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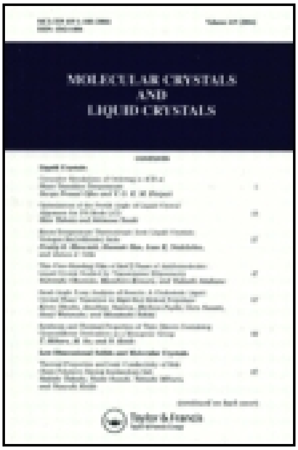

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Photorefractive Effect of Liquid Crystalline Polymers Possessing Azobenzene Chromophores

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Photorefractive Effect of Liquid Crystalline Polymers Possessing Azobenzene Chromophores

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A series of liquid crystalline polymers possessing azobenzene chromophores were synthesized, and in each polymer the photorefractive effect of the isotropic phase was investigated. The photorefractive effect was evaluated by a four-wave mixing experiment. The diffraction efficiency of a side-chain liquid crystalline polymer possessing chiral moieties was measured and compared with that of a polymer possessing achiral chromophores. Chiral polymers exhibited unusual electric-field dependence on diffraction efficiency. The effects of liquid crystallinity and chiral substituents on photorefractivity are discussed.

Keywords Photorefractive effect, polymer liquid crystal, four-wave mixing

INTRODUCTION

The photorefractive effect is defined as an optical modulation of the refractive index [1, 2], and the photorefractive effect of polymer materials has recently attracted great interest. When laser beams interfere in a photorefractive material, a photovoltaic effect occurs between the bright and dark areas of the interference. The resultant electric field causes a change in the refractive index via the electrooptic effect and produces a refractive index

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grating. It is a characteristic of the photorefractive effect that the phase of the index grating is shifted by $\pi/2$ from the interference pattern. This phenomenon enables us to create various photonic applications, such as optical image processing, parallel optical logic, pattern recognition, and phase conjugators. The photorefractive effect of organic materials was first reported in 1990 [3]. Since then, many studies on organic materials have been reported, and extremely high photorefractivity has been achieved in organic polymer materials [4–16]. The high photorefractivity of polymer materials arises from a change in chromophoric orientation induced by an electric field, termed orientational enhancement [4, 15, 17].

Recently, we investigated the photorefractive effects of liquid crystalline polymers and compared the effects with those of amorphous polymers [18]. Our investigation revealed that the photorefractive effect is significantly enhanced in the isotropic phase of the liquid crystalline polymers, and that the diffraction efficiency of the isotropic phase of the liquid crystalline polymers is much greater than that of amorphous polymers, even though these polymers have almost identical molecular structures. Although the exact mechanism of the enhancement effect has not yet been elucidated, the enhancement is considered to arise from the presence of the microscopically ordered structure of component chromophores in the isotropic phase. If the microscopically ordered structure plays an important role in the enhancement, the effect of the introduction of a chiral structure into the component chromophores is interesting. The chiral liquid crystals tend to form a specific phase structure [19, 20], which suggests that the chiral moiety may affect the microscopic structures that exist in the isotropic phase, thereby influencing photorefractivity. In this study, we investigated the photorefractivity of a liquid crystalline polymer that possesses a series of azobenzene chromophores. The azobenzene chromophore with an electron withdrawing substituent exhibits a large hyperpolarizability, so that a large Pockels constant of the polymer film can be expected. The effects of liquid crystallinity and chiral moiety on photorefractivity are discussed.

EXPERIMENTAL

Preparation of Samples

The structures of the liquid crystalline polymers and photoconductive compounds used in this study are shown in Figure 1, and the thermal properties of these polymers are listed in Table 1. The polymers AZO*-8 and AZO-8 were synthesized according to Figure 2. The photoconductive

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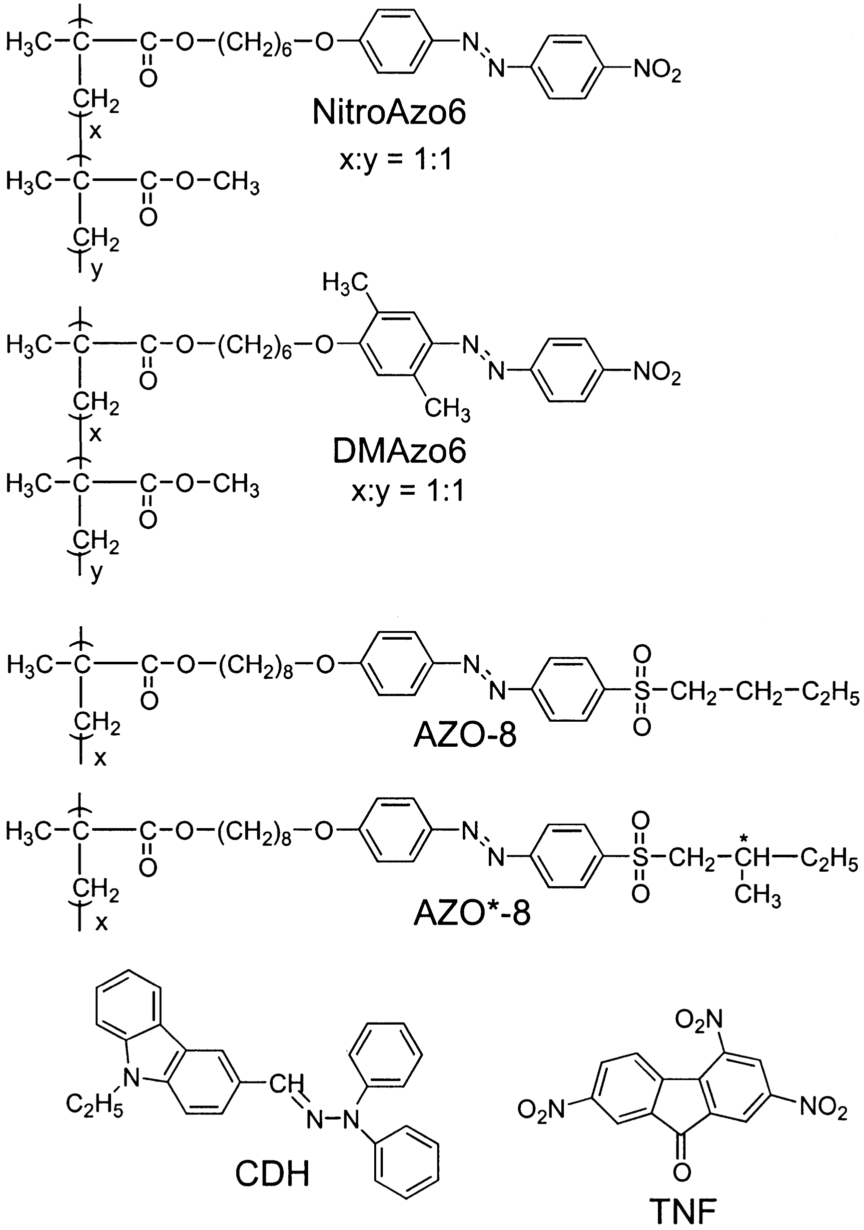

FIGURE 1 Structures of compounds used in this study.

TABLE 1 Molecular weights and phase transition temperatures of the polymers used in this study

Abbrev.	*Mn*	*Mw/Mn*	*Phase transition temperature*[a]				*°C*
NitroAzo6	9000	3.3	g	91	N	169	I
DMAzo6	8500	3.4	g	80			
AZO-8	8500	2.2	g	71	N	103	I
AZO*-8	8300	2.5	g	67	N*	82	I

[a] g, glassy state; N, nematic phase; I, isotropic phase.

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compound, CDH, was synthesized via reaction of disphenylhydrazine and and N-ethlycarbazolylaldehyde in pyridine. TNF (sensitizer/electron trap reagent) was obtained from Tokyo Kasei Co. and purified by re-crystallization from a mixture of hexane-ethylacetate. The photorefractive sample was prepared by casting on an ITO-patterned glass a dichloroethane solution of the polymer mixed with CDH and TNE. The ratio of CDH in the film was 40 wt%, and the concentration of TNF was 1 wt%. No phase separation was observed under the polarizing microscope or during DSC measurements. In order to obtain a flat film, the casting solution was prepared at rather high concentration (200 mg in 1 mL). The film was dried under vacuum for a week 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 μm, as governed by a Teflon spacer.

Synthesis of Azobenzene Monomer AZO*-8

1) 4-((S)-2-methylbutyl)sulfonyl nitrobenzene

4-Nitrothiophenol (14.5 g, 0.093 mol) and (S)-1-chloro-2-methylbutane (Tokyo Chemical Co. 10.0 g, 0.093 mol) were dissolved in 200 mL of N,N-dimethlyformamide (DMF), and 0.5 g of potassium iodide and 40 g of potassium carbonate were added. The mixture was stirred vigorously at 80°C for 6 h. After the solution was cooled to ambient temperature, 400 mL of water was added to the solution, and the sulfide was extracted with diethylether. After the diethylether solution was dried over sodium sulfate the solvent was evaporated, and the resultant solid was dissolved in 400 mL of methanol. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, 0.6 g) in 30 mL of water was added to the solution. The solution was stirred and heated to 40°C, and 50 mL of 30% H_2O_2 was added dropwise over 2 h. The solution was then heated to 80°C, 25 mL of H_2O_2 was added, and the resultant mixture was refluxed for 2 h. The solution was cooled to ambient

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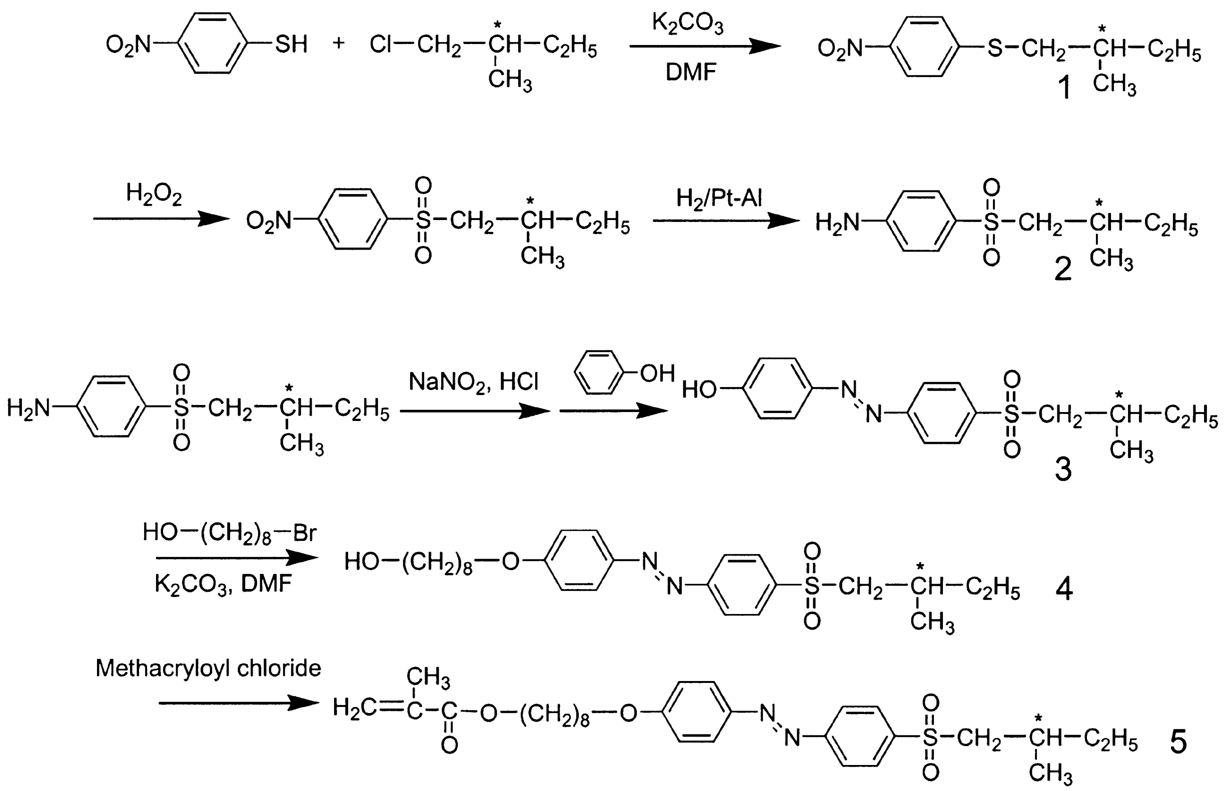

FIGURE 2 Synthetic route for AZO*-8.

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temperature, and slightly yellow crystals were deposited and collected by filtration. The product was purified by recrystallization from methanol-water (3:1) (yield: 61%). Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 51.35; H, 5.88; N, 5.44. Found: C, 51.30; H, 5.91; N, 5.40. ^{1}H NMR ($CDCl_3$) δ 0.83 (t, CH_3), 1.03 (d, CH_3), 1.24–1.47 (m, CH_2), 1.95 (m, CH), 2.86–3.07 (m, SO_2CH_2), 6.98 and 7.71 (aromatic, 4H).

2) 4-((S)-2-methylbutyl) sulfonyl aminobenzene

4-((S)-2-Methylbutyl)sulfonyl nitrobenzene (14.8 g, 0.057 mol) was dissolved in 300 mL of methanol, and 1.0 g of Pt-Al catalyst (5% Pt on alumina) was suspended under N_2 atmosphere. The flask was flushed with hydrogen and the solution was stirred at ambient temperature for 6 h. After the Pt-Al was removed by filtration, the solvent was evaporated, and the resultant product was purified by column chromatography on silica gel (eluent, dichloromethane) (yield: 89%). Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 58.12; H, 7.54; N, 6.16. Found: C, 58.05; H, 7.57; N, 6.13. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, CH_3), 1.05 (d, CH_3), 1.18–1.50 (m, CH_2), 1.95 (m, CH), 2.83–3.24 (m, SO_2CH_2), 4.19 (s, NH_2), 6,70 and 7.64 (aromatic, 4H).

3) 4-Hydroxy-4′-((S)-2-methylbutyl)sulfonyl azobenzene

4-((S)-2-Methylbutyl)sulfonyl aminobenzene (11.0 g, 0.048 mol) was dissolved in 200 mL of a 1:1 mixture of acetone and 1N HCl. The solution was cooled to 0°C, and 3.8 g (0.055 mol) of sodium nitrite in 100 mL of water was added slowly. The resultant diazonium solution was added dropwise to an aqueous solution of phenol (3.6 g, 0.048 mol) and sodium hydroxide (4.0 g, 0.10 mol) at 0°C. After stirring for 2 h, the solution was brought to ambient temperature and neutralized with HCl, and the resultant precipitate was collected by filtration. The product was purified by column chromatography on silica gel (eluent, dichloromethane), followed by recrystallization from methanol (yield: 68%). Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.39; H, 6.10; N, 8.41. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, CH_3), 1.05 (d, CH_3), 1.18–1.50 (m, CH_2), 2.05 (m, CH), 2.95–3.16 (m, SO_2CH_2), 6.97, 7.91 and 7.98–8.11 (aromatic, 8H).

4) 4-(8-Hydroxyoctyloxy)-4′-((S)-2-methylbutyl)sulfonyl azobenzene

4-Hydroxy-4′-((S)-2-methylbutyl)sulfonyl azobenzene (6.8 g, 0.02 mol) and 2.2 g (0.02 mol) of 8-bromooctanol were dissolved in 100 mL of DMF, 10 g of potassium carbonate were added, and the mixture was vigorously stirred at 60°C for 12 h. The solution was poured into 500 mL of water, and the resultant precipitate was collected by filtration. The product was purified by

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column chromatography on silica gel (eluent, dichloromethane), followed by recrystallization from methanol (yield: 51%). Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 65.19; H, 7.88; N, 6.08. Found: C, 65.15; H, 7.89; N, 6.05. ^1H NMR ($CDCl_3$) δ 0.85 (t, CH_3), 1.05 (d, CH_3), 1.25–1.76 (m, CH_2, 14H), 2.05 (m, CH), 2.95–3.16 (m, SO_2CH_2), 3.65 (t, HO-CH_2), 4.15 (t, -O-CH_2), 7.01, 7.94 and 8.00–8.05 (aromatic, 8H).

5) 4-(8-Acryloyloxyoctyloxy)-4′-((S)-2-methylbutyl)sulfonyl azobenzene (AZO-8 monomer)*

4-(8-Hydroxyoctyloxy)-4′-((S)-2-methylbutyl)sulfonyl azobenzene (4.7 g, 0.01 mol) and 3 mL of pyridine were dissolved in 100 mL of dichloromethane, and 2.3 g (0.02 mol) of methacryloyl chloride in 50 mL of dichloromethane was added dropwise and stirred for 5 h. The solution was washed with an aqueous solution of saturated sodium bicarbonate and dried over sodium sulfate. After the solvent was evaporated, the product was purified by column chromatography on silica gel (eluent, dichloromethane), followed by recrystallization from 2-propanol (yield: 61%). Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 65.88; H, 7.63; N, 5.30. Found: C, 65.85; H, 7.60; N, 5.26. ^1H NMR ($CDCl_3$) δ 0.85 (t, CH_3), 1.05 (d, CH_3), 1.25–1.76 (m, CH_2, 14H), 2.05 (m, CH), 2.95–3.16 (m, SO_2CH_2), 3.99 (t, HO-CH_2), 4.15 (t, -O-CH_2), 5.55 and 6.10 (s, C=CH_2), 7.01, 7.94 and 8.00–8.05 (aromatic, 8H).

Polymerization

Thermal radical polymerization of AZO*-8 was carried out in a 10 wt% benzene solution with azobis(isobutylonitrile) (AIBN, 3 mol%) serving as an initiator. All solutions were degassed by a freeze-pump-thaw cycle and heated at 70°C for 20 h. The resulting polymers were purified by repeated reprecipitation from chloroform solution into methanol.

Measurement

The number-average molecular weight (Mn) of the polymers was determined by gel permeation chromatography (GPC; Toyo-soda TSK-GEL G3000HHR; eluent, THF), and the glass transition temperature (Tg) and phase transition temperature were 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 photorefractive property was evaluated via a four-wave mixing experiment. Figure 3 shows a schematic illustration of the experimental

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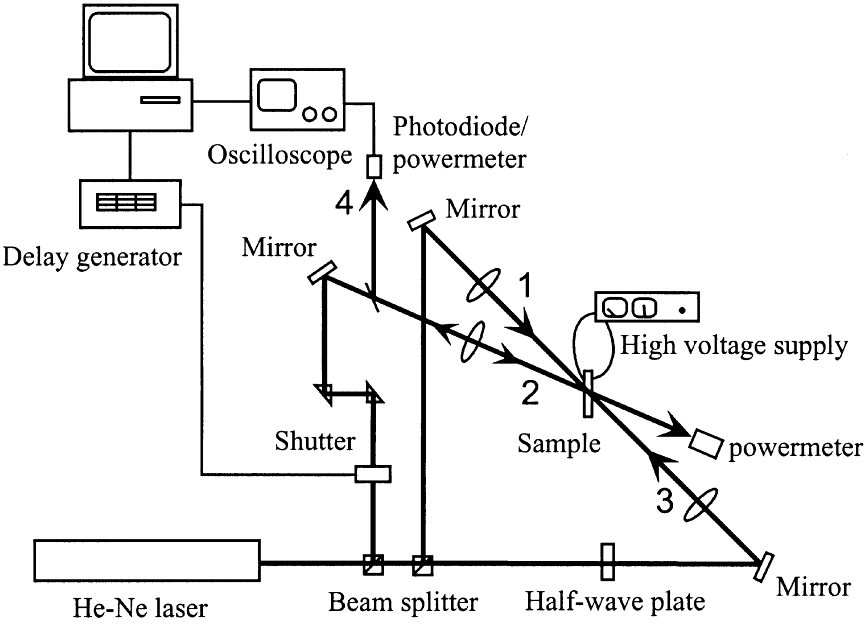

FIGURE 3 Schematic illustration of experimental setup used in this study.

setup. Four-wave mixing experiments were performed using s-polarized writing beams and a p-polarized probe beam counterpropagating to one of the writing beams. A He-Ne laser (Mellesgriot, 633 nm, 7 mW output) was used as a light source. Beam 1 and beam 2 interfered in a sample film, and the intensity of the diffraction of beam 3 (phase conjugate wave, beam 4) was measured by a photodiode (E-O TECH ET2010, response < 1 ns) and recorded by a storage-oscilloscope. The angle between the two writing beams was 72° inside the film (refractive index $= 1.75$), and the grating period was 2.9 μm. The diffraction efficiency is defined as the ratio of intensity of the diffracted beam and the intensity of the probe beam that is transmitted when no grating is being written in the sample by the writing beams. The temperature of the sample was controlled by a thermo-controller (Chino Co. DB1000). An electric field of $10 \sim 40$ V/μm was applied to the sample by a high voltage supply unit (Glassman High Voltage, Inc., PS/EL1OR4.0-10). For two-beam coupling experiments, the transmitted intensities of beams 1 and 2 were measured by power meters. SHG intensities were measured by the Maker fringe method (Tokyo Instruments NL-100 NLO evaluation system). A 1064 nm Nd:YAG laser was used as a fundamental source. The generated 532 nm signals were detected by a photomultiplier and integrated by a boxcar averager.

RESULTS AND DISCUSSION

Photorefractivity of the Isotropic Phase of a Liquid Crystalline Polymer NitroAzo6 and Amorphous Polymer DMAzo6 Doped with Photoconductive Compounds

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A 1:1 copolymer of methylmethacrylate and 4-methacryloyloxyhexyloxy-4′-nitroazobenzene (NitroAzo6) exhibits a nematic liquid crystal phase, whereas a 1:1 copolymer of methylmethacrylate and 4′-methacryloyloxyhexyloxy-2′5′-dimethyl-4-nitroazobenzene (DMAzo6) does not exhibit a liquid crystal phase. The diffraction efficiencies of polymers NitroAzo6 and DMAzo6 mixed with photoconductive compounds (CDH and TNF) were investigated. The sample composition was TNF:CDH:polymer = 1:40:59 wt%. The photoconductive dopant, CDH, is not a liquid crystal, and therefore the mixture of NitroAzo6 and 40 wt% of CDH did not exhibit a liquid crystal phase. The sample film was isotropic and transparent. A two-beam coupling experiment was performed on the sample. An asymmetric energy exchange was observed as applying an external electric field (Figure 4). The diffraction efficiencies were evaluated by the four-wave mixing experiments. When an external electric field was applied to the sample, the diffraction of beam 3 (phase conjugate wave 4) was clearly observed (Figure 5). When the field was turned off, the diffraction disappeared. The diffraction efficiency is defined as $\Delta I/I_0$, where I_0 represents the transmitted intensity of beam 3 through the sample without beams 1 and 2, and ΔI represents the intensity of the diffracted beam. The dependence of diffraction efficiency on the magnitude of the electric field is shown in Figure 6, where we can see that diffraction efficiency increases with the intensity of the applied electric field.

The four-wave mixing experiment was also performed on the amorphous polymer DMAzo6. The concentrations of CDH and TNF were 40 wt% and 1 wt%, respectively. Both samples induced less scattering of the laser beam and neither sample produced any XRD peaks. The diffraction efficiency of DMAzo6 was found to be much smaller than that of NitroAzo6, although their molecular weights are almost the same and DMAzo6 exhibits a lower glass transition temperature than does NitroAzo6. As compared with the amorphous polymer, the isotropic phase of the liquid crystalline polymer

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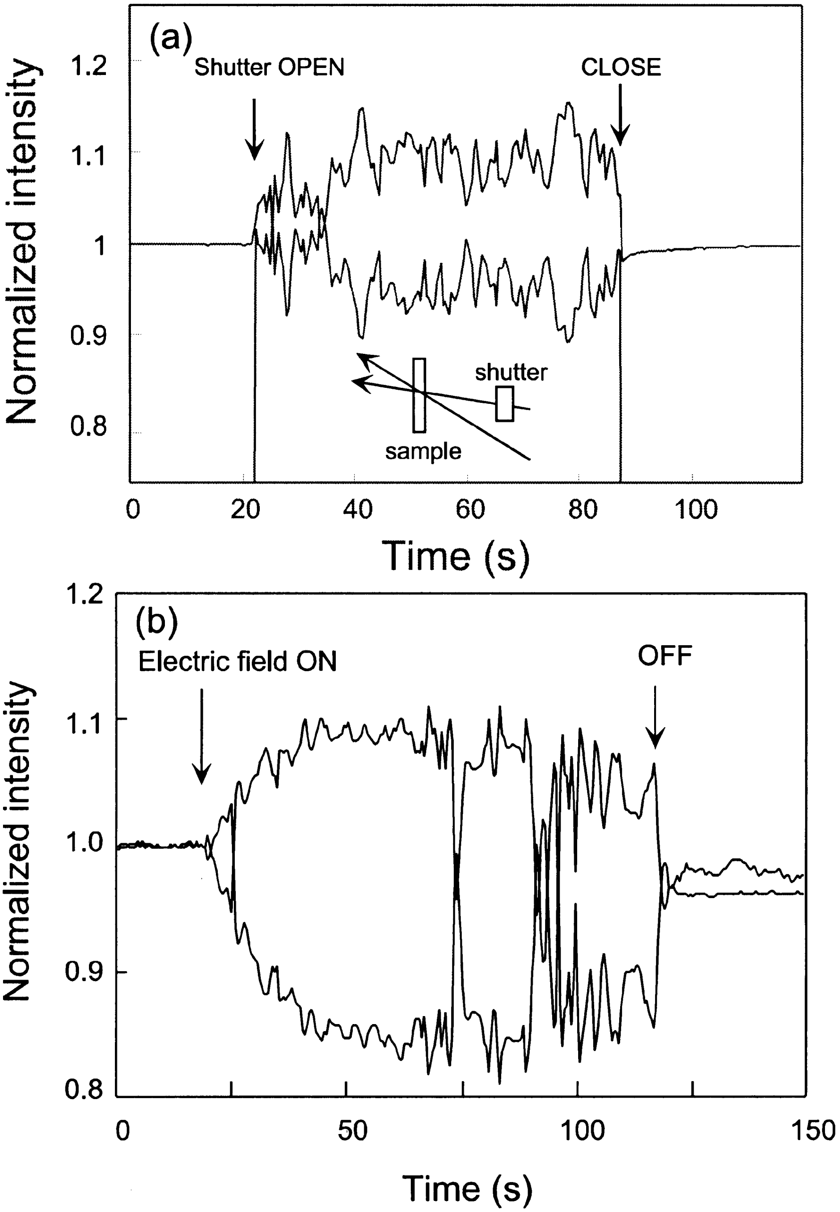

FIGURE 4 Typical example of asymmetric energy exchange in two-beam coupling experiment for NitroAzo6 doped with 40 wt% CDH and 1 wt% TNF. (a) An electric field of 20 V/μm was applied to the sample and the shutter was open at t = 22 s and closed at t = 86 s. (b)An electric field of 20 V/μm was applied to the sample at t = 20 s and cut off at t = 115 s.

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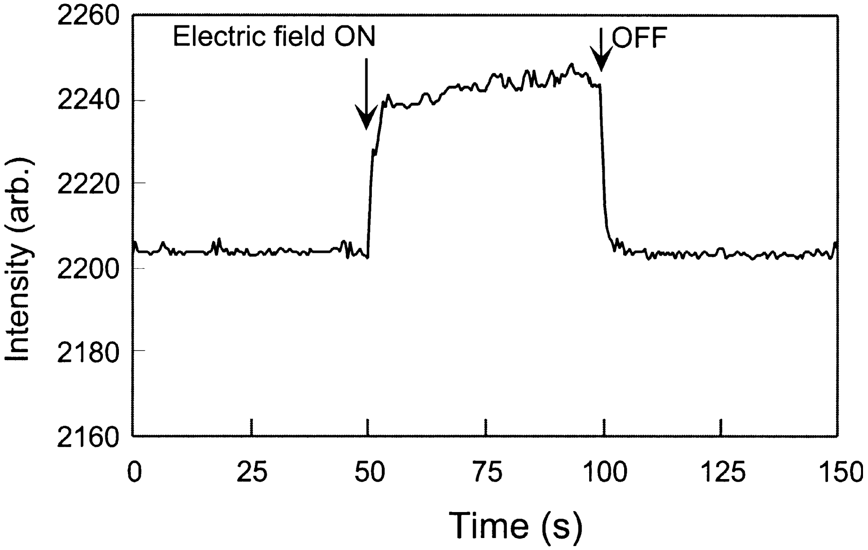

FIGURE 5 Diffracted beam observed in four-wave mixing experiment conducted on NitroAzo6 doped with 40 wt% CDH and 1 wt% TNF. An electric field of 40 V/μm was applied to the sample at t = 50 s and cut off at t = 100 s.

exhibits higher photorefractivity, which supports the enhancement effect in the isotropic phase of liquid crystalline polymers recently reported [18]. The enhancement of photorefractivity in the isotropic phase of liquid crystalline polymer is considered to arise from the microscopic ordering of mesogens (chromophores) in the isotropic phase. The mesogens of the liquid crystalline polymer NitroAzo6 tend to align with each other even in the isotropic phase, producing a temporal microscopic ordering of chromophores. The existence of a small domain is considered to enhance the change in the refractive index through an orientational effect.

The Photorefractive Effect of AZO-8 and AZO*-8

We also investigated the photorefractivity of liquid crystalline polymers possessing alkylsulfon-substituted azobenzene poly 4-(8-methacryloyloxyoctyloxy)-4′-butylsulfonylazobenzene (AZO-8) and poly 4-(8-methacryloyloxyoctyloxy)-4′-((s)-2-methylbutyl)sulfonylazobenzene (AZO*-8), by measuring the diffraction efficiencies of the isotropic phase of each of these polymers. The sample composition was TNF:CDH:polymer = 1:40:59 wt%. Figure 7 shows the diffraction efficiency of AZO-8 as a function of the

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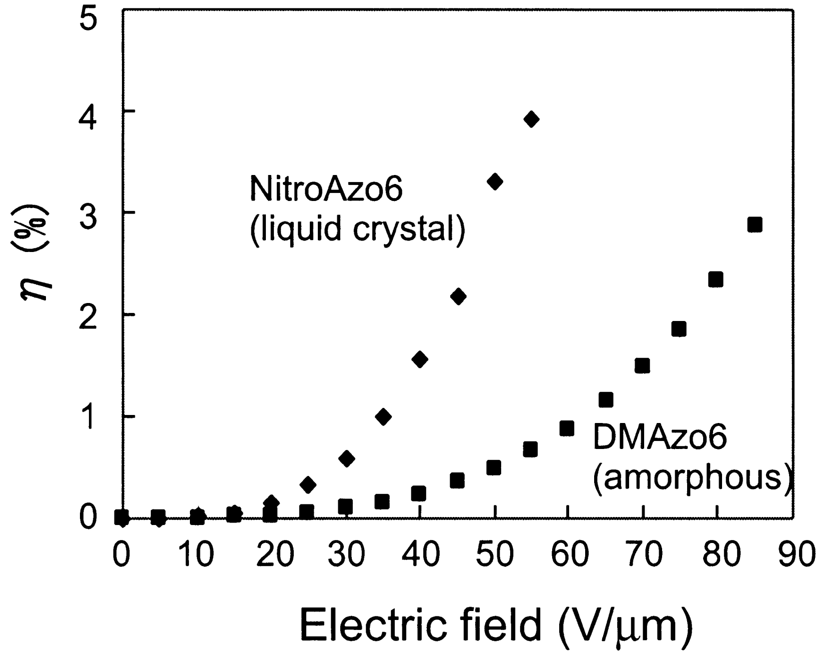

FIGURE 6 Electric field dependence of diffraction efficiency of NitroAzo6 and DMAzo6 doped with 40 wt% CDH and 1 wt% TNF. ◆, NitroAzo6; ■, DMAzo6.

magnitude of an applied electric field. Diffraction efficiency showed $\sin^2$ functional dependence on the electric field, which can be related to Kogelnik's theory of a coupled wave in a thick medium [21]. The mechanism of the photorefractive effect of AZO-8 is considered to consist primarily of the photovoltaic effect and the succeeding electrooptic effect. Figure 8 shows the diffraction efficiency of the chiral polymer AZO*-8 as a function of the magnitude of an applied electric field. The diffraction efficiency of AZO*-8 showed no clear dependence on the magnitude of the applied electric field, which indicates that for AZO*-8 the polarization of the film (and thus the Pockels constant of the film) is not important in four-wave mixing. The diffraction was observed even when the external electric field was not applied. If the diffraction at an electric field of 0 V/μm arises from the chiral structure of the microscopic domain, the second order nonlinear optical properties of AZO*-8 must be active in the absence of the electric field. However, no SHG was observed in AZO*-8 films when no external electric field was applied. Thus, the change in the refractive index of AZO*-8 at 0 V/μm is not via the Pockels effect. Although the asymmetric energy

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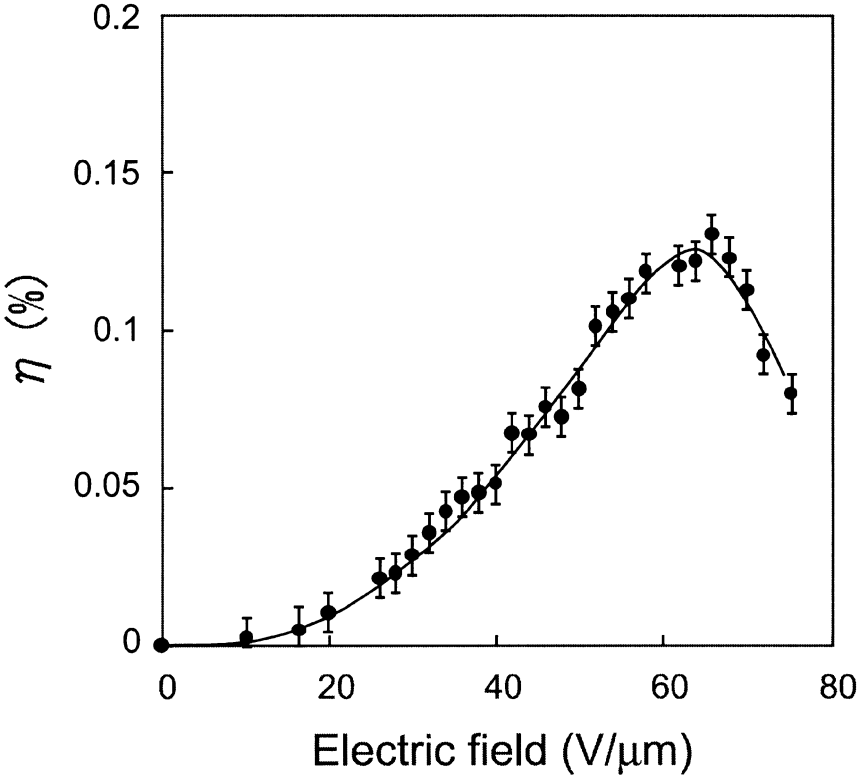

FIGURE 7 Electric field dependence of diffraction efficiency of AZO-8 doped with 40 wt% CDH and 1 wt% TNF.

exchange was observed in AZO*-8 at 0 V/μm in the two-beam coupling experiment, the intensity of the signal was unstable and fluctuated with time. The azobenzene chromophore can exhibit trans-cis photoisomerization. If the chromophore absorbs the laser beam, the refractive index grating can be created by photoisomerization. However, distinct from the photorefractive effect, the phase of the grating created by photoisomerization is not shifted from the interference pattern. The asymmetric energy exchange cannot be observed if the index grating was made by the photoisomerization. In addition, the azobenzene chromophore of AZO*-8 does not exhibit an absorption band at 633 mn, and therefore the diffraction at 0 V/μm is considered not to be induced by trans-cis photoisomerization. Figure 9 shows the SHG signal measured by the Maker-fringe method under application of an electric field of 40 V/μm. The SHG signal of AZO*-8 was

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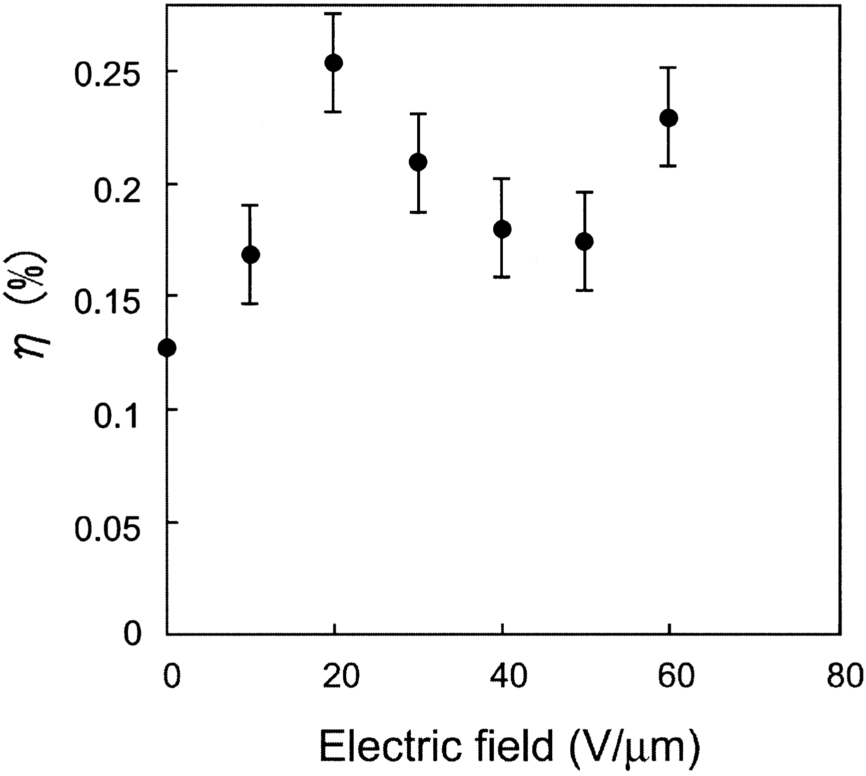

FIGURE 8 Electric field dependence of diffraction efficiency of AZO*-8 doped with 40 wt% CDH and 1 wt% TNF.

larger than that of AZO-8 under identical conditions. This indicates that the AZO*-8 films can be polarized more easily than can the AZO-8 films, because the films exhibit almost identical hyperpolarizabilities [22, 23]. Also, the glass transition temperature of AZO*-8 is lower than that of AZO-8. The chromophores of AZO*-8 may be able to move more easily than those in AZO-8.

The data on distribution of free volume can be obtained by investigating trans-cis photoisomerization behavior in the film [24–28]. Figure 10 shows the absorption spectra of the polymer films before and after irradiation of 366 nm UV light. Reversible changes in UV spectra are induced by irradiation in both films. These polymers differ only in the structure of the alkyl tail unit of the mesogens; no difference is observed in photoisomerization behavior in dichloroethane solution. Figure 11 shows the change in

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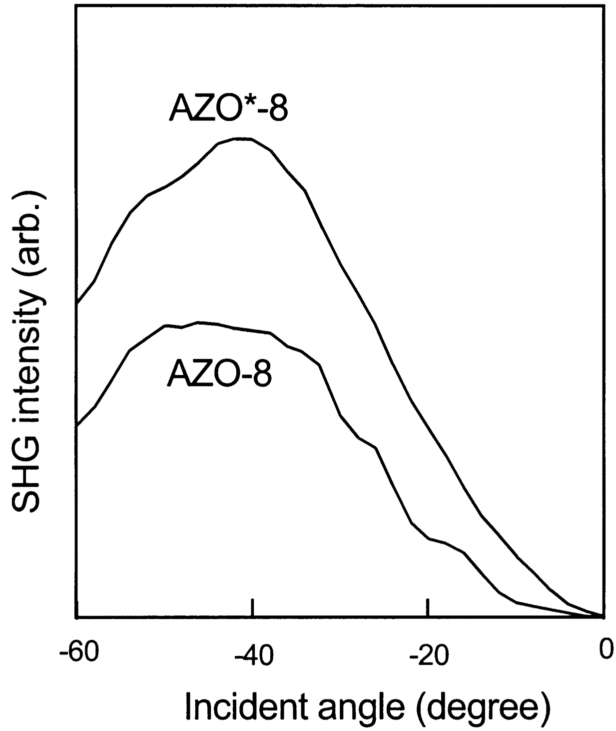

FIGURE 9 Second harmonic signal intensities of AZO-8 and AZO*-8 films doped with 40 wt% CDH and 1 wt% TNF measured by the Maker-fringe method. An electric field of 40 V/μm was applied to the films.

absorption of the films at 350 nm as a function of irradiation time. Measurement of the two films was conducted under the same conditions. AZO*-8 exhibited a faster rate of photoisomerization and a larger change in absorption spectra, and AZO*-8 films are considered to possess larger inner free volume than AZO-8 films. The chiral group in the alkyl tail unit generates a larger free volume in the film and enhanced the mobility of the chromophores. The directions of the chromophores of AZO*-8 are more responsive to the electric field than are those in AZO-8. The diffraction in four-wave mixing in AZO*-8 may be partially due to thermal gratings. However, the asymmetric energy exchange observed in two-beam coupling indicates the occurrence of the orientational photorefractive effect. The orientations of azobenzene chromophores of AZO*-8 were affected by the photoinduced internal electric field and produced an orientational grating.

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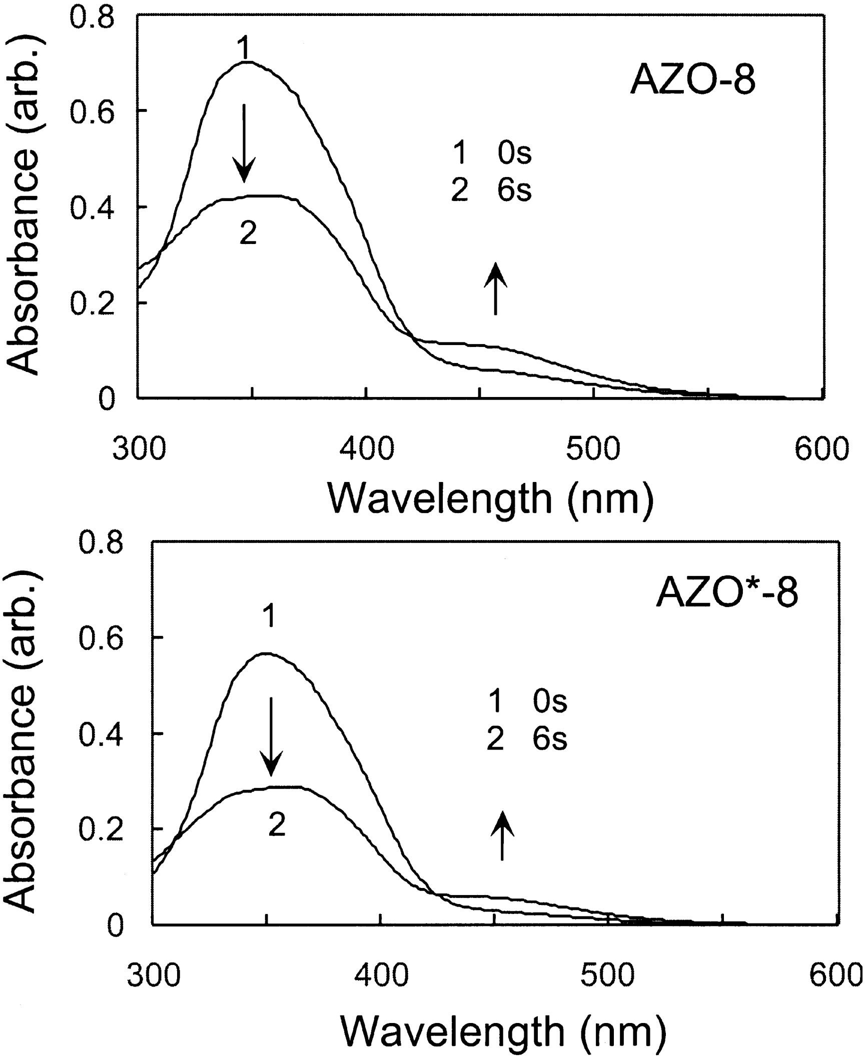

FIGURE 10 Absorption spectra of AZO-8 and AZO*-8 films before and after irradiation with 366 nm light.

The existence of both thermal grating and orientational grating may have caused the unstable fluctuation of the signal intensities. In contrast, the AZO-8 polymer is rather rigid, so that the orientations of chromophores were less affected by the internal electric field.

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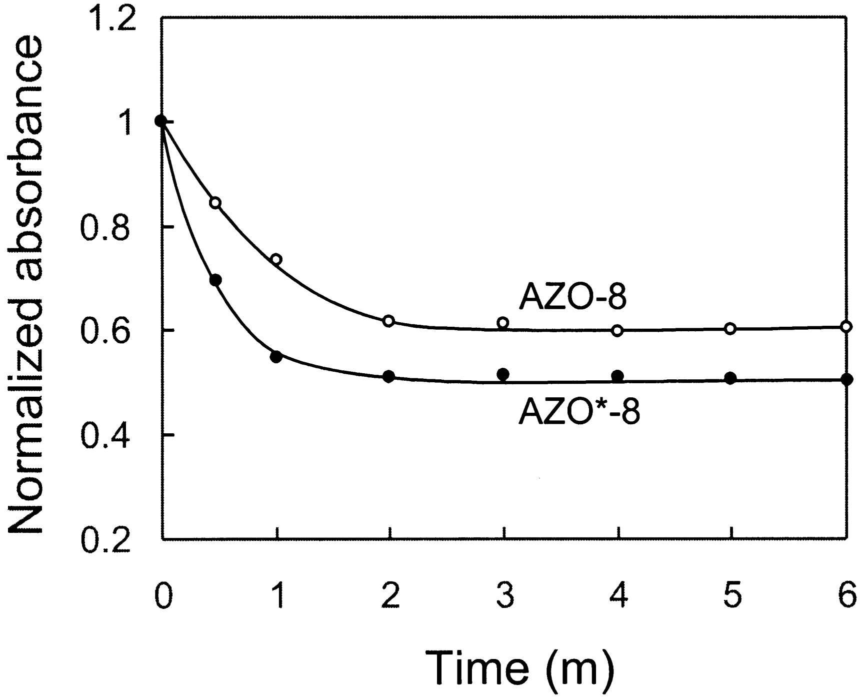

FIGURE 11 Absorption at 350 nm of AZO-8 and AZO*-8 films as a function of irradiation time.

CONCLUSION

The photorefractive effects of a series of side-chain polymers that possess azobenzene chromophores were investigated. Diffraction efficiency was found to be significantly higher in the isotropic phase of the liquid crystalline polymer than in an amorphous polymer of almost identical molecular structure. AZO*-8 exhibited unusual behavior in the photorefractive effect. Chromophores of the AZO*-8 film are considered to exhibit large mobility and exhibit an orientational photorefractive effect.

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