out on surface-stabilized ferroelectric liquid crystals (SS-FLCs) mixed with a photoconductive polymer. In a polymer/FLC mixture the local concentration of photoconductive chromophore is believed to be higher than in monomeric compound/FLC mixtures, and

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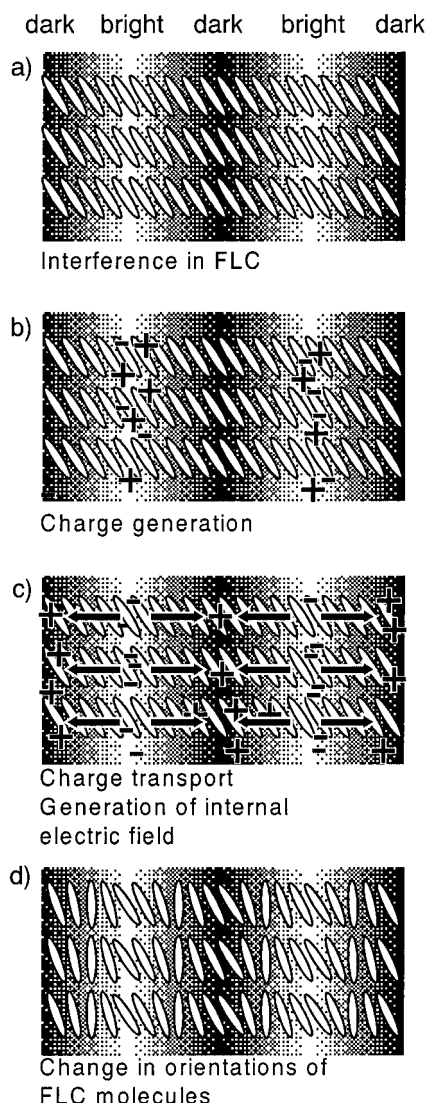


Figure 2. Schematic illustration of the mechanism of the photorefractive effect in FLCs: (a) two laser beams interfere in the photoconductive compound/FLC mixture; (b) charge generation occurs at the bright area of the interference; (c) while the electrons are trapped at the trap site in the bright area, holes migrate by diffusion or drift in the presence of an external electric field and generates an internal electric field between the bright and the dark positions; (d) the orientation of the spontaneous polarization vector (thus the orientations of mesogens) is altered by the internal electric field.

the higher photoconductivity is expected to lead to a higher photorefractivity. The effects on the photorefractivity of temperature, magnitude of external electric field, and the concentration of the polymer are discussed.

Experimental Section

Samples. A commercially available FLC, CS1011 (Chisso Corp., $\text{Ps} = 13.0 \text{ nC/cm}^2$ in $2 \mu\text{m}$ gap cell, phase transition temperatures $\text{Sc}^* 56 \text{ S}_\text{A} 77 \text{ N}^* 91 \text{ I} (^{\circ}\text{C})$) was used in this study. The photoconductive methacrylate polymer, PDPH, used in this study possesses a diphenylhydrazine chromophore in its side chains. The chromophore was synthesized by reacting diphenylhydrazine and 4-alkyloxy-4'-benzaldehyde in pyridine. To increase the miscibility of the polymer with FLCs, a flexible spacer was incorporated between the chromophore and the polymer main chain. The number-average molecular weight of PDPH is 12 000 ($M_w/M_n = 1.21$), as measured by gel permeation chromatography (GPC). The sensitizer, TNF, was

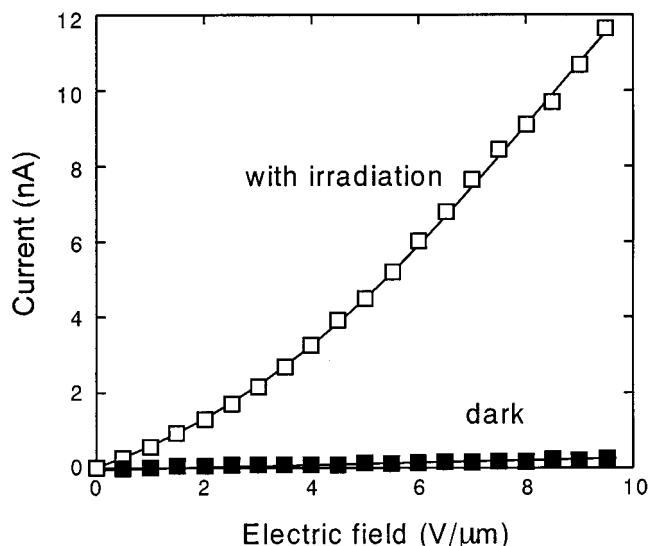


Figure 3. Electric field dependence of photocurrent of PDPH film ($100 \mu\text{m}$ thick) doped with 1 wt % TNF. A beam from an Ar^+ laser (488 nm, CW) of diameter 1 mm and intensity 10 mW was used as the light source. \square , with irradiation; \blacksquare , dark.

obtained from Tokyo Kasei Co. and used without further purification. The structures of PDPH and TNF are shown in Figure 1. Figure 3 shows clear photoconductivity in a PDPH film doped with 1 wt % TNF.

The CS1011, PDPH, and TNF were dissolved in dichloroethane, and the solvent was evaporated. Three samples with PDPH concentrations of 0.5, 1.0, and 2.0 wt % were prepared for the measurement of photorefractivity. The mixture was then dried in a vacuum at room temperature for 1 week. The samples were injected into a $10 \mu\text{m}$ gap glass cell equipped with 1 cm^2 ITO electrodes and a polyimide alignment layer. A $2\text{--}5 \mu\text{m}$ gap cell is typically used to obtain a surface-stabilized FLC;¹⁵ however, the surface-stabilized states of CS1011 samples were established even in the $10 \mu\text{m}$ gap cell.

Photographs of the textures observed in the samples under a polarizing microscope are shown in Figure 4. Zigzag defects are observed in all samples, implying that the CS1011 molecules form a chevron structure.¹⁴ The alignment of the CS1011 molecules was disturbed to some extent by the incorporation of PDPH; however, no phase separation was observed at the concentration of 2 wt % (phase separation was observed at PDPH concentrations exceeding 3 wt %).

Measurement. The two-beam coupling experiment was performed with a p-polarized Ar^+ laser (Laser Graphics 165LGS-S, 488 nm, continuous wave) divided into two by a beam splitter and refocused 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 $1.9 \mu\text{m}$ inside the material ($n = 1.65$). The sample was thermostated using a thermocontroller (Chino Co. DB1000). An electric field of $0\text{--}0.7 \text{ V}/\mu\text{m}$ was applied to the sample from a regulated dc power supply (Kenwood DW36-1). The change in transmitted beam intensity was monitored by a power meter (Advantest, Inc., TQ8210+TQ82014) and recorded by a computer. The photoconductivity was measured using a R8340 ultrahigh-resistance ohmmeter (Advantest). The spontaneous polarizations of the samples were measured by triangular voltage method ($10 \text{ V}_{\text{p-p}}$, 100 Hz).

Results and Discussion

Asymmetric Energy Exchange in PDPH/TNF/CS1011 Mixtures. Figure 5 shows a typical example of asymmetric energy exchange observed in a PDPH/TNF/CS1011 sample with a PDPH concentration of 2

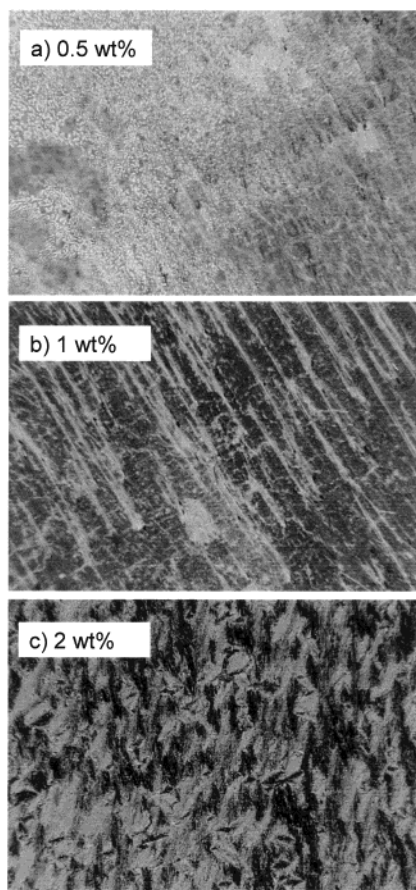


Figure 4. Photographs of the textures of PDPH/TNF/CS1011 mixtures with three different concentrations of PDPH in a 10 μm gap cell observed under polarizing microscope ($\times\sim 40$).

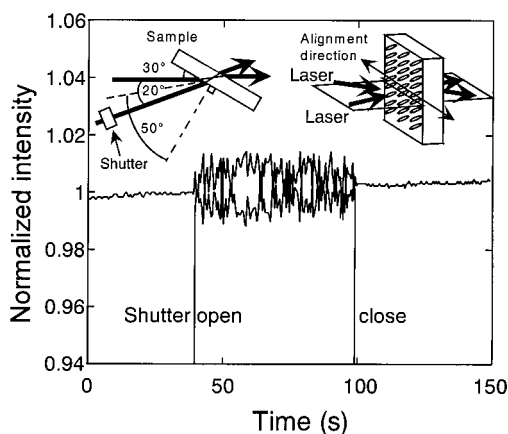


Figure 5. An example of asymmetric energy exchange observed in CS1011 mixed with 2 wt % PDPH and 0.1 wt % TNF. The intensities of the transmitted laser beams in a two-beam coupling experiment normalized at $t = 43$ s (initial beam intensity) are plotted as a function of time.

wt % and an applied electric field of 0.1 V/ μm . The interference of the divided beams in the sample results in an increased transmittance of one of the beams and a decreased transmittance of the other beam. These transmittance characteristics are reversed when the polarity of the applied electric field is reversed. Asymmetric energy exchange was only observed when an electric field was applied, indicating that beam coupling is not caused by a thermal grating. As $2\pi\lambda L/n\Delta^2 > 1$ (L , interaction length = 11 μm), the diffraction observed in this experiment is in the Bragg regime.² The energy

exchange between the two beams is characterized by the two-beam coupling gain coefficient, Γ , which is calculated according to^{1,2}

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

where $D = L/\cos(\theta)$ is the interaction path for the signal beam (L = sample thickness, θ = 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. The gain coefficient at 30 $^{\circ}\text{C}$ was calculated to be 17.4 cm^{-1} for a sample under the application of a 0.1 V/ μm external electric field and 34.0 cm^{-1} for an applied field of 0.2 V/ μm . The total optical loss (including absorption, scattering, reflection, etc.) was found to be 30 cm^{-1} , primarily attributable to reflection. The reflection loss of the LC cell used in this study was large; however, it could be reduced to be less than 5 cm^{-1} by the antireflection coating.

Temperature Dependence of the Gain Coefficient. The temperature dependence of the gain coefficient of PDPH/TNF/CS1011 mixtures at three concentrations of PDPH is shown in Figure 6. For each concentration of PDPH the gain coefficient increases with temperature from 25 $^{\circ}\text{C}$ and shows a maximum at 40–50 $^{\circ}\text{C}$, then decreases at higher temperatures, and vanishes by 55–60 $^{\circ}\text{C}$. No asymmetric energy exchange is observed at the higher temperatures. The spontaneous polarizations of the PDPH/TNF/CS1011 mixtures in the 10 μm gap cell are plotted as a function of temperature in Figure 7. The spontaneous polarization vanishes when the temperature is raised above 55 $^{\circ}\text{C}$. Thus, asymmetric energy exchange was observed only in the temperature range in which the sample exhibits ferroelectric properties (Sc^* phase). Figures 6 and 7 show that the temperature dependences of the gain coefficient and of the spontaneous polarization are similar. This indicates that the photorefractive effect in PDPH/TNF/CS1011 mixtures is caused by the response of the spontaneous polarization to the internal electric field.

Electric Field Dependence of the Gain Coefficient. The dependence of the gain coefficient of PDPH/TNF/CS1011 mixtures on external electric field strength is shown in Figure 8. The gain coefficient increases as the strength of the external electric field increases up to 0.2 V/ μm , above which the gain coefficient becomes constant. This is quite different from the electric field dependence reported for amorphous polymers.^{3,4} In amorphous polymers, the gain coefficient exhibits a \sin^2 dependence on the electric field, consistent with Kogelnik's theory.¹⁵ In PDPH/TNF/CS1011 mixtures, as the external electric field is increased from 0 to 0.2 V/ μm , a greater charge separation is induced and the formation of the orientational grating is enhanced. However, when the external electric field exceeds 0.2 V/ μm , many defects (zigzag defect) appear as increasing the intensity of the external electric field. The defects scatter the laser beam so that the refractive index grating cannot be created clearly under the large external electric field.

Effect of the Concentration of PDPH on the Gain Coefficient. In a previous study, the photore-

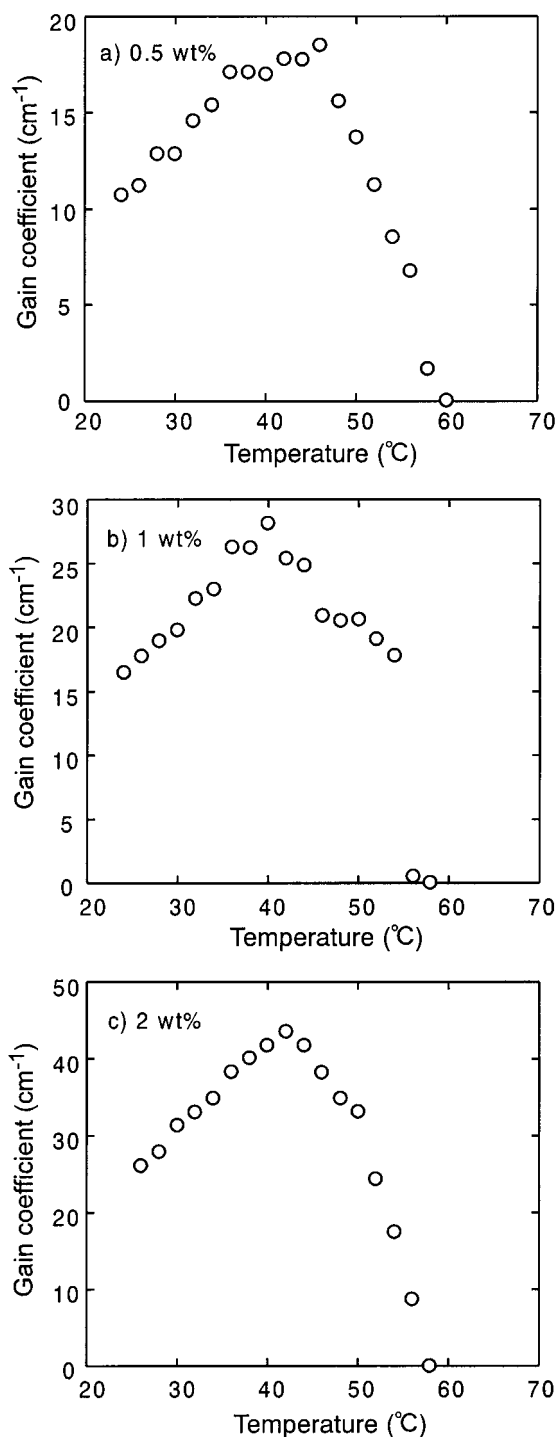


Figure 6. Temperature dependence of gain coefficient of PDPH/TNF/CS1011 mixtures with three different concentrations of PDPH. An electric field of 0.1 V/ μ m was applied to the sample.

fractivity of CS1011 doped with 2 wt % CDH (Figure 1) and 0.1 wt % TNF was investigated, and diffraction efficiencies of 2–3% were measured in samples in 10 μ m gap cells.^{13c} The alignment of the FLC was very fine in these CDH/TNF/CS1011 samples compared to that of the PDPH/TNF/CS1011 samples where the alignment of the FLC molecules is disturbed. Since orientational gratings with higher contrast can be created in finely aligned samples, it is expected that the gain coefficient would be lower in PDPH/TNF/CS1011 samples. However, there was no significant difference in the gain coefficient between PDPH/TNF/CS1011 and CDH/TNF/

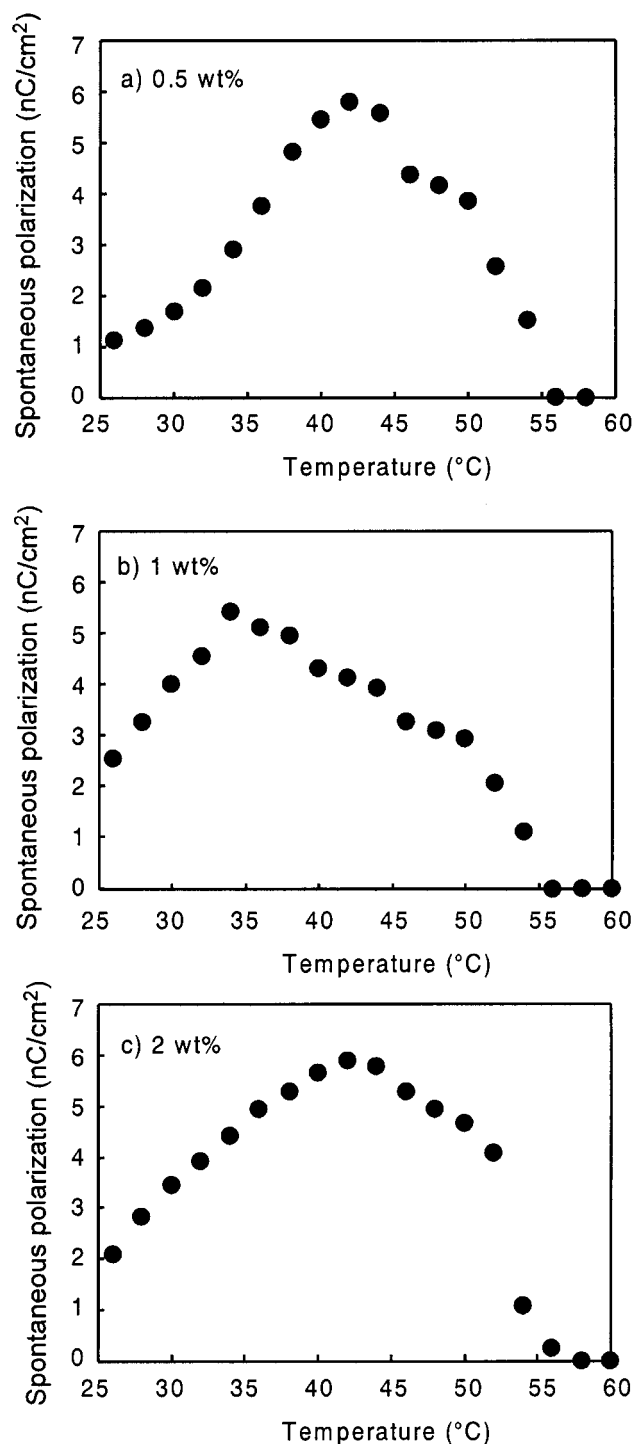


Figure 7. Temperature dependence of spontaneous polarization of PDPH/TNF/CS1011 mixtures with three different concentrations of PDPH measured by the triangular voltage method (100 Hz, 10 V_{p-p}) in a 10 μ m gap cell.

CS1011. However, the local concentration of the photoconductive chromophore is higher in polymers such as PDPH; hence, charge separation is more effective in PDPH/TNF/CS1011 than in CDH/TNF/CS1011. It is believed that the higher photoconductivity compensates for the poorer alignment of FLC molecules in the PDPH/TNF/CS1011 samples.

Conclusion

The photorefractivity of mixtures of a ferroelectric liquid crystal and a photoconductive polymer was

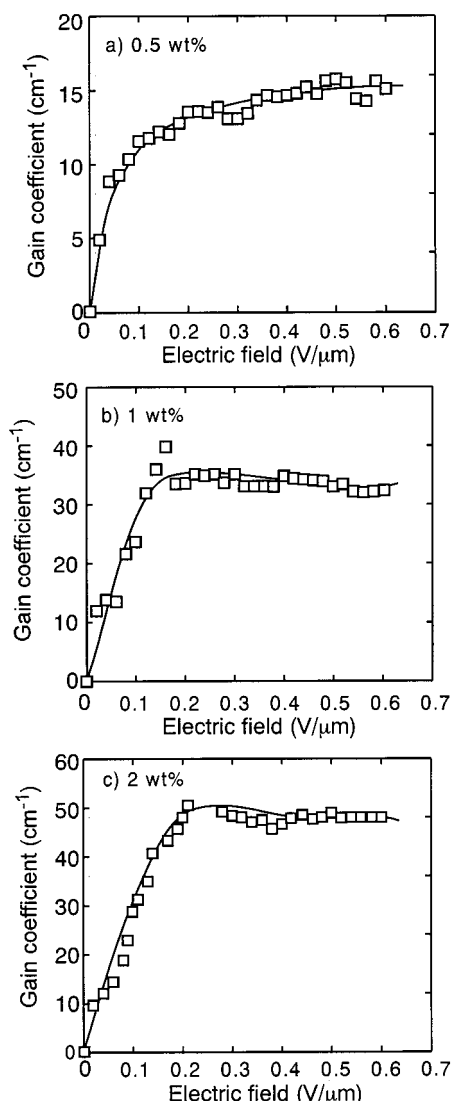


Figure 8. Electric field dependence of gain coefficient of PDPH/TNF/CS1011 mixtures with three different concentrations of PDPH measured at 30 °C.

investigated through two-beam coupling experiments. The orientational photorefractive effect was observed in

these mixtures. That the photorefractivity was only observed in the ferroelectric phase of the samples indicates that the mechanism responsible for refractive index grating formation in FLCs is a change in the spontaneous polarization vector induced by the internal electric field. The low gain coefficients observed in PDPH/FLC mixtures were due to the low solubility of polymer to FLC. The gain coefficient can be improved by the optimal choice of the photoconductive polymer/FLC combinations. Since the photoconductivity of polymers is higher than that of monomeric chromophores, it can be concluded that photoconductive polymer/FLC systems have a greater potential as high-performance photorefractive materials.

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