

Photorefractive smectic liquid crystalline mixtures and their application to remote sensing

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*This article is dedicated to Prof Kehar Singh for his significant contributions to Optics and Photonics
on the occasion of his 80th Birth Day (July 3, 2021)*

The photorefractive effect of flexoelectric smectic liquid crystal mixtures was investigated. Smectic liquid crystal mixtures, composed of smectic-C liquid crystals, photoconductive chiral compounds and a sensitizer, are known to exhibit a large photorefractive effect. The chiral compound plays a critical role in the exhibition of large photorefractivity in smectic liquid crystals. The concentration of the chiral compound was varied and the photorefractive properties of the liquid crystal mixture were examined. It was found that smectic-C liquid crystals containing small amounts of a chiral compound show a large photorefractivity even though they do not possess spontaneous polarizations. The application of the photorefractive liquid crystals to a remote sensing device was demonstrated. © Anita Publications. All rights reserved.

Keywords: Photorefractive effect, Liquid crystals, Asymmetric energy exchange, Remote sensing.

1 Introduction

The photorefractive properties of ferroelectric liquid crystal (FLC) mixtures composed of smectic-C (SmC) liquid crystal (LC) compounds and photoconductive chiral compounds have been reported [1]. When laser beams interfere in a photorefractive material, a refractive index grating is formed [2-6]. The photorefractive effect induces a change in the refractive index by a mechanism that involves both photovoltaic and electro-optic effects (Fig 1). The directions of dipole moments of molecules are changed by the space-charge field that formed between the bright and the dark positions of the interference fringe. FLCs possess spontaneous polarization and show large photorefractive effect because the spontaneous polarization responds to the space-charge field. The most characteristic phenomenon of the photorefractive effect is an asymmetric energy exchange, in which the energy of one of the interfering laser beams transfers to the other [3]. This asymmetric energy exchange can be utilized in optical signal amplification, and the amplification of moving optical signals by photorefractive FLC mixtures has been demonstrated [6]. The FLCs used for practical applications are mixtures of several liquid crystalline compounds and chiral compounds. To obtain a photorefractive FLC, a photoconductive compound is also added to the FLC mixture. However, in most cases, the photoconductive compounds are not liquid crystalline materials and the addition of the photoconductive compound to the FLC mixture disturbs the alignment of the FLC molecules. Thus, light scattering in the FLC medium increases. Light scattering in the photorefractive material is not desirable, because the light scattering distorts the interference fringes. To avoid this problem, photoconductive compounds that also possess a chiral structure have been synthesized [7]. A photorefractive FLC can be obtained by mixing of a photoconductive chiral compound with a smectic LC mixture. We have reported that photorefractive FLC

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mixtures containing photoconductive chiral compounds exhibit large photorefractivity and a fast response [1]. However, when the concentration of a photoconductive chiral compound is changed, the concentrations of both the photoconductive moiety and the chiral moiety are changed. The present study investigates the effect of the concentration of chiral moiety on the photorefractive effect of smectic LC mixtures. A terthiophene photoconductive chiral compound and a terthiophene compound that does not possess a chiral structure were synthesized (Fig 2). These compounds were mixed without changing the concentration of the terthiophene unit. The photoconductive chiral mixtures are then added to smectic LCs. The effect of the chiral concentration on the photorefractive effect of the smectic LC mixtures was then investigated.

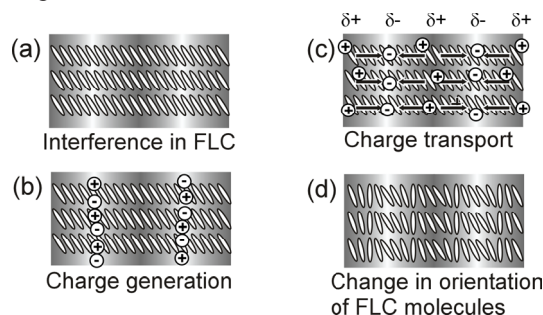


Fig 1. Schematic illustration of the mechanism of the photorefractive effect in the FLCs. (a) Two laser beams interfere in the SS-state of the FLC/photoconductive compound mixture; (b) charge generation occurs in the bright areas of the interference fringes; (c) electrons are trapped at trap sites in the bright areas, holes migrate by diffusion or drift in the presence of an external electric field to generate an internal electric field between the bright and dark positions; and (d) the orientation of the spontaneous polarization vector (i.e., orientation of mesogens in the FLCs) is altered by the internal electric field.

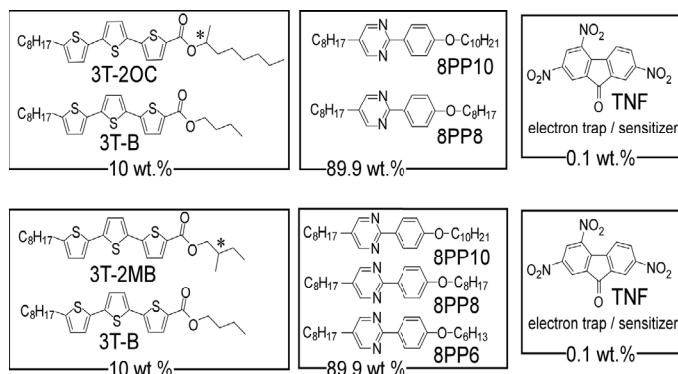


Fig 2. Structures of the smectic LCs (8PP8, 8PP10 and 8PP6), photoconductive chiral dopants (3T-2MB and 3T-2OC) and the sensitizer TNF.

2 Experimental

2.1 Samples

The structures of the compounds used in this study are shown in Fig 2. Terthiophene-type photoconductive chiral compounds, 3T-2MB and 3T-2OC, were synthesized as previously reported [7]. 3T-B was used as a photoconductive compound without a chiral structure. The photoconductive chiral compounds were mixed with 3T-B, keeping the concentration of the terthiophene moiety constant. Mixtures of photoconductive chiral compounds and 3T-B with mixing ratios of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8

and 1:9 were prepared. The terthiophene mixtures were blended with an LC mixture. The concentration of the terthiophene moiety was set to 10 wt.%. Mixtures of phenylpyrimidine-type smectic liquid crystalline compounds, 8PP8, 8PP10 and 8PP6, were used as host liquid crystals (base-LCs). The miscibility of the photoconductive chiral compound differs due to the combination of the base-LC and the compound. The composition of the base-LC had to be optimized. Two types of LC mixtures were incorporated in order to keep the SmC phase of the samples at room temperature. When 3T-2MB was used as a photoconductive chiral compound, a ternary mixture of 8PP6, 8PP8 and 8PP10 (2:2:1 weight ratio) was used as the base-LC. While 3T-2OC was used as a photoconductive chiral compound, a binary mixture of 8PP8 and 8PP6 (1:1) was used as the base-LC. The phase sequences were identical in these base-LCs. Only the phase transition temperatures were different between binary and ternary mixtures. The phase transition temperatures of these base-LCs are listed in Table 1. Trinitrofluorenone (TNF, Tokyo Kasei Co.) was used as an electron trap reagent. A mixture of the base-LC (89.9 wt.%), TNF (0.1 wt.%) and a mixture of terthiophene compounds (3T-2MB+3T-B or 3T-2OC+3T-B, 10 wt.%) was injected into a glass-cell equipped with an ITO electrode and a polyimide alignment layer (Fig 3). The thickness of the LC was adjusted to 10 μm .

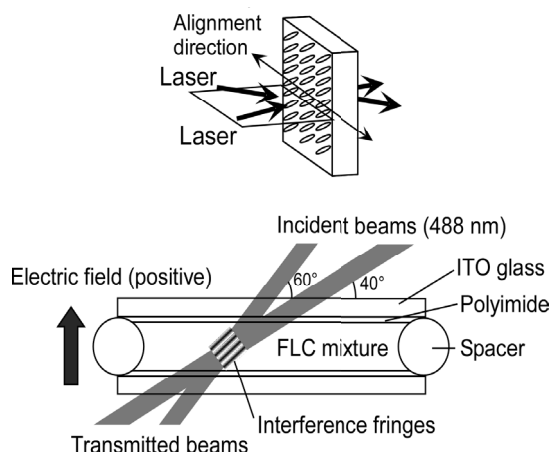


Fig 3. Laser beam incidence condition and the structure of the LC cell.

2.2 Measurements

Phase transition temperatures were determined using differential scanning calorimetry (DSC; DSC822, Mettler) and microscopic observations (FP-80, FP-82, Mettler; BX-50 polarizing microscope, Olympus). Spontaneous polarization (P_s) was measured by the triangular waveform voltage method (10 V_{p-p} , 100 Hz). The photorefractive effect was measured in a two-beam coupling experiment. A linearly polarized beam from a diode-pumped solid state laser (DPSS laser, Spectra Physics, Cyan-PC13689, 488 nm, continuous wave or Oxixious, 473S-50-COL-PP, 473 nm, continuous wave) was divided into two by a beam splitter; the two beams were then interfered in the sample film. A p -polarized beam was used in most of the experiments in this study. The laser intensity was 1 mW/cm^2 for each beam (1 mm diameter). The orientation of the rubbing direction and the beam incidence plane are shown in Fig 4. The incident beam angles to the glass plane were 40° and 60° . Each interval of the interference fringe was 1.87 mm. The sample was maintained at 25°C using a thermo-controller (DB1000, Chino Co.). An electric field in the range of 0 to 10 V/mm was applied to the sample from a regulated DC power supply (Kenwood DW36-1), and the change in the transmitted beam intensity was monitored by photodiodes (ET-2040, Electro-Optics Technology, Inc.) and recorded by an oscilloscope. The formation time for the refractive index grating in the FLC was measured based on the simplest single-carrier model of photorefractivity [4,5], in which the gain transient is exponential. The rising signal of the two-beam coupling was fitted by a single exponential function.

3 Results and Discussions

3.1 Photorefractive effect of the smectic LC mixtures containing photoconductive chiral dopants

The photorefractive properties were evaluated by a two-beam coupling experiment. A 488-nm laser beam was split into two and directed to interfere within a sample. A typical example of a two-beam coupling experiment (asymmetric energy exchange) is shown in Fig 4. The transmitted intensity of one beam through the sample decreases and that of the other beam increases because of the formation of a phase-shifted grating. The photorefractive effect was evaluated by gain coefficients (Γ) and refractive index grating formation times (τ) obtained from the data of the two-beam coupling experiments [6].

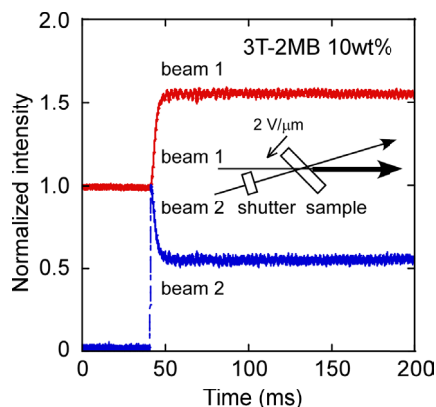


Fig 4. Typical results of two-beam coupling experiments for a ternary mixture base LC, 3T-2MB, and TNF measured at 25 °C.

3.2 Dependence of the photorefractive effect of the smectic LC mixtures on the chiral concentration

In order to distinguish the contribution of the concentration of the chiral moiety, LC mixtures that contain different concentrations of the chiral moiety while maintaining a constant concentration of the photoconductive moiety were prepared. The photoconductive chiral compounds were mixed with the achiral photoconductive compound 3T-B. The mixing ratio was varied to prepare mixtures with different concentrations of the chiral moiety while keeping a constant concentration of the photoconductive moiety (terthiophene). Figure 5 shows the gain coefficient and refractive index grating formation times of LC mixtures containing 3T-2OC and 3T-B as a function of the concentration of the chiral unit keeping the concentration of the photoconductive moiety at 10 wt.%. As the concentration of the chiral unit (3T-2OC) is increased, the gain coefficient decreases and the response time decreases. The decrease in response time is due to the increase in spontaneous polarization. The decrease in gain coefficient is considered to be related to the change in dielectric properties of the LC. The origin of the decrease in the gain coefficient will be discussed in the later section after the measurements of dielectric properties and the tilt angles of the LC mixtures.

Figure 6 shows the gain coefficient and refractive index formation times of LC mixtures containing 3T-2MB and 3T-B as a function of the concentration of the chiral unit keeping the concentration of the photoconductive moiety at 10 wt.%. At chiral concentrations higher than 3 wt.%, the gain coefficient increased linearly and the formation time decreased as the concentration of the chiral unit increased. However, at chiral concentrations lower than 3 wt.%, large gain coefficients and a fast response was obtained. This change in properties is possibly due to a phase transition of the LC. At chiral concentrations higher than 3 wt.%, chiral smectic C phase (SmC*) is induced by the chiral unit. The SmC* phase possesses a helical structure. The chiral unit induces asymmetric interactions between the LC molecules and the achiral SmC phase turns into the SmC* phase. The SmC* phase exhibits a ferroelectricity when formed into a thin film. However, when the

concentration of the chiral unit is lower than 3 wt.%, the ferroelectric SmC^* phase cannot be wholly induced. It was considered that the mechanism of the photorefractive effect observed at the 3T-2MB concentrations lower than 3 wt.% was different from that of the photorefractive effect of the ferroelectric SmC^* phase. At chiral concentrations lower than 3 wt.%, the LC medium can not possess a spontaneous polarization and the chiral unit induces asymmetric interactions between the LC molecules and the achiral SmC phase turns into the SmC^* phase. The SmC^* phase exhibits a ferroelectricity when formed into a thin film. However, when the concentration of the chiral unit is lower than 3 wt.%, the ferroelectric SmC^* phase cannot be wholly induced. It was considered that the mechanism of the photorefractive effect observed at the 3T-2MB concentrations lower than 3 wt.% was different from that of the photorefractive effect of the ferroelectric SmC^* phase. At chiral concentrations lower than 3 wt.%, the LC medium can not possess a spontaneous polarization and the mechanism of the photorefractive effect at that concentration is not based on the response of the spontaneous polarization. The behavior of the LC mixtures containing 3T-2MB is quite different from that of the mixtures containing 3T-2OC. Although the response time of the photorefractive effect was fast, the LC mixtures containing 3T-2MB were not considered to be ferroelectric. It was considered that a flexoelectric effect was induced when an electric field was applied to the LC mixtures containing 3T-2MB. The electro-optical response and the photorefractive response were made faster through the flexoelectric effect.

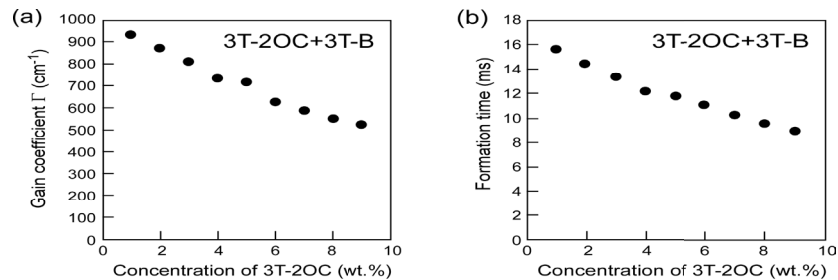


Fig 5. Gain coefficients and refractive index grating formation times of LC mixtures containing a photoconductive mixture (3T-2OC and 3T-B). (a) Dependence of the magnitude of the gain coefficient on the concentration of the chiral unit (3T-2OC). (b) Dependence of the refractive index grating formation time on the concentration of the chiral unit. The concentration of the photoconductive chromophore (terthiophene) was kept constant (10 wt.%). An electric field of 2 V/mm was applied to the sample. The measurement was conducted at room temperature.

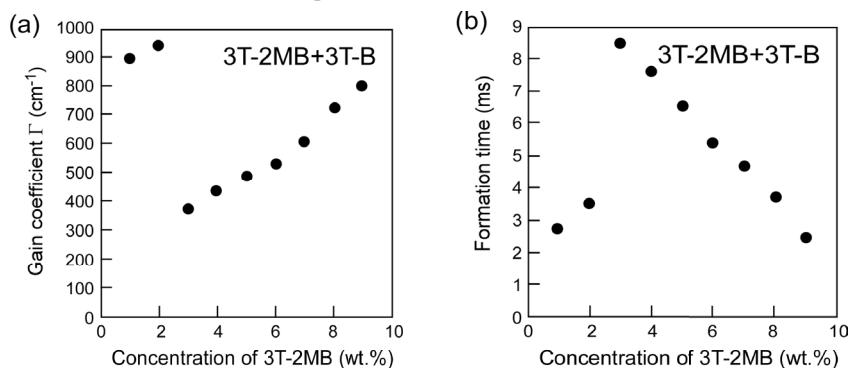


Fig 6. Gain coefficients and refractive index grating formation times of LC mixtures containing a photoconductive mixture (3T-2MB and 3T-B). (a) Dependence of the magnitude of the gain coefficient on the concentration of the chiral unit (3T-2MB). (b) Dependence of the refractive index grating formation time on the concentration of the chiral unit. The concentration of the photoconductive chromophore (terthiophene) was kept constant (10 wt.%). An electric field of 2 V/mm was applied to the sample. The measurement was conducted at room temperature.

3.3 Application to a remote sensing device

The application of the photorefractive LC mixture to a remote sensing was demonstrated by a set-up as shown in Fig 7. A continuous wave (CW) laser beam (473 nm) is divided into two beams, one of which (reference light) is injected into a liquid crystal, and the other (object light) is irradiated onto an object (aluminum plate, 2 mm thickness), and the reflected light from the object is injected into the liquid crystal and interferes with the reference light. The intensity with which each light is transmitted through the liquid crystal is then measured. A photorefractive two-wave coupling occurs, amplifying the object light and attenuating the reference light, both of which settle to a constant value. The object is now irradiated with a 1064 nm pulsed laser with a pulse width of less than 7 nanosecond, which generates ultrasonic waves at the object surface. The ultrasound wave travels through the object and is reflected by each surface of the object and by defects and structures inside the object. These reflected waves appear on the surface of the object and cause variations in the reflection of the object light. The phase of the interference fringes in the liquid crystal also changes because the phase of the reflected light is modulated by the changes in the object surface caused by the reflected waves. This causes a shift in the amplification and attenuation of the light due to a deviation from the two lightwave coupling conditions. By measuring the time between the irradiation of pulsed light to an object and the change in the object light, the thickness of the object can be investigated. The transmission intensities of these pulses are shown in Fig 8. The pulsed laser irradiation generates ultrasonic vibrations on the surface of the aluminum plate, which can be longitudinal or transverse. The transmission velocities of the longitudinal and transverse waves in the aluminum plate are 6240 m/s and 3040 m/s, respectively. The transmission of ultrasonic vibrations from the back to the surface causes variations in the steady-state light reflection. This appears as a signal in the two-light wave coupling. By measuring the time between the pulse laser irradiation and the appearance of the signal, the thickness of the aluminium plate can be determined.

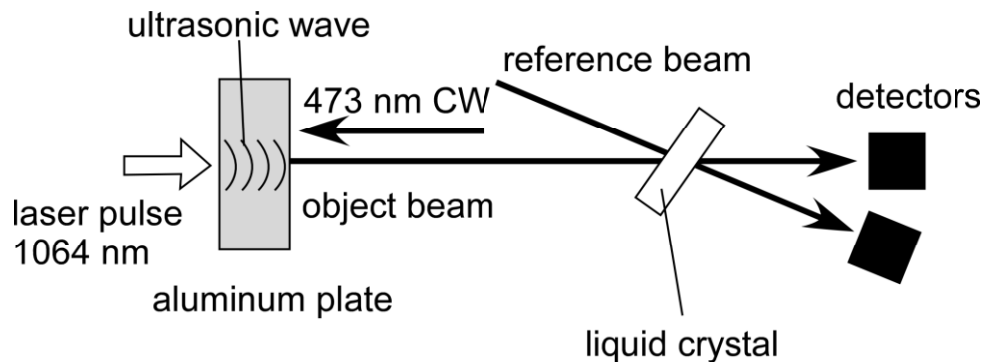


Fig 7. A schematic illustration of experimental set-up for the measurement of the thickness of an aluminium plate.

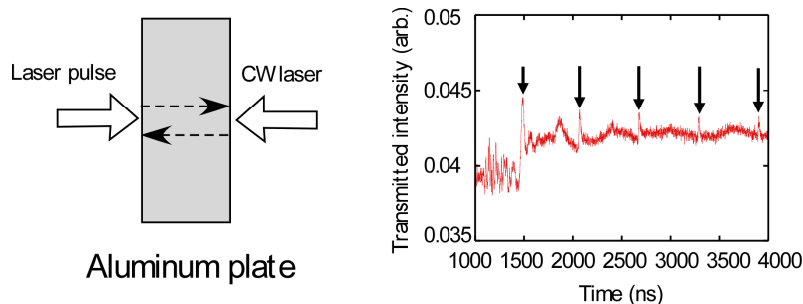


Fig 8. An example of the measured signal. The ultrasonic signals reflected by the front and back surfaces of the aluminium plate are observed in the two-beam coupling measurement.

4 Conclusion

The effect of the concentration of the chiral unit on the photorefractive effect of an LC mixture containing a photoconductive chiral compound was investigated. The photorefractive effect in LC mixtures containing various concentrations of the chiral unit was evaluated by a two-beam coupling experiment. A large photorefractive effect was observed in LC mixtures containing small amounts of 3T-2MB. It can be concluded that the LC mixtures containing 3T-2MB concentrations lower than 3 wt.% are not FLCs. The large photorefractive effect can be attributed to an electro-clinic effect and a flexoelectric effect induced in the SmC phase containing a small amount of chiral compound that is not sufficient to introduce a full SmC* phase. The large photorefractivity of LC materials can be utilized in many applications including remote sensing devices.

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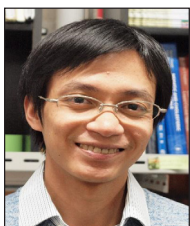
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