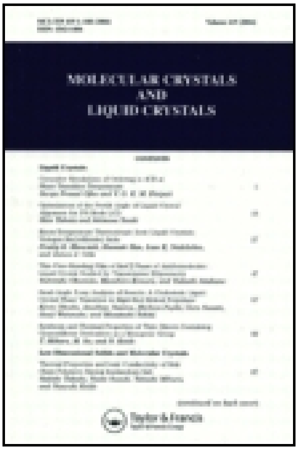

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Spontaneous Polarization Reorientation Photorefractive Effect in Ferroelectric Liquid Crystals

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SPONTANEOUS POLARIZATION REORIENTATION PHOTOREFRACTIVE EFFECT IN FERROELECTRIC LIQUID CRYSTALS

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The photorefractive effect of a series of low-molecular-weight ferroelectric liquid crystals (FLCs) doped with photoconductive compounds was investigated using two-beam coupling experiments. Asymmetric energy exchange was observed only in the ferroelectric phase, and the refractive index formation time was found to be ~30 ms, which is faster than that of nematic photorefractive LCs. These results indicate that the mechanism of the photorefractive effect in FLCs is different from that in nematic LCs. The photorefractivity of a photoconductive polymer and FLC mixture was also investigated, and the effects of temperature, the strength of the applied electric field and spontaneous polarization on the diffraction efficiency were examined.

Keywords: ferroelectric liquid crystals; photorefractive effect; spontaneous polarization

1. INTRODUCTION

The photorefractive effect is defined as the optical modulation of the refractive index of a medium as a result of a number of processes. The interference of two laser beams in a photorefractive material establishes a refractive index grating. The mechanism responsible for the formation of this refractive index grating is the generation of a space-charge field (internal electric field) due to charge separation between bright and dark areas of the interference and a subsequent change in the refractive index via an electrooptic effect (Pockels effect). A characteristic of the

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photorefractive effect is that the phase of the refractive index grating is shifted by $\pi/2$ from the interference pattern [1–3]. The laser beams are themselves diffracted by the grating, resulting in a change in the intensities of the transmitted beams; the intensity of one beam appears to increase while that of the other appears to decrease. This phenomenon is known as asymmetric energy exchange in photorefractive two-beam coupling. One class of materials that exhibit high diffraction efficiency are glassy photoconductive polymer materials doped with high concentrations of NLO compounds. These materials have been studied extensively [4–13] and have been shown to exhibit high diffraction efficiency (η) under the application of a $\sim 80\,\mathrm{V}/\mu\mathrm{m}$ electric field. The photorefractivity of organic materials is greater than that of inorganic materials due to the higher Pockels constant and the ability of component chromophores to reorientate in the internal electric field. The photorefractive effect primarily induced by chromophoric reorientation is known as the orientational photorefractive effect. Recently, the photorefractive effect of low-molecular-weight nematic liquid crystals has been investigated, [14–19] and the photoinduced changes in refractive index in such crystals has been shown to be caused by changes in the orientation of liquid crystal molecules induced by the photoinduced space charge field. The effect of the reorientation of liquid crystal molecules on the apparent refractive index is particularly strong. Despite the apparent advantages of organic photorefractive materials, their response time is too slow (usually $\sim 100\,\mathrm{ms}$) for practical applications, attributable to the slow reorientation of chromophores. The use of high-Tg polymers has been investigated as one means of addressing this problem [20,21]. In such stiff materials, the reorientation of chromophores is restricted, and refractive index modulation is solely due to the electrooptic effect. Although rapid response times have been achieved in these materials, the reported diffraction efficiencies are lower than in low-Tg materials due to the absence of a supplementary orientational mechanism.

In this study, we carried out a two-beam coupling experiment on surface-stabilized ferroelectric liquid crystals (SS-FLCs) doped with photoconductive compounds. Recently, the present authors [22,23,25–27] and Wasielewski *et al.* [24] independently reported the first observation of asymmetric energy exchange in FLCs, however, the photorefractivity of FLCs has yet to be characterized in detail. FLCs exhibit spontaneous polarization and are known to be sensitive to electric fields, [28] and the direction of spontaneous polarization is expected to be governed by the internal space-charge field. The refractive index grating is then considered to be created through the orientation of FLC molecules according to the direction of polarization (Fig. 1). We prepared a series of FLC samples with differing properties, and examined the effects of temperature, applied electric field and magnitude of spontaneous polarization on the photorefractive properties of these SS-FLCs. The response of the spontaneous polarization to the internal space-charge field was clearly exemplified.

2. EXPERIMENTAL SECTION

2.1 Samples

The ferroelectric liquid crystals used in this study are commercially available from Chisso Chemical Corporation. The properties of these FLCs are listed in Table I.

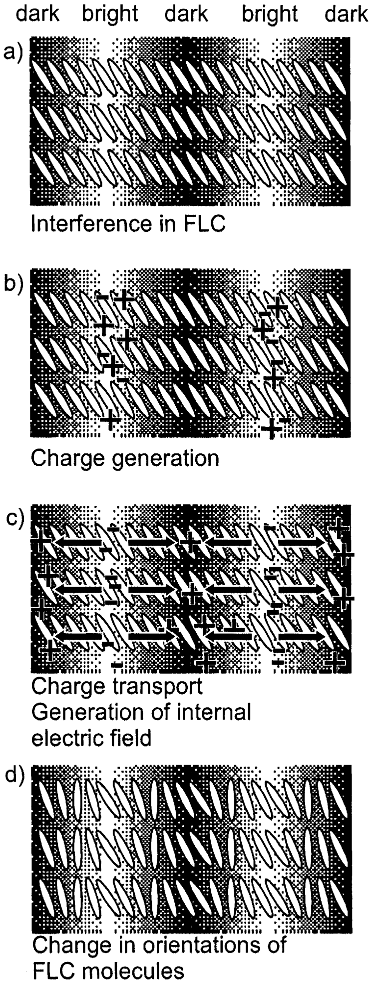

FIGURE 1 Proposed mechanism of photorefractive effect in FLCs.

TABLE I Physical Properties of FLCs Used in this Study

	Ps at 25°C (nC/cm^2)	Phase transition temperature[a] (°C)	Response time τ[b] (µs)	Tilt angle (deg.)
CS1011 (in 2-μm-gap cell)	13.0	– Sc* 56 S_A 77 N* 91 I	899	22
CS1015 (in 2-µm-gap cell)	6.6	C – 17 Sc* 58 S_A 68 N* 78 I	188	26
CS1022 (in 2-µm-gap cell)	34.7	C – 11 Sc* 61 S_A 73 N* 85 I	56	25
CS1030 (in 2-µm-gap cell)	20.2	C -5 Sc* 70 S_A 74 N* 88 I	82	28

[a] C, crystal; Sc*, chiral smectic C phase; S_A, smectic A phase; N* chiral nematic phase; I, isotropic phase

[b] Response time to 10 V/µm electric field at 25°C in a 2-µm cell.

The structures of photoconductive compounds and the electron trap reagent are shown in Figure 2. The photoconductive compound, CDH, was synthesized via the reaction of diphenylhydrazine and N-ethylcarbazole-3-carboxaldehyde in pyridine. TNF (sensitizer/electron trap reagent) was obtained from Tokyo Kasei Co. and purified by recrystallization from a hexane-ethylacetate mixture. The concentration of CDH was 2 wt%, and that of TNF was 0.1 wt%. The FLCs and dopants were dissolved in dichloroethane and the solvent was evaporated. The mixture was then dried in a vacuum at room temperature for one week. At this concentration, no phase separation was observed under a polarizing microscope or in differential scanning calorimeter (DSC) measurements. Phase separation was observed at CDH concentrations exceeding 3 wt%. The samples were injected into a 10-µm-gap glass cell equipped with 1 cm^2 ITO electrodes and a polyimide alignment layer. A 2 to 5-µm-gap cell is typically used to obtain a surface-stabilized FLC, [25] however, finely aligned FLC samples were obtained using the 10-µm-gap cell.

2.2 Measurement

The phase transition temperatures were determined using a DSC (Seiko I&E SSC-5000) and by microscopic (Mettler FP-80, FP-82 and Olympus BX-50 polarizing microscope). The photoconductivity was measured using

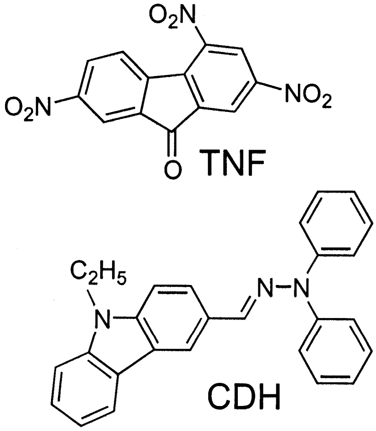

FIGURE 2 Structure of photoconductive compound and sensitizer used in this study.

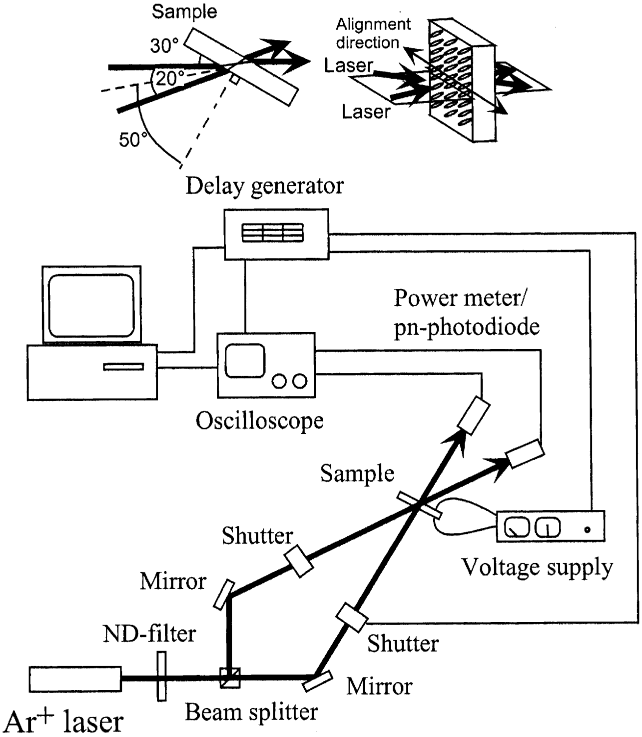

FIGURE 3 Schematic illustration of experimental setup.

a R8340 ultra-high-resistance ohmmeter (Advantest). The photorefractive effect was measured in a two-beam coupling experiment. A schematic illustration of the experimental setup is shown in Figure 3. A p-polarized beam from an Ar^+ laser (Laser Graphics 165LGS-S, 488 nm, continuous wave) was divided by a beam splitter and refocused in the sample film. The intensity of the laser was 2.4 mW for each beam (1-mm-diameter). The sample was inclined at 50°, and the angle between the two incident beams was set to 20°, producing a grating spacing (Λ) of 1.9 μm inside the material ($n = 1.65$). The sample was thermostated using a thermo-controller (Chino Co. DB1000). An electric field of 0 ~ 10 V/μm was applied to the sample from a regulated DC power supply (Kenwood DW36-1), and the change in transmitted beam intensity was monitored by photodiodes (Electro-Optic Technology, Inc. ET-2040) and recorded by a computer. The spontaneous polarization of FLCs was measured by the triangular voltage method (10 Vp-p, 100 Hz).

3. RESULTS AND DISCUSSION

3.1 Two-beam Coupling Experiment on FLCs

Figure 4 shows a typical example of the asymmetric energy exchange observed in the CDH/TNF/CS1011 sample. An electric field of 0.1 V/μm was applied to the sample. The interference of the divided beams in the sample resulted in the increased transmittance of one of the beams and the decreased transmittance of the other beam. These transmittance characteristics were reversed when the polarity of the applied electric field was reversed. Asymmetric energy exchange was only observed when an electric field was applied, indicating that beam coupling was not caused by a thermal grating. In order to calculate the two-beam coupling gain coefficient, it must be determined whether the diffraction condition is in Bragg regime or in Raman-Nath regime. These diffraction conditions are distinguished by a dimensionless parameter Q [2].

$$\mathrm{Q} = 2\pi\lambda L/n\Lambda^2 \tag{1}$$

When $\mathrm{Q} > 1$ it is defined as the Bragg regime of optical diffraction. In this regime, multiple scattering is not permitted and only one order of diffraction of light is produced. Conversely, when $\mathrm{Q} < 1$ it is defined as the Raman-Nath regime of optical diffraction. In this regime, many orders of diffraction can be observed. Usually $\mathrm{Q} > 10$ is required to guarantee that the diffraction is entirely in Bragg regime. In the present experimental condition, Q is calculated to be 6.6 (L: interaction length = 13 μm), so that the diffraction observed in this experiment is predominantly but not

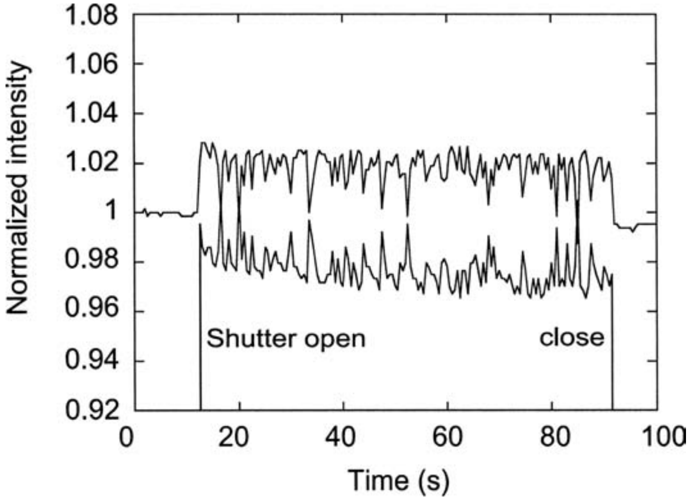

FIGURE 4 Typical example of asymmetric energy exchange obserced in CDH/TNF/CS1011.

entirely in the Bragg regime and Raman-Nath type diffraction partly contributes. However, since we could not observe higher order diffraction, we calculated the two-beam coupling gain coefficient Γ according to the equation assuming the Bragg diffraction [1,2,9]

$$\Gamma = \frac{1}{D}\ln\left(\frac{gm}{1+m-g}\right) \tag{2}$$

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°C was calculated to be $31.3\,\mathrm{cm}^{-1}$ for a CDH/TNF/CS1011 sample. The total optical loss (including absorption, scattering, reflection etc.) was found to be $30\,\mathrm{cm}^{-1}$, primarily attributable to reflection.

3.2. Effect of Temperature

The temperature dependence of the gain coefficient of CS1011 doped with 2 wt% CDH and 0.1 wt% TNF is shown in Figure 5. Asymmetric energy exchange was observed only at temperatures below 45°C. The spontaneous polarization of the CS1011/CDH/TNF mixture in the 10-μm-gap cell are

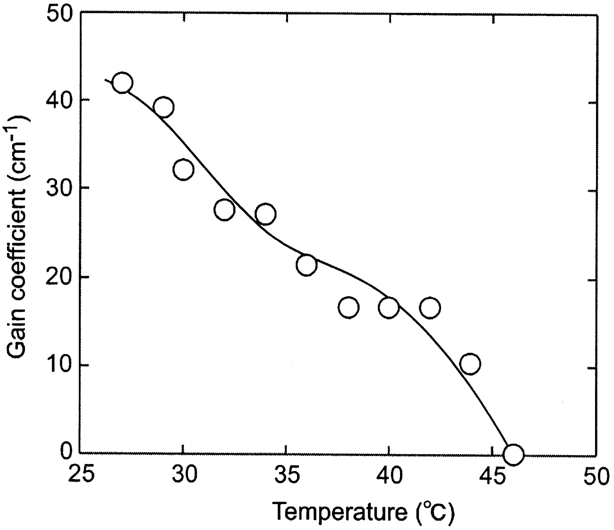

FIGURE 5 Temperature dependence of gain coefficient of CDH/TNF/CS1011.

plotted as a function of temperature in Figure 6. The spontaneous polarization vanished when the temperature was raised above 45℃. Thus, asymmetric energy exchange was observed only in the temperature range

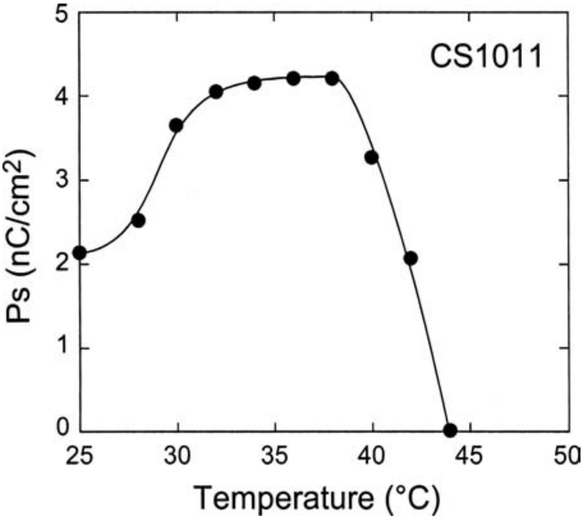

FIGURE 6 Temperature dependence of spontaneous polarization of CDH/TNF/CS1011.

in which the sample exhibits ferroelectric properties (Sc* phase). The two-beam coupling experiment was also performed on the FLCs listed in Table I. The results are similar to those for CS1011. Asymmetric energy exchange was observed only in the Sc* phase. Many of the nematic liquid crystalline photorefractive materials reported to date, usually cyanobiphenyl liquid crystals, possess a large dipole moment aligned in the same direction as the molecular axis. In these nematic liquid crystals, a refractive index grating is generated as a result of orientational fluctuation along the director axis caused by the photoinduced internal electric field. In contrast, the molecular dipole moment of FLCs is small and the dipole moment is aligned perpendicular to the molecular axis. Large changes in the orientation of the molecular axis cannot be induced by the internal electric field in the S_A or N* phase of the FLCs used in this study. However, in the Sc* phase, reorientation associated with spontaneous polarization occurs due to the internal electric field. The spontaneous polarization causes the orientation of mesogens in the corresponding area to change accordingly.

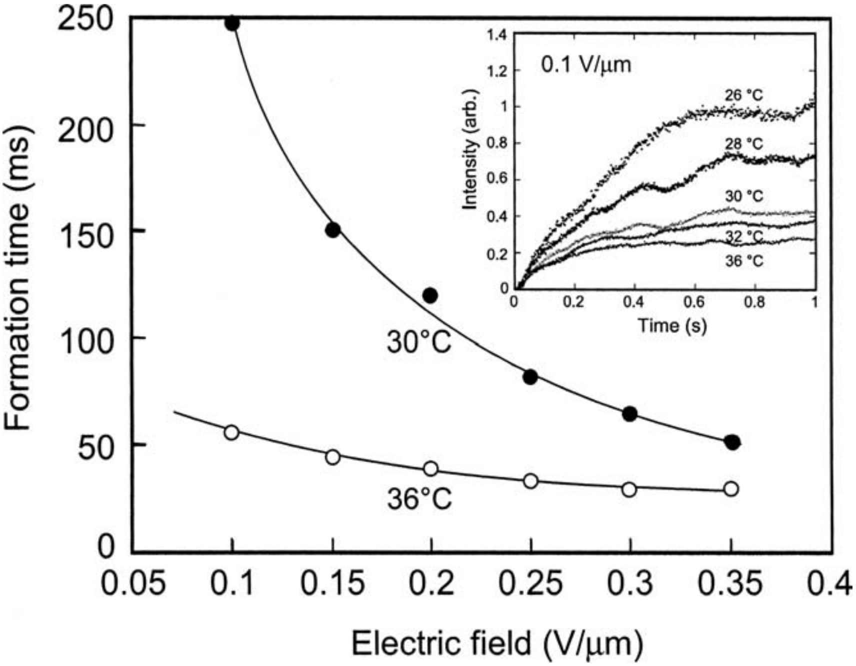

FIGURE 7 Dependence of refractive index grating formation time of CDH/TNF/CS1011 on the strength of external electric field.

3.3. Refractive Index Grating Formation Time

The refractive index grating formation time in CDH/TNF/CS1011 was measured based on the simplest single-carrier model of photorefractivity [2], in which the gain transient is exponential. The rising signal of the diffracted beam was fitted by a single exponential function:

$$\gamma(t) - 1 = (\gamma - 1)[1 - \exp(-t/\tau)] \tag{2}$$

where $\gamma(t)$ represents the transmitted beam intensity at time t divided by the initial intensity ($\gamma(t) = I(t)/I_0$) and τ is the formation time. The grating formation time in CDH/TNF/CS1011 is plotted as a function of the strength of the external electric field in Figure 7. The grating formation time decreases with increasing electric field strength, presumably due to the increased efficiency of charge generation. The formation time was shorter at higher temperatures. The viscosity of FLC decreases with rising temperature, such that the formation time decreases at higher temperatures. The formation time was found to be 28.8 ms at 36°C.

4. CONCLUSION

The photorefractivity of a series of FLC mixtures was investigated through two-beam coupling experiments. The reorientational photorefractive effect was observed in dye-doped FLC samples. Photorefractivity was observed only in the ferroelectric phase of these samples, and the refractive index formation time was found to be shorter than that of nematic LCs. These results indicate that the mechanism responsible for refractive index grating formation in FLCs is different from that for non-ferroelectric materials, and is clearly related to the ferroelectric properties of the material.

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