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Enhancement of Photorefractivity in the Isotropic Phase of Polymer Liquid Crystals

Takeo Sasaki,* Masatomo Goto, Yuichi Ishikawa, and Takeshi Yoshimi

Department of Applied Chemistry, Faculty of Engineering, Oita University, Dannoharu, Oita 870-1192, Japan

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The photorefractivity of a series of polymer liquid crystals that possess a 4-nitrobenzylideneaniline moiety or a cyanobiphenyl moiety as a mesogen and simultaneously as a nonlinear optical chromophore was investigated using two-beam coupling experiments. A large diffraction efficiency (η) of 65% under application of a 37 V/ μm external electric field was obtained in the isotropic phase of a polymer liquid crystal mixed with charge transporting compounds. The photorefractivity was compared between the liquid crystalline polymers and amorphous polymers. The photorefractivity was found to be significantly enhanced in the isotropic phase of the liquid crystalline polymers compared to that of the amorphous polymers with almost the same molecular structure.

Introduction

The photorefractive effect is a phenomenon in which a change in the refractive index of a material is induced by the absorption of light. This phenomenon enables us to create various types of photonic applications. The photorefractive material exhibits both photoconductivity and a second-order nonlinear optical effect (Pockels effect).^{1–3} When two coherent laser beams are in interference in a photorefractive material, a refractive index grating is created. It is characteristic of the photorefractive effect that the phase of the refractive index grating is $\pi/2$ shifted from the interference pattern. The laser beams are diffracted by the grating resulting in a change in the intensities of these beams. This phenomenon is known as asymmetric two-beam coupling^{1–3} in which one beam gains intensity and the other one loses intensity. The photorefractive property of a material is often evaluated by the two-beam coupling experiment. Recently, a photorefractive organic material with a large diffraction efficiency was reported in which a large amount of nonlinear optical compounds (*p*-nitroazobenzene derivative and trinitrofluorenone) was mixed with a photoconductive polymer (poly(vinylcarbazole)).^{4,5} The diffraction efficiency of this mixture at 670 nm was reported to be 86% under application of an external electric field of 61 V/ μm .⁴ The photorefractive effect (diffraction efficiency) of organic materials is several times that of inorganic photonic crystals, and the organic polymers can easily be processed into fine wide films and also into fibers.^{4–13} This is considered to be advantageous for photonic applications. The photorefractive effect of low-molecular-weight liquid crystals has also been reported.^{14–20} The refractive index of a liquid crystal doped with a small amount of charge-generating compounds was changed by Ar⁺ laser irradiation under application of a weak electric field. The photoinduced refractive index change in the low-molecular-weight liquid crystals is caused by a change in the orientation of the liquid crystalline molecules induced by the photoinduced space charge field. The reorientation of the liquid crystal molecules significantly changes the apparent refractive index.^{21,22} However, the liquid crystal phase diffracts light to some extent; thus it is disadvantageous for photonic applications. On the other hand, in the isotropic

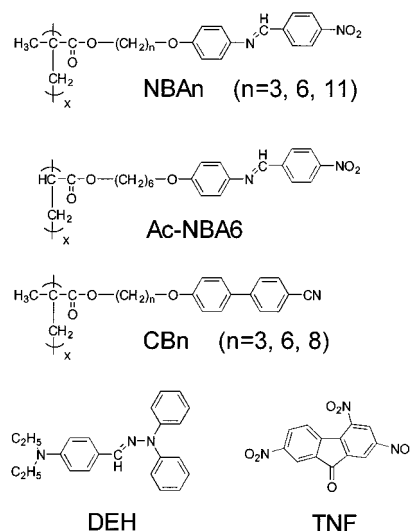


Figure 1. Structures of compounds used in this study.

phase of liquid crystals, each molecule is randomly oriented and does not strongly diffract light. Moreover, each liquid crystalline molecule still tends to create an ordered structure in the microscopic region even in the isotropic phase.²² Thus, the isotropic phase of a liquid crystalline material is considered to possess a potential for large photorefractivity and high transparency. In this study, the photorefractive effect of the isotropic phase of a series of polymer liquid crystals that possessed 4-nitrobenzylideneaniline and cyanobiphenyl moieties was investigated. A large diffraction efficiency of over 65% under 37 V/ μm was obtained in the isotropic phase of the polymer liquid crystal. The photorefractive effect of the liquid crystal phase and of the isotropic phase was investigated and compared to that of a glassy polymer which possesses a very similar molecular structure. The effects of liquid crystallinity on the photorefractive properties are discussed.

Experimental Section

Preparation of Samples. The structures of the polymer liquid crystals and photoconductive compounds used in this study are shown in Figure 1. Polymer NBA6 exhibited a nematic liquid

* To whom correspondence should be addressed.

TABLE 1: Molecular Weights and Phase Transition Temperatures of the Polymers Used in This Study

abbrev	M_n	M_w/M_n	phase transition temperature, ^a °C						$\Delta H_{lc/iso}$, ^c kJ/mol
NBA3	4200	1.2	g	63				amorphous	
NBA6	4000	1.2	g	49	N	120		I	0.45
NBA11	6200	1.3	g	29	S	62	N	140	0.70
Ac-NBA6	4500	1.2	g	43				amorphous	-
CB3	6300	1.3	g	29	S	88		I	0.37
CB6	5500	1.1	g	27	S	61	N	96	0.76
CB8	6200	1.2	g	<i>b</i>	S			116	2.33

^a g, glassy state; S, smectic phase; N, nematic phase; I, isotropic phase. ^b Lower than room temperature. ^c Enthalpy required for liquid crystal phase to isotropic phase transition.

crystal phase and NBA11 exhibited both nematic and smectic liquid crystal phases. The polymers NBA3 and Ac-NBA6 did not exhibit a liquid crystal phase. These polymers were synthesized according to the literature.^{23,24} The thermal properties of the polymers used in this study are listed in Table 1. The number-average molecular weight (M_n) of the polymer liquid crystals was determined by gel permeation chromatography (GPC; Toyo-soda TSK-GEL G3000HHR; eluent, THF), and the glass transition temperature (T_g) and the phase transition temperature were respectively determined by a differential scanning calorimeter (DSC; Seiko I&E SSC-5000) and by microscopic observation (Mettler FP-80, FP-82, and Olympus BX-50 polarizing microscope). The photoconductive compound, DEH, was synthesized via the reaction of diphenylhydrazine and diethylaminobenzaldehyde in pyridine. TNF (sensitizer) was obtained from Tokyo Kasei Co. and purified by recrystallization from a mixture of hexane-ethyl acetate. The photorefractive sample was prepared by casting a dichloroethane solution of the polymer mixed with DEH and TNF on an ITO patterned glass. The ratio of DEH in the film ranged from 0 to 30 wt % with the concentration of TNF maintained at 1 wt %. No phase separation was observed under the polarizing microscope and during the DSC measurements. In order to obtain a flat film, the casting solution was prepared at a rather high concentration (about 200 mg in 1 mL). The film was dried under vacuum for 6 h and sandwiched between two ITO glasses at 70 °C. The film was softened at this temperature and completely filled the space between the ITO electrodes. The film thickness was 100 μ m as determined by a Teflon spacer.

Measurement. The photorefractive property was evaluated using a two-beam coupling experiment and a four-wave mixing experiment. A schematic illustration of the experimental setup is shown in Figure 2. A P-polarized beam from a He-Ne laser (Mellesgriot, 633 nm, 7 mW output, P-polarized) was separated by a beam splitter and refocused in the sample film. The sample was tilted 30°, and the angle between the two incident beams was 40° which gave a grating spacing of 1.07 μ m. The sample was thermostated using a thermo-controller (Chino Co. DB1000). An electric field of 10–40 V/ μ m was applied to the sample by a high-voltage supply unit (Glassman High Voltage, Inc., PS/EL10R4.0-10), and 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 R8340 ultrahigh resistance meter (Advantest) and 750W halogen-tungsten lamp with an IR-cut filter (Toshiba IRA25S).

Results and Discussion

Photorefractivity of the Isotropic Phase of a Polymer Liquid Crystal NBA6 Doped with Photoconductive Compounds. A typical example of the asymmetric energy exchange in a two-beam coupling experiment is shown in Figure 3. The

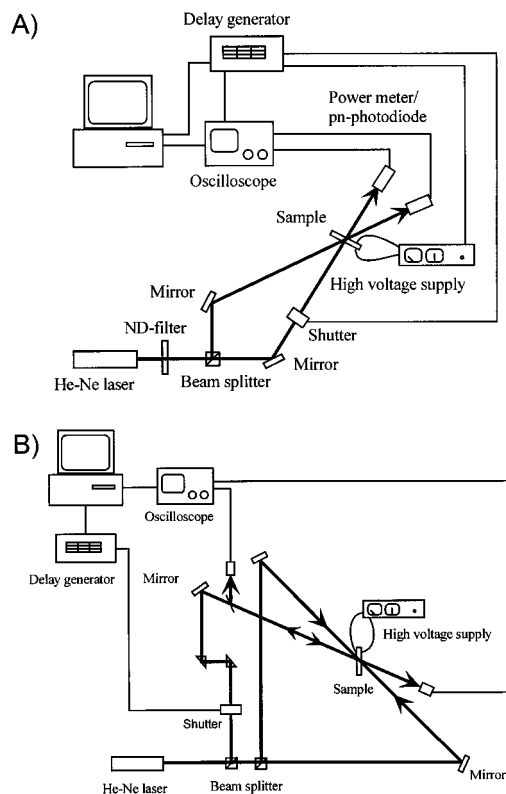


Figure 2. Schematic illustration of experimental setup used in this study: (A) two-beam coupling configuration, (B) four-wave mixing configuration.

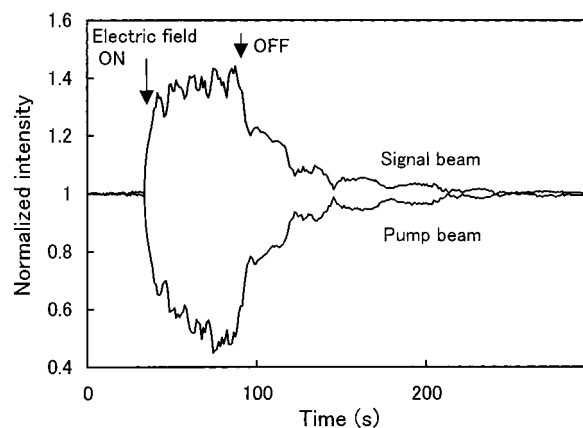


Figure 3. Typical example of asymmetric energy exchange in two-beam coupling experiment for NBA6 doped with 30 wt % DEH and 1 wt % TNF. An electric field of 30 V/ μ m was applied to the sample at $t = 35$ s and cutoff at $t = 90$ s.

transmitted intensities of the He-Ne laser beams through the sample film are indicated as a function of time. The sample composition was TNF:DEH:NBA6 = 1:30:69 wt %. The sample

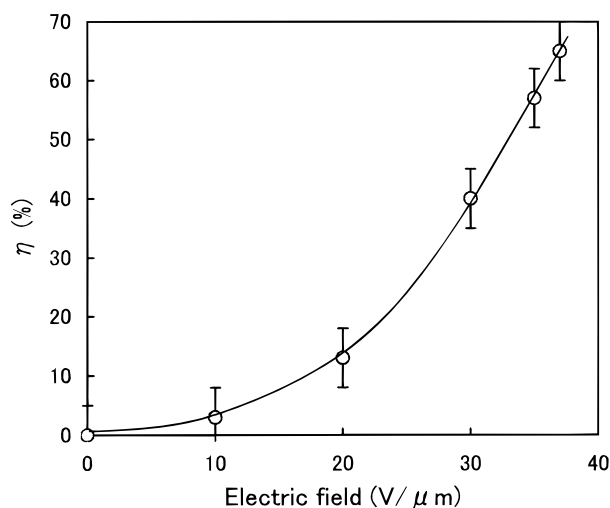


Figure 4. Dependence of diffraction efficiency on the applied electric field for NBA6 doped with 30 wt % DEH and 1 wt % TNF.

film was isotropic and transparent. The photoconductive dopant, DEH, is not a liquid crystal, so that the addition of 30 wt % DEH disturbed the liquid crystal phase of the host polymer. The beam intensity was 7 mW total, and an electric field of 30 V/μm was applied to the sample at $t = 35$ s and cutoff at $t = 90$ s. When an electric field of 30 V/μm was applied to the sample, the transmitted intensity of one beam increased while that of the other beam decreased. An energy exchange of about 40% was observed under these conditions. The response to an external electric field was rather slow in this case.^{11,12} When the field was turned off, the intensities of the two beams gradually returned to their original values. The diffraction efficiency is defined as $\Delta I/I_0$, where I_0 is the transmitted beam intensity without an electric field, and ΔI is the change in transmittance under application of an external electric field. The dependence of the electric field intensity on the diffraction efficiency is shown in Figure 4. The diffraction efficiency was increased as the intensity of the applied electric field increased. In the results reported here, the diffracted beams appeared only in the presence of an applied electric field, eliminating the possibility of beam coupling due to thermal gratings. The energy exchange between the two beams is characterized by the two-beam coupling gain coefficient, Γ , which is calculated according to^{1,2,9}

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

where $D = L/\cos(\theta)$ is the interaction path for the signal beam (L is the sample thickness, θ the propagation angle of the signal beam in the sample), g is a ratio of intensities of the signal beam after the sample with and without the presence of the pump beam, and m is the ratio of the beam intensities (pump/signal) before the sample. The gain coefficient of the mixture of NBA6/DEH/TNF (69:30:1 wt %) at 37 V/μm was calculated to be 118.8 cm⁻¹. The diffraction in NBA6 sample was also measured using a four-wave mixing configuration (Figure 2B). Two laser beams interfered in the sample, and the diffraction of third beam which counterpropagates to one of the writing beams was monitored. The diffracted beam was clearly observed when the electric field was applied to the sample (Figure 5). The photoconductivity of the sample film was measured using the visible light from a 750 W halogen-tungsten lamp with an IR-cut filter. The photoconductivity was clearly observed as shown in Figure 6.

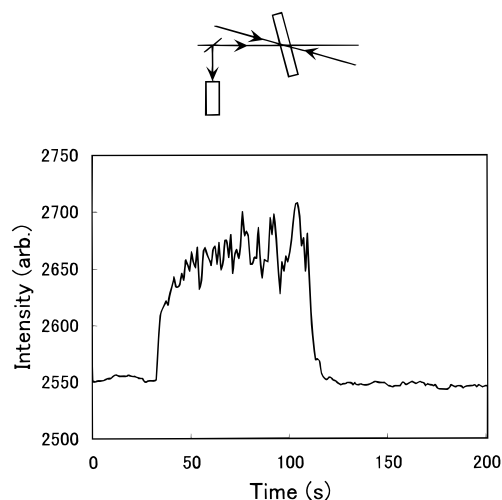


Figure 5. Diffracted beam observed in four-wave mixing experiment on NBA6 doped with 30 wt % DEH and 1 wt % TNF. An electric field of 30 V/μm was applied to the sample at $t = 33$ s and cutoff at $t = 110$ s.

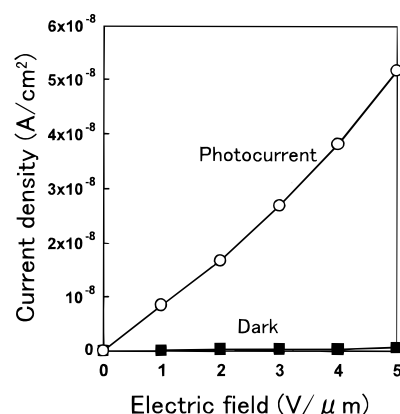


Figure 6. Electric field dependence of the photocurrent of NBA6 doped with 30 wt % of DEH and 1 wt % of TNF, with irradiation of visible light from 750 W halogen-tungsten lamp (160 mW/cm²); ■, dark.

Effect of Spacer Length of Polymer Liquid Crystals. The properties of side-chain polymer liquid crystals depend on the length of the spacer which connects the mesogen with the polymer main chain. NBA6 exhibits only a nematic liquid crystal phase, while NBA11 exhibits both nematic and smectic phases. These liquid crystal phases are observed at room temperature as long as the DEH content is maintained below 20 wt % for NBA6 and 40 wt % for NBA11. Above this critical additive concentration, the polymer loses the properties of a liquid crystal in return for acquiring transparency. The diffraction efficiency of NBA6 and NBA11 at room temperature (22 °C) is plotted as a function of the concentration of DEH in Figure 7. Both NBA6 and NBA11 show a significant increase in the diffraction efficiency at 20 and 40 wt % DEH content, respectively. This concentration of DEH is coincident with the critical values for the formation of a liquid crystal phase. The presence of the liquid crystal phase scatters the laser beams, providing a poor interference pattern, so that a refractive index grating was induced less than in their transparent isotropic phases. Transmittance of laser beam was 63% in isotropic sample (NBA6, 30 wt % DEH) and 2% in liquid crystal sample (NBA6, 10 wt % DEH). In the isotropic phase, the diffraction efficiency of NBA11 was nearly equal to that of NBA6. The glass transition temperatures of NBA6 and NBA11 containing 30 to 50 wt % DEH with 1 wt % TNF are far below room temperature. In other words, there may be no noticeable

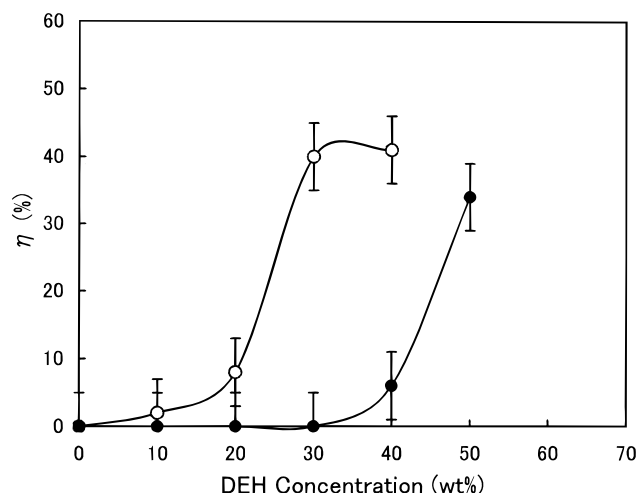


Figure 7. Dependence of diffraction efficiency of NBA6 on the concentration of DEH: (○) NBA6, (●) NBA11. The concentration of TNF was maintained at 1 wt % and an electric field of 30 V/ μ m was applied to the sample.

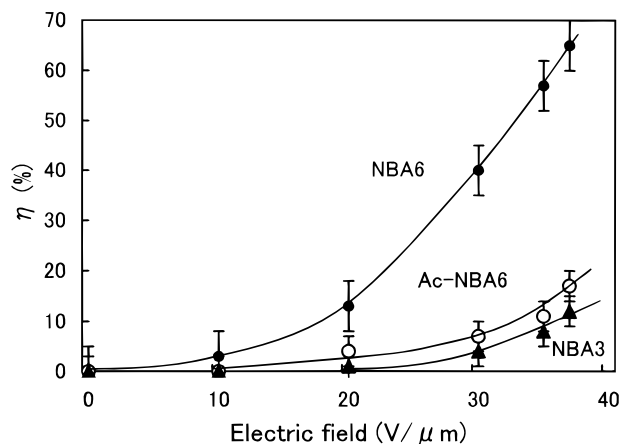


Figure 8. Dependence of diffraction efficiency on the applied electric field for NBA6 doped with 30 wt % DEH and 1 wt % TNF: (●) NBA6, (○) Ac-NBA6, (▲), NBA3.

difference in the mobility of a nonlinear optical chromophore between the two polymers. Therefore, an increase in transparency was responsible for the higher diffraction efficiency in Figure 7.

The diffraction efficiency of NBA3 was also investigated. The diffraction efficiency of NBA3 (7% at 37 V/ μ m) is inferior to those of NBA6 and NBA11, although NBA3 is an amorphous transparent polymer. Thus, the large photorefractivity cannot be explained only by the transparency of the film.

Effect of Liquid Crystallinity. The two-beam coupling experiment was performed on the acrylate Ac-NBA6 (the structure is shown in Figure 1). Ac-NBA6 did not exhibit a liquid crystal phase even though the molecular structure is almost the same as that of NBA6. The only difference is that the structure of the main chain (Ac-NBA6 is an acrylate polymer while NBA6 is a methacrylate polymer). The thermal property of Ac-NBA6 is listed in Table 1. The two-beam coupling experiments were conducted under the condition of transparent isotropic phase of the polymers at room temperature. Both polymers, in fact, caused less scattering of the laser light and did not produce any XRD peaks. The diffraction efficiencies of Ac-NBA6 and NBA6 are plotted as a function of the applied electric field in Figure 8. The concentrations of DEH and TNF were 30 and 1 wt %, respectively. The diffraction efficiency of Ac-NBA6 was found to be much smaller than that of NBA6,

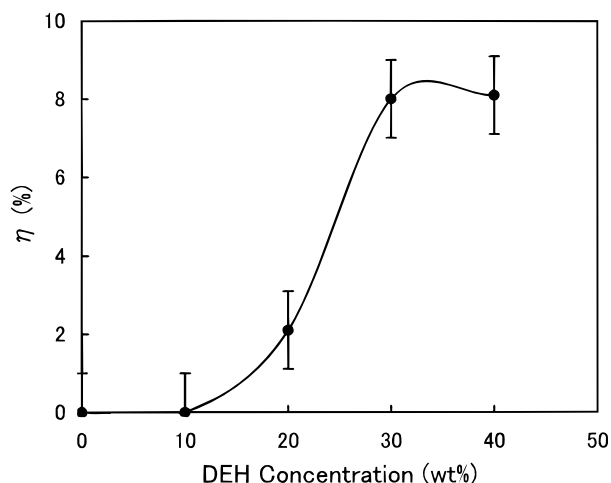


Figure 9. Dependence of diffraction efficiency of CB6 on the concentration of DEH. The concentration of TNF was maintained at 1 wt % and an electric field of 30 V/ μ m was applied to the sample.

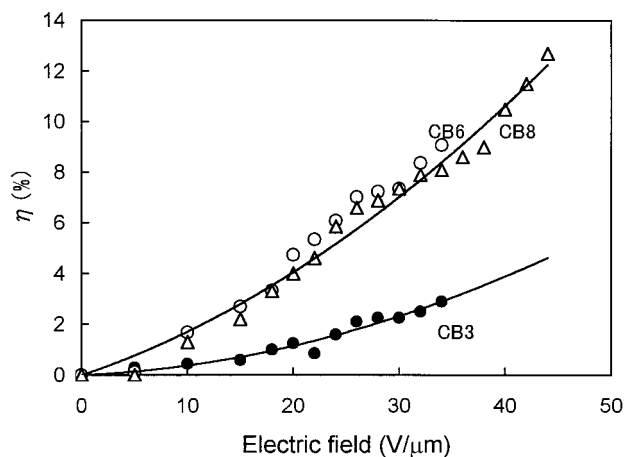


Figure 10. Dependence of diffraction efficiency on the applied electric field for CB6 doped with 30 wt % DEH and 1 wt % TNF: (○) CB6, (Δ), CB8, (●), CB3.

although the molecular weight was almost the same for NBA6 and Ac-NBA6 and the glass transition temperature of Ac-NBA6 was lower than that of NBA6. In addition to the spacer chain effect, the main chain effect also exemplifies the fact that the photorefractivity is larger in the isotropic phase of the liquid crystalline polymers compared to the amorphous polymers. Thus, the difference in the diffraction efficiency is considered to come from the difference in the morphology.

Photorefractive Effect of Cyanobiphenyl PLCs. In order to clarify the effect of liquid crystallinity on the photorefractive effect, the photorefractive properties of the cyanobiphenyl PLCs (polymethacryloyloxyalkoxy-4-cyanobiphenyl) were also investigated. Pure CB6 and CB8 exhibited both nematic and smectic phases. CB3 exhibited a nematic phase; however, the order parameter was very small and required several hours to exhibit birefringence. CB3 is clearly inferior to CB6 and CB8 in terms of the ability to form a liquid crystal phase. The effect of DEH concentration on the diffraction efficiency of CB6 is shown in Figure 9. The asymmetric energy exchange was observed at concentrations higher than 20 wt %, where CB6 did not exhibit a liquid crystal phase at room temperature. The diffraction efficiencies of CB6, CB8, and CB3 are plotted as a function of the applied electric field in Figure 10. The concentrations of DEH and TNF were 30 and 1 wt %, respectively. At this DEH concentration, CB6, CB8, and CB3 did not exhibit a liquid crystal phase. The diffraction efficiency

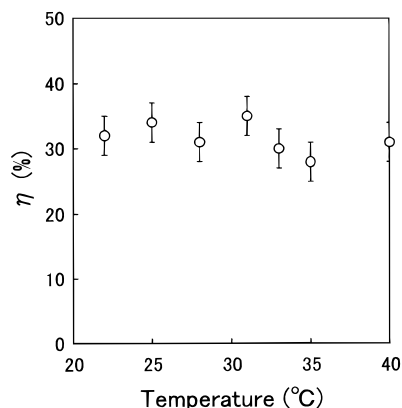


Figure 11. Dependence of diffraction efficiency on temperature for NBA6 doped with 30 wt % DEH and 1 wt % TNF and an electric field of 25 V/ μ m was applied to the sample.

of CB6 was 10% under application of a 40 V/ μ m electric field. On the other hand, the diffraction efficiency of CB3 was several times smaller than those of CB6 and CB8, although the CB3 sample was transparent and the glass transition temperature was almost the same as that of CB6. It can be concluded that the photorefractivity becomes large in the isotropic phase of the liquid crystalline polymer in comparison with the polymers with low liquid crystallinity.

Photorefractive Property of the Isotropic Phase of Liquid Crystalline Polymers. Thus, the photorefractivity was found to be larger in the isotropic phase of the liquid crystalline polymers than in the amorphous polymers. Recently, optical modulation of the refractive index has been demonstrated in a liquid crystal phase.^{14–20} It was reported that a large photorefractivity was obtained in a liquid crystal phase through orientational enhancement. The liquid crystal molecules can easily change their orientation along the direction of an applied electric field. The photoinduced space-charge field is large enough to affect the orientation of the liquid crystals.²¹ The apparent refractive index is largely changed by the orientational alternation of the liquid crystalline molecules. However, the high sensitivity of a liquid crystal to an electric field is caused by the existence of domain structures. The dipole moment of a domain is much larger than that of a composite mesogen. The isotropic phase of liquid crystalline molecules does not respond to an electric field as does the liquid crystal phase. It is natural to consider that there must be no large difference in the efficiency for the photorefractive effect between amorphous polymers and the isotropic phase of liquid crystalline polymers. However, in this study, the photorefractive property was found to be enhanced in the isotropic phase of liquid crystalline polymers. It is well-known that many properties of a liquid crystal are changed when the temperature is close to the nematic/isotropic phase transition. The dependence of diffraction efficiency of NBA6 doped with 30 wt % of DEH on temperature is shown in Figure 11. The diffraction efficiency did not depend on temperature. NBA6 doped with 30 wt % DEH does not form a liquid crystal phase at the temperatures above 0 °C. The diffraction efficiency of NBA6 was still larger than those of Ac–NBA6 and NBA3 even at 40 °C. Thus the enhancement of photorefractivity in this experiment cannot be attributed to pretransitional effects. These results indicate that the isotropic phase of liquid crystalline polymers is not the same as that of the amorphous polymers. The mesogens (chromophores) of the liquid crystalline polymer NBA6 tend to align with each other

even in their isotropic phase. This produces a temporal microscopic ordering of chromophores. The existence of a small domain enhances the change in the refractive index through a reorientational effect. The reorientation of mesogens is considered to contribute to a large diffraction efficiency in the two-beam coupling experiments in Figures 8 and 10. In addition, the isotropic phase is highly transparent and does not scatter light very strongly. The isotropic phase of liquid crystalline polymers is considered to possess a significantly potential for a wide range of applications.

Conclusion

The photorefractivity of a series of side-chain polymers was investigated by two-beam coupling experiments. The diffraction efficiencies of the isotropic phases of liquid crystalline polymers were compared to that of amorphous polymers. The diffraction efficiency was found to be much larger in the isotropic phase of liquid crystalline polymers compared to those in amorphous polymers. The enhancement of photorefractivity is considered to be produced by the aligned structure-forming nature of the isotropic phase of liquid crystalline polymers and the high transparency.

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