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Photorefractive Effect in Liquid-Crystalline Polymers Containing Hydrogen-Bonding Moiety

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The effect of the introduction of microdomains in polymer films on the photorefractive effect was investigated. The photorefractivity of side-chain liquid-crystalline polymers that possess a hydrogen-bonding moiety was examined using a four-wave mixing experiment. The photorefractivity was compared to that of a polymer which has no hydrogen-bonding moiety. A significant difference was found in the photorefractivity between hydrogen-bonding polymers and non-hydrogen-bonding polymers. This difference was likely due to the presence of microdomain structures in the polymers with the hydrogen-bonding moieties.

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.[1−4] A photorefractive material exhibits both photovoltaic effect and an electro-optic effect. The interference of two laser beams in a photorefractive material establishes a refractive index grating. The change in refractive index through the photorefractive effect occurs only within the interference fringe of the incident laser beams. The mechanism of the formation of a refractive index grating is shown in Figure 1. When laser beams interfere in a photorefractive material, charge separation occurs between the light and the dark positions of the interference fringe. A space-charge field (internal electric field) is built in the area between the light and the dark positions. The refractive index of the corresponding area is changed through electro-optic effects. Thus, a refractive index grating is formed at the interference fringe. Dynamic volume holograms are easily formed through the photorefractive effect and this effect has direct applicability in photonics, including optical image processing, parallel optical logic, pattern recognition, and phase conjugation. It is characteristic of the photorefractive effect that the phase of the refractive index grating is $\pi/2$ shifted from the interference fringe. In such a phase-shifted grating, laser beams have a unique mode of propagation.[2] The interfering laser beams are energetically coupled through the phase-shifted grating, and the transmitted intensity of one beam through the material appears to increase, while that of the other appears to decrease. This phenomenon is known as asymmetric energy exchange in two-beam coupling.[1−3] An organic photorefractive material is composed of D-π-A chromophores and photoconductive compounds. When laser beams interfere in such an organic material, a change in orientations of D-π-A chromophores is induced by the internal electric field. A very high photorefractive performance (diffraction efficiency) has been achieved in various polymeric materials[5−8] and liquid-crystalline materials.[9−14]

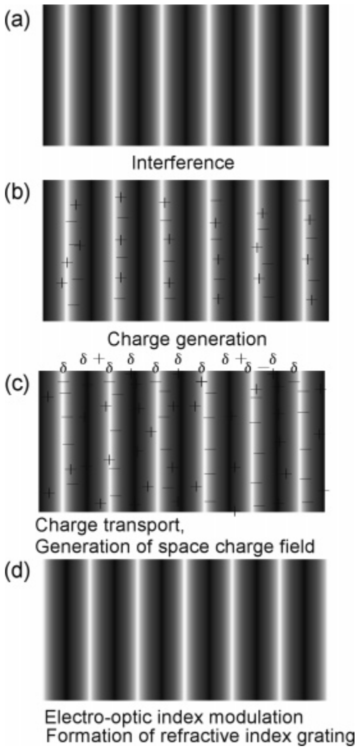

Figure 1. Schematic illustration of the mechanism of the photorefractive effect: (a) two laser beams interfere in the photorefractive material; (b) charge generation occurs in the light area of the interference; (c) while the electrons are trapped at the trap site in the light area, holes migrate by diffusion or drift in the presence of an external electric field and generates an internal electric field between the light and the dark positions; (d) the refractive index of the corresponding area is altered by the internal electric field.

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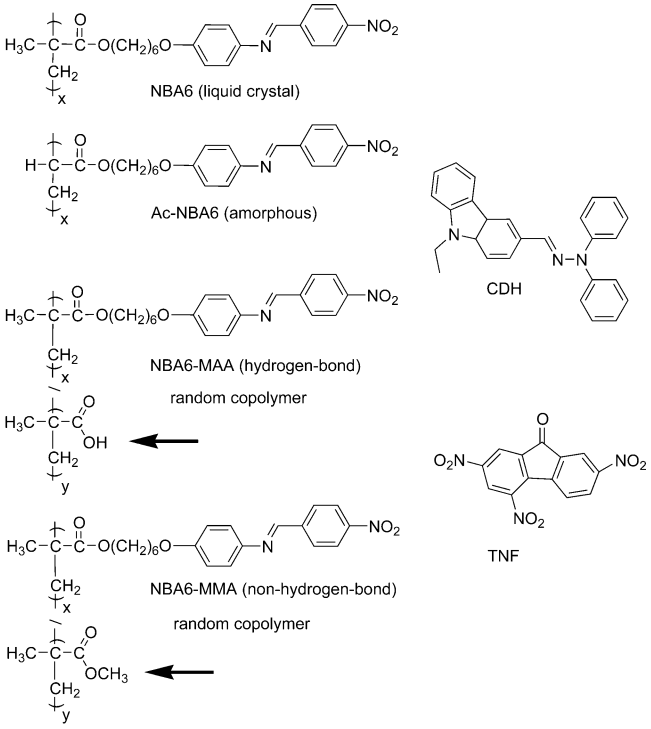

Figure 2. Molecular structures of the compounds used in this study.

In a previous study, we investigated photorefractive effects in liquid-crystalline polymers that possess D-π-A chromophores as mesogens and compared the results with amorphous polymers.[15−19] Our investigation revealed that the photorefractive effect is significantly enhanced in the isotropic phase of the liquid-crystalline polymers. The diffraction efficiency of the isotropic phase of the liquid-crystalline polymers was found to be much greater than that of amorphous polymers, even though these polymers have almost identical molecular structures.[15] Although the exact mechanism of the enhancement effect has not yet been elucidated, it is considered to arise from the microscopically ordered structure of component chromophores in the isotropic phase. If the microscopically ordered structure plays an important role in the enhancement of the photorefractive effect, the introduction of a hydrogen-bonding moiety into the polymer would significantly affect the photorefractivity. To investigate this possibility, in this study, we prepared D-π-A polymers that possess a hydrogen-bond-formable moiety and compared the photorefractivity with that of polymers without hydrogen-bonding moieties. The polymer used in this study is a side-chain polymer possessing nitrobenzylidenaniline chromophore which has been reported to exhibit large diffraction efficiency.[15] Thus, the polymer used in this study potentially exhibits large diffraction efficiency when illuminated with sufficiently intense lasers.

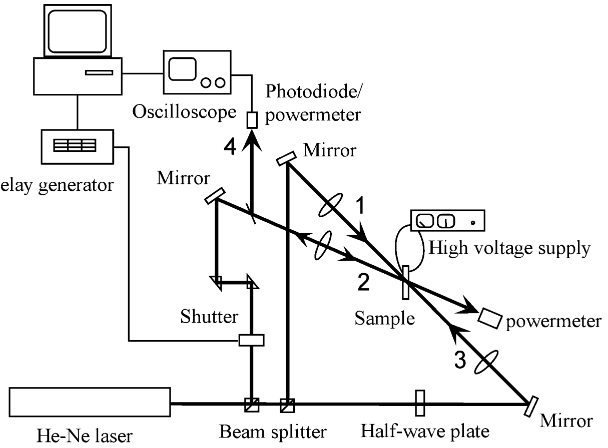

Figure 3. Schematic illustration of the setup for the four-wave mixing experiment. Beams 1 and 2 were interfered in the sample film, and the diffraction of beam 3 was measured. For the two-beam coupling experiment, transmitted intensities of beams 1 and 2 were measured as a function of time.

Table 1. Molecular Weights and Phase Transition Temperatures of the Polymers Used in This Study

	Mn	Mw/Mn	phase transition temperature[a] °C					
NBA6	25000	1.7	g	45	N	109	I
Ac-NBA6	22000	1.8	g	42	I		
NBA6:MMA							
98:2	21000	1.7	g	58	N	105	I
95:5	27000	1.6	g	48	N	98	I
90:10	29000	1.7	g	57	N	105	I
80:20	37000	1.7	g	56	N	93	I
60:40	35000	1.7	g	55	I		
NBA6:MAA							
98:2	28000	1.6	g	56	N	116	I
95:5	29000	1.7	g	58	N	113	I
90:10	23000	1.6	g	60	N	102	I
80:20	37000	1.7	g	65	N	103	I
60:40	35000	1.7	g	53	I		

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

Experimental Section

Preparation of Samples. The molecular structures of the polymers and photoconductive compounds used in this study are shown in Figure 2. Random copolymers of nitrobenzylidenaniline monomer with methacrylic acid (NBA6-MAA) and with methyl methacrylate (NBA6-MMA) were prepared. The thermal properties of these polymers are listed in Table 1. A photoconductive compound, 9-ethyl-3-carbazolcarboxyaldehyde diphenylhydrazone (CDH), and a sensitizer, 2,4,7-trinitro-9-fluorenone (TNF), were mixed with the polymers. Photorefractive samples were prepared by casting a *N*-methylpyrolidon solution of the polymer mixed with CDH and TNF on an ITO patterned glass. No phase separation

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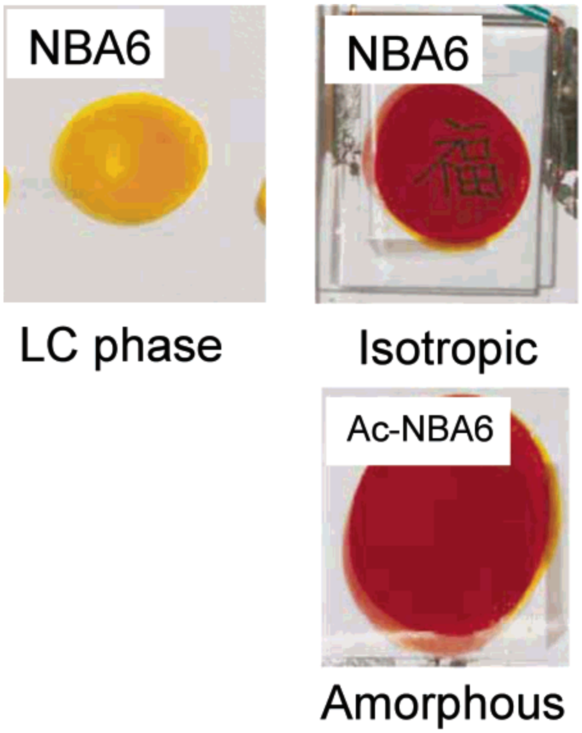

Figure 4. Photographs of the polymer/CDH/TNF (69:30:1) samples showing the transparent nature of the isotropic phase.

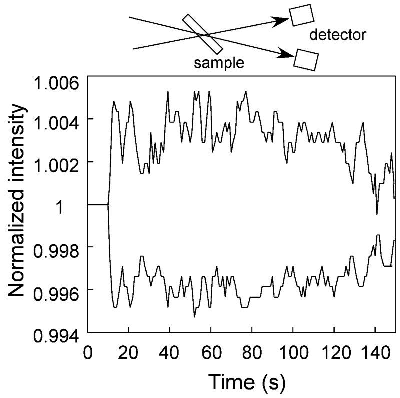

Figure 5. Typical example of asymmetric energy exchange in two-beam coupling experiment for NBA6 doped with 30 wt % CDH and 1 wt % TNF. An electric field of 30 V/μm was applied to the sample at $t = 10$ s.

was observed under a polarizing microscope and during DSC measurements. To obtain a flat film, the casting solution was prepared at a high concentration of about 200 mg in 1 mL. The films were placed in a clean bench for 14 days. The solvent was completely removed from the films after being placed in a vacuum for 6 days. The films were 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 determined by a Teflon spacer.

Measurements. The number-average molecular weight (Mn) of the polymer liquid crystals was determined by gel permeation chromatography (GPC; Shodex K-803; eluent, chloroform), and the glass transition temperatures (Tg) and the phase transition temperatures were respectively determined by differential scanning calorimetry (DSC; DSC20-TS15, Mettler) and by microscopic observation (Mettler FP-80, FP-82 and Olympus BX-50 polarizing microscope). Photorefractive properties were evaluated via a four-wave mixing experiment. Figure 3 shows a schematic illustration of the experimental setup. Four-wave mixing experiments were performed using s-polarized writing beams and a p-polarized probe beam, counter-propagating to one of the writing beams. A He−Ne laser (Mellesgriot, 633 nm, 7 mW output) was used as the light source. Beam 1 and beam 2 interfered within a sample film, and

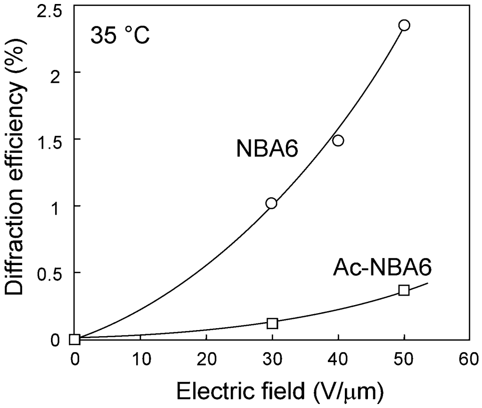

Figure 6. Electric field dependence of the diffraction efficiencies of NBA6/CDH/TNF and Ac-NBA6/CDH/TNF mixtures measured at 35 °C.

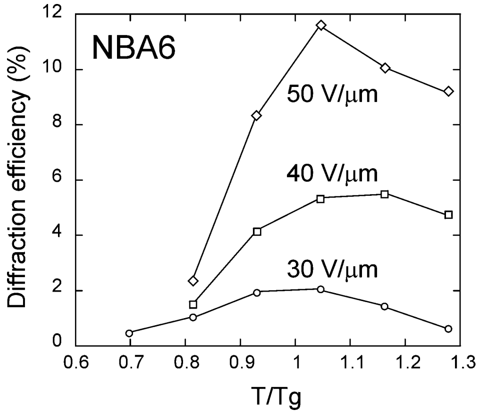

Figure 7. Temperature dependence of the diffraction efficiencies of NBA6/CDH/TNF mixture measured using different strengths of the external electric field. The horizontal axis is the ratio of temperature (K) to the glass transition temperature (K).

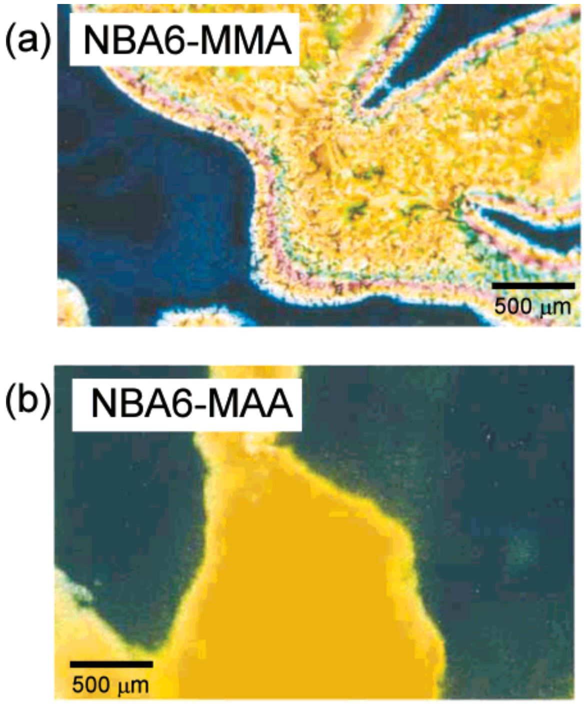

Figure 8. Textures observed under polarizing microscope.

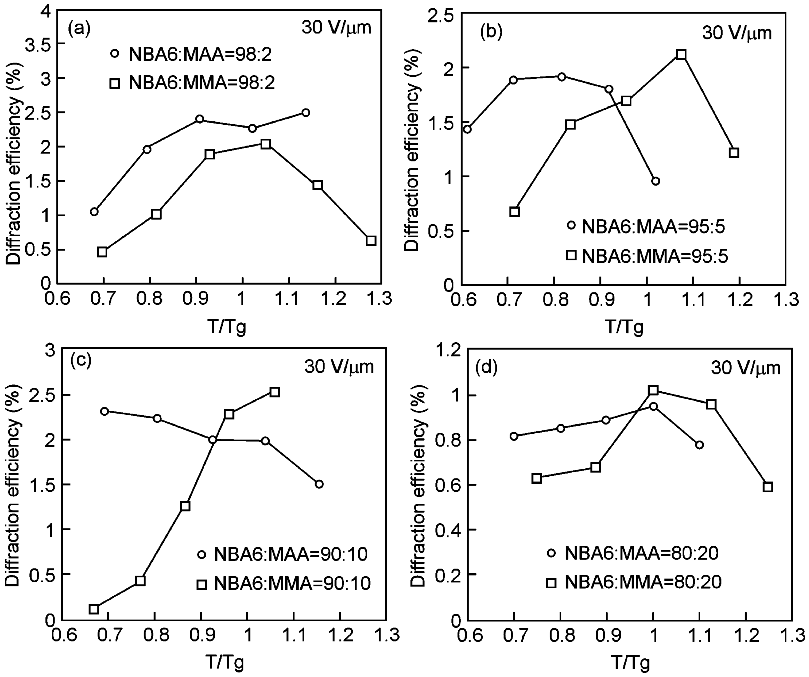

Figure 9. Temperature dependence of the diffraction efficiencies of NBA6/CDH/TNF mixture measured using several strengths of the external electric field. (a) Copolymerization ratio = 98:2; (b) copolymerization ratio = 95:5; (c) copolymerization ratio = 90:10; (d) copolymerization ratio = 80:20.

the intensity of the diffraction of beam 3 (phase conjugate wave, beam 4) was measured using a photodiode (E-O TECH ET2010, response < 1 ns) and recorded on a storage-oscilloscope. The angle between the two writing beams was 7.2° 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 present in the sample due to the writing beams. The temperature of the sample was controlled by a thermo-controller (Chino Co. DB1000). An electric field of 10−40 V/μm was applied to the sample by a high-voltage supply unit (Glassman High Voltage, Inc., PS/EL10R4.0-10). For two-beam coupling experiments, the transmitted intensities of beams 1 and 2 were measured by power meters.

Results and Discussion

Photorefractivity of the Isotropic Phase of a Polymer Liquid-Crystal NBA6 Doped with Photoconductive Compounds. The photorefractivities of the isotropic phases of NBA6/CDH/TNF mixture and Ac-NBA6/CDH/TNF mixture (Figure 2) were investigated. NBA6 exhibited nematic liquid-crystal phase. However, 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 between the two is the structure of the main chain (Ac-NBA6 is an acrylate polymer while NBA6 is a methacrylate polymer). The sample composition was TNF:CDH:polymer = 1:30:69 wt %. The photoconductive dopant, CDH, is not a liquid crystal; therefore, the addition of 30 wt % CDH disturbed the liquid-crystal phase of the host polymer. The CDH-doped NBA6 film was thus isotropic and transparent, as shown in Figure 4. A typical example of the asymmetric energy exchange observed in the two-beam coupling experiment on the CDH-doped NBA6 film is shown in Figure 5. Transmitted intensities of two laser beams are plotted as a function of time. An external electric field of 30 V/μm was applied to the film at $t = 10$ s. When the electric field was applied to the film, the transmitted intensity of one beam increased while that of the other beam symmetrically decreased. The result indicates that the CDH-doped NBA6 film exhibits photorefractivity. The diffraction efficiencies of NBA6/CDH/TNF mixture and Ac-NBA6/CDH/TNF mixture was measured by the four-wave mixing experiment. The diffraction efficiencies of the polymers are plotted as a function of the strength of the external electric field in Figure 6. The diffraction efficiency 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 diffraction efficiency of Ac-NBA6 was found to be much smaller than that of NBA6, even though the molecular weight and the glass transition temperature were almost the same for NBA6 and Ac-NBA6. The absorption and light scattering were also nearly the same in NBA6 and Ac-NBA6 samples. No birefringence was observed in the NBA6 sample. As the molecular structure of NBA6 is almost identical to that of Ac-NBA6, the enhancement of photorefractivity may arise from the morphology of the isotropic phase. In the case of the isotropic phase of a LC, it is believed that the orientations of mesogens are completely random. However, in the case of the isotropic phase of NBA6/CDH mixture, the orientations of mesogens are randomized not by rising temperature, but by lowering of the phase transition temperature through the introduction of an impurity (CDH) into the LC polymer. The formation of an ordered structure is thermodynamically prevented by the presence of the impurity. However, the local concentration of CDH is not unity throughout the highly viscous medium like polymer film. Thus, some fractions of mesogens tend to form locally ordered structure in the microscopic region. It is likely that the electro-optic effect was enhanced

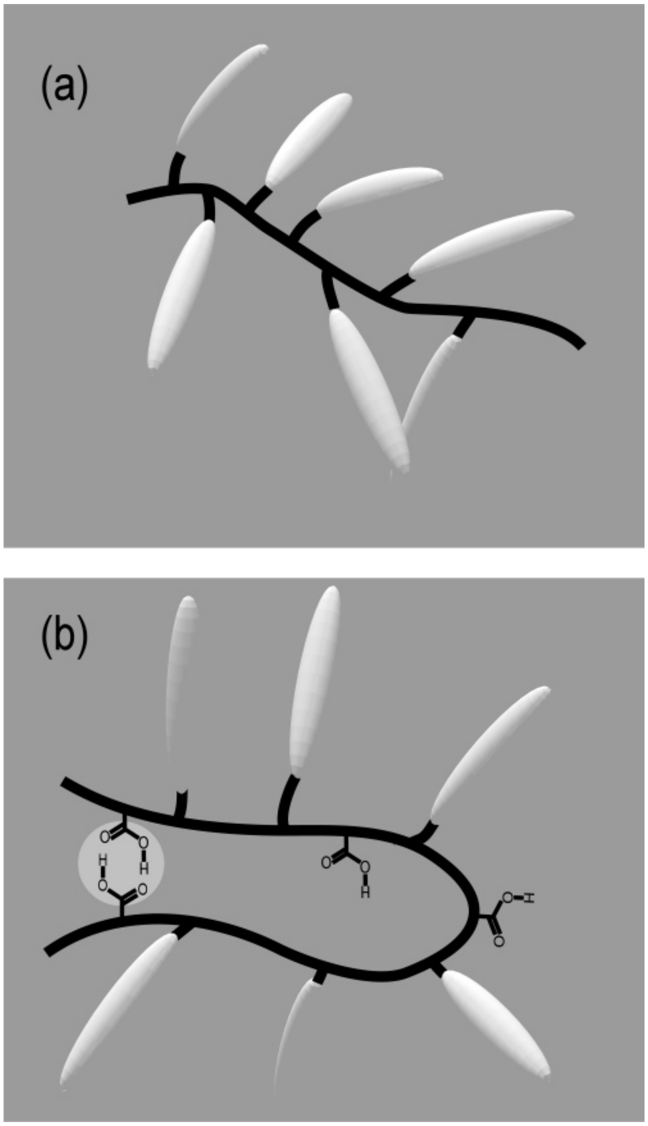

Figure 10. Illustration of a polymer without hydrogen bonding (a) and a polymer with a hydrogen-bonding moiety (b).

by the presence of the microdomain structure, leading to larger photorefractivity.

Temperature Dependence of the Photorefractivity of Liquid-Crystalline Polymer. Figure 7 shows the temperature dependence of the diffraction efficiency of NBA6 doped with 30 wt % CDH and 1 wt % TNF. The diffraction efficiency increased at around the glass transition temperature (Tg). A change in the refractive index in organic polymers is caused mainly by the change in orientations of D-π-A chromophores induced by an internal electric field. The mobility of the D-π-A chromophores increases with increasing temperature above Tg. Thus, the refractive index grating was formed by weaker internal electric fields at temperatures around Tg. However, the diffraction efficiency decreased at higher temperatures, above T/Tg values of 1.2. This is because of increased excess thermal motion of D-π-A chromophores. The orientational grating is distorted by thermal motions at higher temperatures.

The Diffraction Efficiencies of Polymers with Hydrogen-Bonding Moiety. The photorefractivity of copolymers of a nitrobenazylideneaniline monomer and methacrylic acid (NBA6-MAA) were investigated. The carboxylic acid moieties are capable of forming hydrogen bonds and this introduces microdomains in the polymer film. Copolymers of nitrobenzylidenaniline monomer and methyl methacrylate (NBA6-MMA) were used as reference polymers. Since the polymer used in this study contains several carboxylic groups, the formation of hydrogen bonding could not be verified by IR-absorption measurements. Textures of NBA6-MMA and NBA6-MAA films observed under polarizing microscope are shown in Figure 8. While NBA6-MAA exhibited schlieren texture, LC domains of NBA6-MAA were very small and did not exhibit distinguishable texture. The glass transition temperature and nematic−isotropic phase transition temperature are both higher in NBA6-MAA compared to NBA6-MMA (Table 1). Conformational changes of the main chain of NBA6-MAA are restricted by the hydrogen bonding and could lead to higher phase transition temperatures.

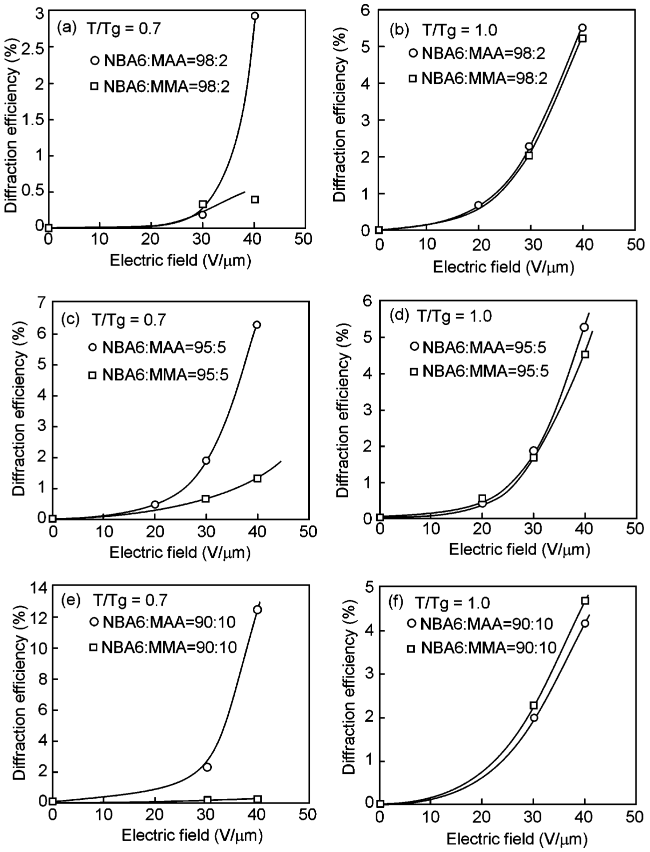

Figure 11. Electric field dependence of the diffraction efficiencies of the copolymers mixed with 30 wt % CDH and 1 wt % TNF. (a) Copolymerization ratio = 98:2, measured at T/Tg = 0.7; (b) copolymerization ratio = 98:2, measured at T/Tg = 1.0; (c) copolymerization ratio = 95:5, measured at T/Tg = 0.7; (d) copolymerization ratio = 95:5, measured at T/Tg = 1.0; (e) copolymerization ratio = 90:10, measured at T/Tg = 0.7; (f) copolymerization ratio = 90:10, measured at T/Tg = 1.0.

The temperature dependence of the diffraction efficiencies of NBA6-MAA and NBA6-MMA mixed with 30 wt % CDH and 1 wt % TNF are shown in Figure 9. The diffraction efficiency of the non-hydrogen-bonding polymer NBA6-MMA increased with increasing temperature around Tg and decreased at higher temperatures. However, the hydrogen-bonding polymer NBA6-MAA exhibited larger diffraction efficiencies at temperatures below Tg, which decreased as the temperature was raised above Tg. For the copolymerization ratios considered, the diffraction efficiencies of NBA6-MAA at temperatures T/Tg = 0.7−0.9 were much larger than those of NBA6-MMA. The larger diffraction efficiencies in NBA6-MAA are considered to originate from the large mobility of the side-chain D-π-A chromophores below Tg and due to an enhancement in the electro-optic effect caused by the presence of microdomains. A change in the refractive index for the photorefractive effect in organic polymers arises chiefly from the orientational change of D-π-A chromophores. However, in common photorefractive polymers, the mobility of side-chain D-π-A chromophores in the film is low at temperatures below Tg. It was considered that the mobility of D-π-A chromophores in NBA6-MAA films at temperatures below Tg was enhanced by the presence of the hydrogen bonding. The conformation of the main chain of NBA6-MAA is restricted by the hydrogen bonding and is likely to be in a stressed state. This results in a larger inner-free volume around the chromophores as shown in Figure 10. The glass transition temperature, below which the main chains freeze, was higher in NBA6-MAA. However, the free volumes around the side chains likely swelled because of the stressed conformation of the main chains. When the temperature was raised above Tg, the hydrogen bonding was broken and the conformation of the main chain relaxed to the thermally stable state. The side chains are closely packed and this leads to smaller free volumes around the D-π-A chromophores. Moreover, the microdomains formed via the hydrogen bonding are disorganized at temperatures above Tg and this lowers the photorefractivity.

The dependence of the diffraction efficiency on the external electric field strength is shown in Figure 11. The diffraction efficiencies at T/Tg = 0.7 and at T/Tg = 1.0 are compared. At T/Tg = 0.7, the diffraction efficiencies of MBA6-MAA were much larger than those of NBA6-MMA. However, when the temperature was raised to T/Tg = 1.0, the polymers showed almost the same electric field dependence. For the copolymer with a copolymerization ratio of 98:2, the magnitude of the diffraction efficiency was larger at higher temperatures. The behavior of the MBA6-MAA 98:2 copolymer is similar to that of non-hydrogen-bonding polymers. The diffraction efficiencies of the NBA6-MAA 95:5 copolymer and the NBA6-MAA 90:10 copolymer were smaller at higher temperatures. The larger amount of hydrogen bonding likely introduced larger inner-free volumes and microdomains at lower temperatures.

Conclusion

The photorefractivity of a series of side-chain polymers which possess a hydrogen-bonding moiety was investigated and compared to that of a polymer with no hydrogen-bonding moiety. The hydrogen-bonding polymer exhibited large diffraction efficiencies at temperatures below the grass transition temperature. The origin of this larger diffraction efficiency at lower temperatures was considered to be a larger free-volume distribution and the existence of microdomain structures.

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