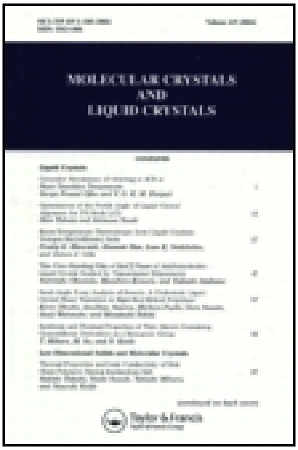

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Enhancement of Photorefractive Effect in the Isotropic Phase of Liquid Crystalline Polymers

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The photorefractive effect of the isotropic phase of liquid crystalline polymers was investigated. A large photorefractivity was observed in polymers which exhibit a liquid crystalline phase even though they were in the isotropic phase. The photorefractivity was compared between the liquid crystalline polymers and amorphous polymers. The photorefractive effect 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.

Keywords: Photorefractive effect; Liquid crystalline polymer; Isotropic phase; Diffraction efficiency; Four-wave mixing

INTRODUCTION

The photorefractive effect has been attracting great interest from both fundamental and practical view points.[1-3] Photorefractive materials exhibit both photoconductivity and a second order nonlinear optical effect (Pockels effect). 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 phase shifted grating can cause asymmetric diffraction of laser beams. The photorefractivity of a material is evaluated by the diffraction efficiency which is measured by the two-beam coupling and four-wave mixing experiments.[3] The photorefractive effect (diffraction efficiency) of organic materials is several times that of inorganic photonic crystals.[4, 5] Recently, we

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reported that the photorefractive effect was enhanced in the isotropic phase of liquid crystalline polymers.[6] The origin of this enhancement has not yet been identified. In this study, the photorefractive effect of the copolymers consist of nitroazobenzene monomer and methylmethacrylate (MMA) was investigated. We prepared both liquid crystalline polymers and amorphous polymers. The effects of the liquid crystallinity on the photorefractive properties are discussed.

EXPERIMENTAL

Preparation of samples.

The structures of the polymer liquid crystals and photoconductive compounds used in this study are shown in Figure 1. The 1:1 copolymer of the nitroazobenzene monomer with methylmethacrylate (MMA), CoAZO6(1:1), exhibited a nematic liquid crystal phase. The 1:2 copolymer CoAZO6(1:2) and 1:1 copolymer of the dimethyl-substituted nitroazobenzene with MMA (MAZO6(1:1)) did not exhibit a liquid crystal phase. The cyanobiphenyl polymers CB6 and CB11 exhibited nematic and smectic liquid crystal phases. These polymers were synthesized according to the literature.[6] The thermal properties of the polymers used in this study are listed in Table 1. 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-ethylacetate. The photorefractive sample was prepared by casting a dichloroethane solution of the polymer mixed with DEH and TNF on an ITO patterned glass. The film was dried under vacuum for 6 h and sandwiched between two ITO glasses at 70 °C. The film thickness was 100 μm as determined by a Teflon spacer.

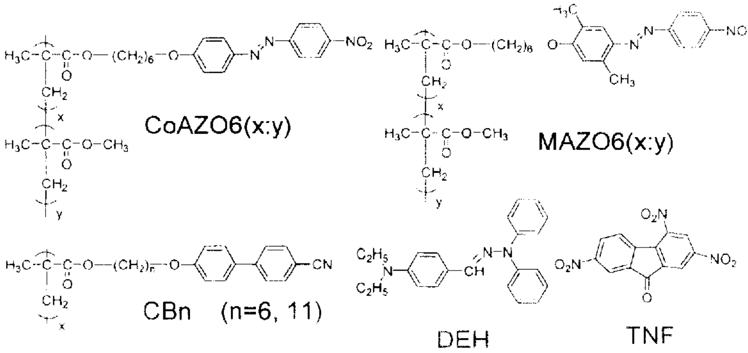

FIGURE 1 Structures of compounds used in this study.

Measurement.

The photorefractive property was evaluated using a four-wave mixing experiment (Figure 2). A P-polarized beam from a He-Ne laser (633 nm, 7 mW output, P-polarized) was used as the light source. The angle between the two incident beams (1 and 2) was 15°, and the probe beam (3) was incident to the sample from exactly the opposite direction of the beam (1). An electric field of 10~40 V/μm was applied to the sample by a high voltage supply unit, and the generated phase conjugate wave (4) was monitored by a power meter (Advantest, Inc., TQ8210+TQ82014) and recorded by a computer. The diffraction efficiencies were calculated as the intensity of the phase conjugate wave divided by the intensity of incident probe beam (3).

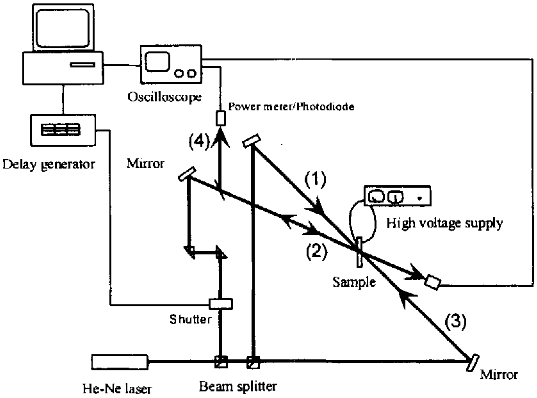

FIGURE 2 Schematic illustration of the experimental setup used in this study.

RESULTS AND DISCUSSION

Diffraction efficiencies of liquid crystalline polymers in the isotropic phase.

A typical example of the results from the four-wave mixing experiment is shown in Figure 3. The intensities of the phase conjugate wave are indicated as a function of time. The sample composition was TNF:DEH:CoAZO6(1:1) = 1:30:69 wt%. 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 sample film was isotropic and transparent. The phase conjugate wave appeared when an electric field of 40V/μm was applied and disappeared when the electric field was turned off. A diffraction efficiency of about 2 % was obtained under these conditions. The diffraction efficiency increased as the intensity of the applied electric field increased. The diffracted beams appeared only in the presence of an applied electric field, thus eliminating the possibility of beam coupling due to thermal gratings.

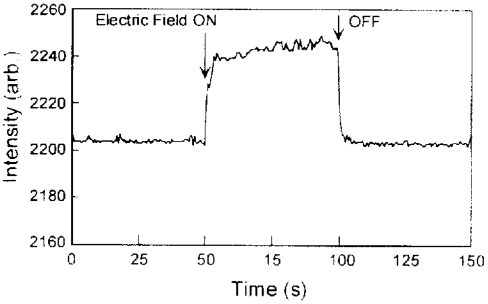

FIGURE 3 Typical example of the generation of phase conjugate wave in four-wave mixing experiment on TNF:DEH:CoAZO6(1:1) = 1:30:69 wt%

Effect of liquid crystallinity.

The four-wave mixing experiments were also conducted on the amorphous polymers at room temperature. The copolymer MAZO6(1:1) and CoAZO6(1:2) did not exhibit a liquid crystal phase. The diffraction efficiencies of CoAZO6(1:1), CoAZO6(1:2) and MAZO6(1:1) are plotted as a function of the applied electric field in Figure 4. The concentrations of DEH and TNF were 30 wt% and 1 wt%, respectively. The diffraction efficiency of MAZO6(1:1) was found to be much smaller than that of CoAZO6(1:1).

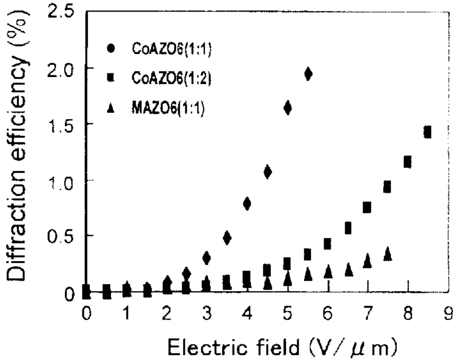

FIGURE 4 Electric field dependence of diffraction efficiencies of CoAZO6(1:1), CoAZO6(1:2) and MAZO6(1:1) doped with 30wt% of DEH and 1 wt% of TNF.

The photorefractive property of the isotropic phase of liquid crystalline polymers.

The photorefractivity was larger in the isotropic phase of the liquid crystalline polymers compared to that in the amorphous polymers. Recently, the photorefractive effect of side-chain liquid crystalline polymers possessing nitrobenzylidene aniline chromophores was investigated.[6] It was reported that the photorefractivity was larger in the isotropic phase of the liquid crystalline polymer in comparison with amorphous polymers. The mesogens (chromophores) of the liquid crystalline polymer tend to align with each other even in their isotropic phase.[7] 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 the large diffraction efficiency in the two-beam coupling experiments. In addition, the isotropic phase is highly transparent and does not strongly scatter light. The isotropic phase of the liquid crystalline polymers is considered to possess a significant potential for a wide range of applications.

Photorefractive effect of cyanobiphenyl PLCs with long spacer chain.

In order to investigate the effect of liquid crystallinity on the photorefractive effect, the photorefractive properties of the cyanobiphenyl PLCs (CBn; poly methacryloyloxy-alkoxy-4-cyanobiphenyl) were also investigated. Pure CB6 and CB11 exhibited both nematic and smectic phases. Typical examples of the experimental results of the four-beam mixing of CB6 and CB11 are shown in Figure 5. The intensities of the phase conjugate wave are plotted as a function of time. The concentrations of DEH and TNF were 30 wt% and 1 wt%, respectively. At this DEH concentration, both CB6 and CB11 did not exhibit a liquid crystal phase. The electric field of 30V/μm was applied to the sample. In the CB6 sample, the phase conjugate wave appeared as the external electric field was applied and immediately disappeared when the electric field was turned off. The diffraction efficiency of CB6 was 10 % upon application of a 40 V/μm electric field. The increase in CB11/DEH/TNF was very slow and showed a prolonged phase conjugate wave signal. The signal was observed even 30 min after the electric field was removed. This indicates that the refractive index grating remained for a long time without an applied external electric field. The exact mechanism of this unusual behavior of CB11 in the photorefractive effect is not yet clarified, however, the difference in the photorefractive effect between CB6 and CB11 may arise from the mobility of mesogens.

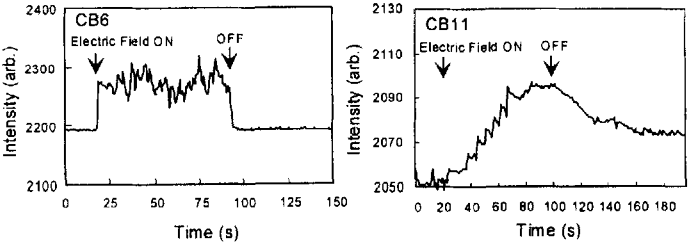

FIGURE 5 Intensity of the phase conjugated wave observed in for-wave mixing experiments on CB6 and CB11 plotted as a function of time.

CONCLUSION

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

Acknowledgments
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