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Photoalignment and Holographic Properties of Azobenzene-Containing Block Copolymers with Oxyethylene and Alkyl Spacers

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*Two azobenzene-containing block copolymers with an oxyethylene (**P1**) or an alkyl (**P2**) spacer in the side chain were prepared by atom transfer radical polymerization (ATRP). Neither of the block copolymers with a low azobenzene content showed a liquid-crystalline phase. However, their glass transition temperatures (T_g s) were lowered by introducing flexible spacers. In particular, T_g was lowered by about 30°C in **P1**. Their photoalignment and holographic behavior was investigated at various temperatures in thin films. Rapid changes in refractive index were induced in the **P1** films upon irradiation at a temperature below T_g . But the photoinduced birefringence in the **P1** film was lower than that in the **P2** films. Similar results were obtained in holographic recording. The azobenzene-containing block copolymer with the oxyethylene spacer (**P1**) used in this study has potential application for dynamic hologram.*

Keywords: atom transfer radical polymerization (ATRP); azobenzene; block copolymer; holography; oxyethylene

INTRODUCTION

Generally, holographic materials require various properties such as high diffraction efficiency, high transparency, quick response, heat-, moisture- and light-resistance. However, it is difficult to attain all of these requirements. Polymeric materials containing azobenzene moieties have been studied for holograms, because of their preferable properties to holograms such as reversible storage and high diffraction

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efficiency [1–11]. Holographic gratings can be formed by photoisomerization and photoinduced alignment of azobenzene molecules.

In our previous studies, azobenzene-containing polymers with alkyl chains as spacers were selected for holographic materials [2–8]. Recently, it was found that the photoinduced birefringence (Δn) of block copolymer films was higher than that of random copolymer films with a similar azobenzene content, thanks to the cooperative motion of liquid crystals in the block copolymer films [5,6]. However, photoisomerization and alignment of azobenzene molecules take place slowly in the block copolymer films than those in the random copolymer films by micro-phase separation upon irradiation. Schmidt *et al.* reported that the higher refractive-index anisotropy was obtained by an increase of free volume and a decrease of the interface layer in block copolymer films [9,10]. Zhao *et al.* indicated that the nanoscale phase separation might restrict the motion of azobenzene moieties in block copolymer films [11].

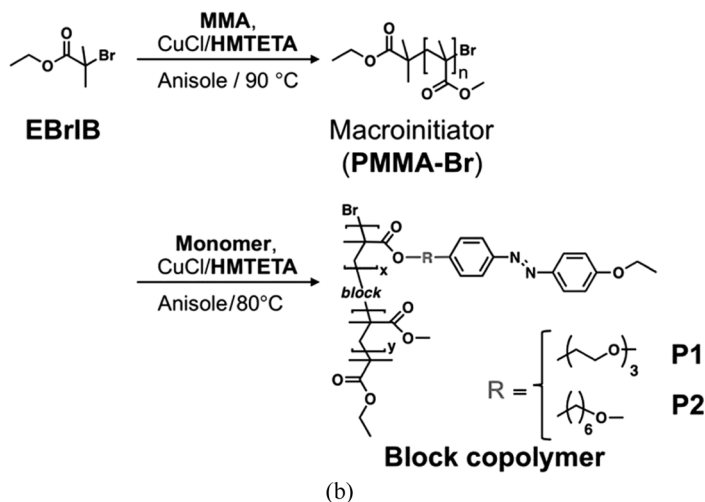
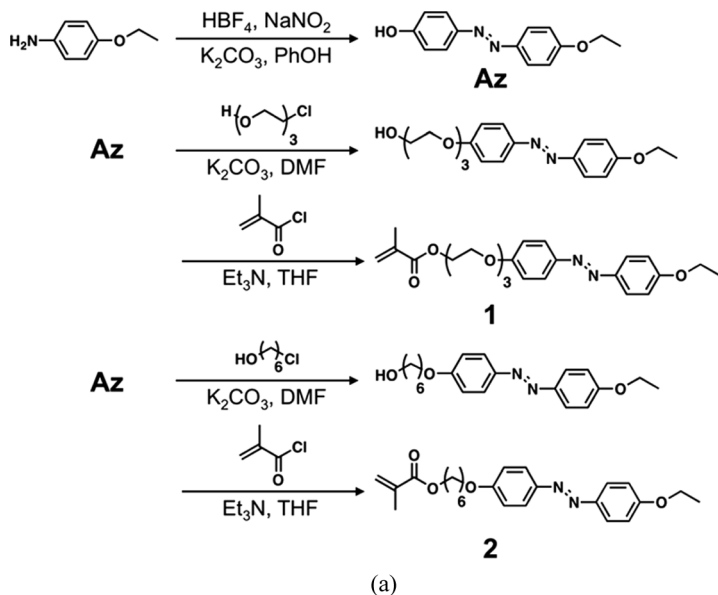
Recently, it has been demonstrated that oxyethylene chains as flexible spacers not only decouple mesogens from the main chains in liquid-crystalline polymers, but also decrease interaction among mesogens [12,13]. The oxyethylene moiety is a very flexible and non-bulky chain. Altomare *et al.* synthesized azobenzene-containing liquid-crystalline polymers with oxyethylene segments and investigated their isomerization behavior [14]. Azobenzene moieties in polymers with the oxyethylene chain may be aligned more easily than those with an alkyl spacer thanks to weak interaction among them in block copolymer films. However, photoinduced changes in alignments of azobenzene moieties have not been reported in block polymers with the oxyethylene spacer.

In this study, photoresponsive and holographic properties were investigated in the block copolymer films with oxyethylene spacers as a flexible unit. For comparison, an azobenzene-containing block copolymer with alkyl spacers was also prepared, and its photoresponsive behavior was explored. The block copolymers with the narrow polydispersity and a similar azobenzene content were prepared by atom transfer radical polymerization (ATRP).

EXPERIMENTAL

Material

As shown in Scheme 1(b), two block copolymers with an oxyethylene or an alkyl spacer in the azobenzene side chain were synthesized by using a bromo-terminated poly(methyl methacrylate) (PMMA-Br) as a macroinitiator by ATRP [5,6], which are named as **P1** and **P2**,



SCHEME 1 Synthetic routes of two azobenzene monomers with an oxyethylene and an alkyl spacer (a) and their corresponding block copolymers (b), **P1** and **P2**, used in this study.

respectively. The two monomers, 4-(8-methacryloyloxy-3,6-dioxaoctyl-1-oxy)-4'-ethoxyazobenzene (**1**) and 4-[6-(methacryloyloxy)hexyloxy]-4'-ethoxyazobenzene (**2**), were prepared according to the reported

procedure shown in Scheme 1(a) [7]. Molecular weight of the polymers was measured by GPC (Japan Spectroscopy Co., model DG-980-50; column, Shodex GPC K802 + K804 + K805; eluent, chloroform) using standard polystyrenes for calibration. The thermodynamic properties of polymers were analyzed with a differential scanning calorimeter (DSC, Seiko I&E SSC-5200 and DSC220C) at heating and cooling rates of 10°C/min. At least three scans were performed to check the reproducibility. The mole fraction of the azobenzene moiety in the copolymers was estimated by the absorbance of the copolymers and the monomers in toluene measured by UV-vis spectroscopy (JASCO, V-550).

Film Preparation

The block copolymer films with a thickness of about 1.9 μm were prepared by casting their toluene solution onto glass substrates. The film thickness was measured with a surface profiler (Veeco Instruments Inc., Dektak 3ST). Before measurement, the films were annealed at 140°C in a vacuum oven for 40 h. The heating and cooling rates were controlled at 0.5°C/min and 0.1°C/min, respectively. Atomic force microscopy (AFM) images of surface modulation were detected with a scanning probe microscope (Veeco Instruments Inc., Nanoscope IV) in a tapping mode at room temperature.

Optical Setups for Photoinduced Alignment and Formation of Gratings

The sample film was first fixed on a rubber heater to control the temperature of the film (Fig. 1(a)). Then an *s*-polarized beam at 488 nm from an Ar⁺ laser (Spectra Physics, Inc., BeamLok2065-7S) (100 mW/cm²) was used to induce alignment of azobenzene moieties in the sample film. Figure 1(b) shows an optical setup for photoinduced alignment. The intensity of a probe beam at 633 nm from a He-Ne laser (NEC, Co., GLS5370) transmitted through a pair of crossed polarizers, with the sample film fixed on the heater between them, was measured with a photodiode.

Gratings with a fringe spacing of 2 μm were formed upon irradiation with two interference beams on a film at an incident angle of 7° (Fig. 1(c)). The total intensity of the beams was 100 mW/cm². The grating formation was evaluated by monitoring the first-order diffraction beam (I_1) at 633 nm from a He-Ne laser with a photodiode in real time. The first-order diffraction efficiency (η) was defined

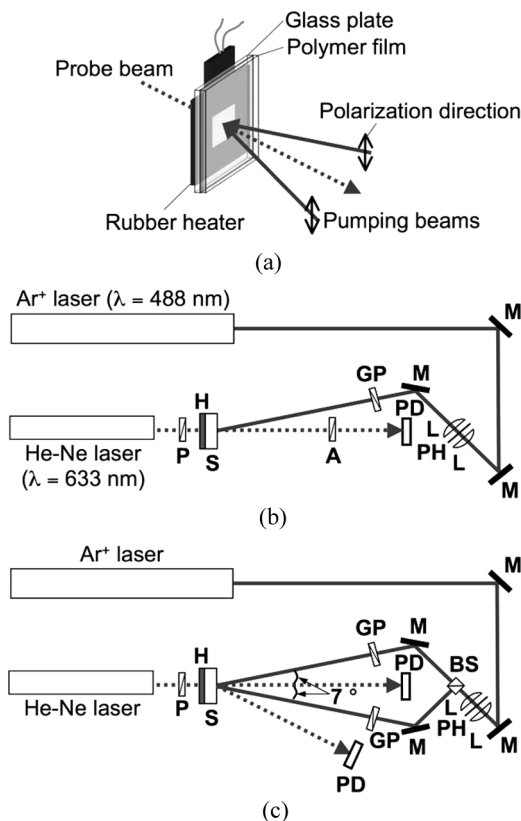


FIGURE 1 Optical setup around the sample (a), for the evaluation of the photoinduced birefringence (Δn) (b) and for the formation of gratings (c). A, analyzer; BS, beam splitter; GP, Glan-Thomson prisms; L, lens; M, mirror; PH, pinhole; S, sample; P, polarizer; PD, photodiode; H, rubber heater.

as the ratio of I_1 to the intensity of the transmitted beam before recording (I_0).

$$\eta = \frac{I_1}{I_0} \quad (1)$$

RESULTS AND DISCUSSION

Properties of Polymers

Results of characterization of the polymers are summarized in Table 1. Although both block copolymers had almost a similar azobenzene

TABLE 1 Summary of Properties of the Block Copolymers Used in this Study

| | M_n | M_w/M_n | Composition ratio (x:y) | Phase transition temperature (°C) |
|----------------|--------|-----------|-------------------------|-----------------------------------|
| PNMA-Br | 12,000 | 1.12 | — | G 118 I |
| P1 | 18,000 | 1.04 | 6.94 | G 87 I |
| P2 | 19,000 | 1.04 | 9.91 | G 105 I |

M_n , number-average molecular weight; M_w , Weight-average molecular weight; G, glassy; I, isotropic.

content as evaluated by UV-vis absorption spectra, their T_g values were different: T_g of **P1** was 87°C, while that of **P2** was 105°C. T_g of a homopolymer with an oxyethylene spacer is lower than that with an alkyl spacer [6,8,15]. It has been reported that a flexible spacer leads to a decrease of T_g and a separation of the motion of a main chain from those of mesogens [12–14]. The oxyethylene spacer in the azobenzene block may decouple azobenzene moieties from the main chain. The **P1** film with an oxyethylene spacer showed microphase separation with spherical microdomains after annealing (Fig. 2(a)). This might be due to the introduction of hydrophilic segments of oxyethylene. Although **P2** has a similar azobenzene content, its film did not show any microphase separation (Fig. 2(b)).

Effect of Temperature on Photoinduced Birefringence

To explore the change in alignment of azobenzene moieties, transmittance was monitored through a pair of crossed polarizers upon irradiation with a linearly polarized beam. The photoinduced birefringence (Δn) was estimated from the change in transmittance by Eq. (2),

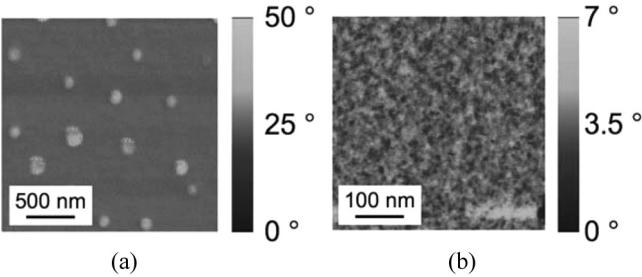


FIGURE 2 AFM phase images of **P1** (a) and **P2** (b) after annealing at 140°C.

$$T = \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \quad (2)$$

where d is the film thickness and λ is the wavelength of the probe beam, respectively. The experiments were carried out at room temperature, at 55°C and at a temperature just below T_g ($T = T_g - 15^\circ\text{C}$), respectively. In both films, birefringence increased and finally reached to a constant value upon irradiation as shown in Figure 3. It was found that the photoinduced birefringence in both block copolymer films was reduced with an increase in temperature (Fig. 3). Moreover, birefringence could not be induced above T_g . This is presumably because the degree of alignment of the azobenzene moieties is suppressed by enhancing the mobility of the main chain at high temperature. After the laser beam was switched off, Δn decreased in the **P1** film, while Δn was kept constant at a maximum value in the **P2** film. These results suggest that the mobility of azobenzene moieties in **P1** with the oxyethylene spacer is higher than that in **P2** with the alkyl spacer at the same temperature. To investigate the alignment of azobenzene moieties, polarized absorption spectra were measured after irradiation with a linearly polarized beam. Figure 4 shows polarized absorption spectra of **P1** and **P2** films at room temperature after photoalignment. A_{\parallel} and A_{\perp} are absorbance parallel and perpendicular to the polarization direction of the actinic beam, respectively. Before irradiation, the same spectra were obtained, while A_{\perp} was higher than A_{\parallel} after irradiation with a linearly polarized beam. These results indicate that *trans*-azobenzene molecules are aligned perpendicular to the

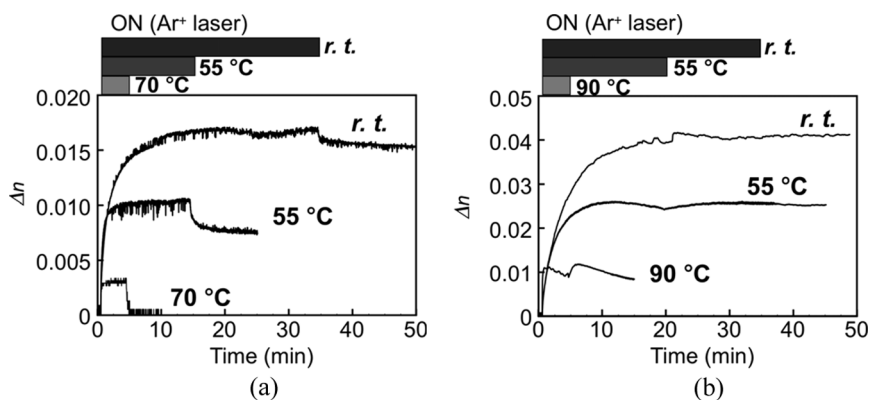


FIGURE 3 Photoinduced birefringence of **P1** (a) and **P2** (b) in film at room temperature, at 55°C, and at a temperature slightly below T_g .

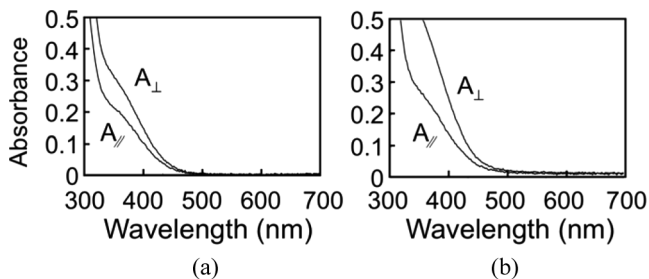


FIGURE 4 Polarized absorption spectra of **P1** (a) and **P2** (b) in film after irradiation with an *s*-polarized beam at 488 nm. A_{\parallel} and A_{\perp} are absorbance parallel and perpendicular to the polarization direction of the actinic beam, respectively.

polarization direction of the actinic beam in film upon irradiation. The order parameter (S) was estimated from A_{\perp} and A_{\parallel} by Eq. (3).

$$S = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + 2A_{\parallel}} \quad (3)$$

A higher alignment order of azobenzene moieties was induced in the **P2** film, similar to the photoinduced birefringence. The values of S were 0.14 (**P1**) and 0.23 (**P2**), respectively.

Modulation of Refractive Index

To investigate the grating formation, the copolymer film was irradiated with two interference beams. All the experiments were performed in the Raman-Nath regime. Modulation of refractive index ($\Delta n'$) between the bright and dark fringes of the interference pattern was estimated by Eq. (4), assuming that the diffraction is due to the change in the refractive index alone,

$$\eta = \left(\frac{\pi \Delta n' d}{\lambda} \right)^2 \quad (4)$$

where d is the film thickness and λ is the wavelength of the probe beam, respectively. When the interference beams were turned on, the $\Delta n'$ increased in both films as shown in Figure 5. Continuous irradiation with the interference beams led to a decay in $\Delta n'$. Since *trans*-azobenzene moieties are also aligned perpendicular to the polarization direction of the actinic beam in the dark area as well as in the bright

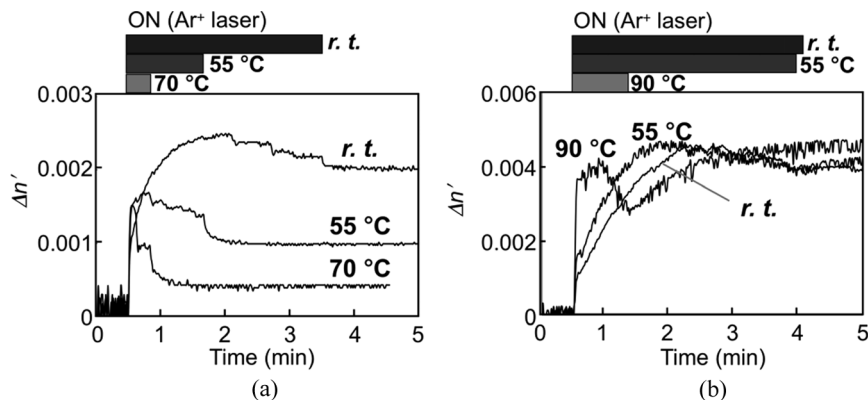


FIGURE 5 Modulation of refractive index in **P1** (a) and **P2** (b) in film at room temperature, at 55°C, and at a temperature slightly below T_g .

areas, the difference in the refractive index between the dark and bright fringes becomes smaller. After the actinic light was switched off, the films of **P1** and **P2** behaved differently. In the **P2** film, the $\Delta n'$ increased rather monotonically and remained unchanged, whereas the $\Delta n'$ decreased after the actinic beam was turned off in the **P1** film. Considering the results of Δn described in the preceding section, it is reasonable to infer that the improvement of motion of azobenzene moieties in the **P1** film is really due to the incorporation of oxyethylene moieties. To explore the effect of temperature on the grating formation, the response time is plotted as a function of temperature of the films in Figure 6. Here the response time is defined as the time

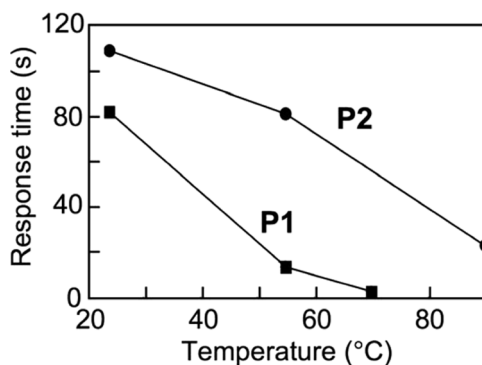


FIGURE 6 Response times of **P1** and **P2** films at various temperatures. (Squares) **P1**; (circles) **P2**.

necessary to reach the maximum value of $\Delta n'$. It was observed that the response time decreased with an increase in temperature in both films. This could be interpreted in terms of the increased mobility of azobenzene moieties as well as their enhanced *cis-trans* thermal isomerization with temperature. The response time of **P1** was shorter than that of **P2** at each temperature. The oxyethylene spacer of **P1** may effectively decouple the azobenzene moieties from the main chain.

CONCLUSIONS

Two block copolymers with oxyethylene (**P1**) and alkyl (**P2**) spacers in the azobenzene block were successfully prepared by ATRP with a low polydispersity of 1.04. The **P1** film showed spherical microphase separation, whereas no nanostructure was observed in the **P2** film. Glass transition temperature (T_g) was lowered by about 20°C in **P1** compared with **P2**. Their photoalignment and holographic properties were investigated in thin films. Although photoinduced birefringence (Δn) in **P2** was kept constant, Δn in **P1** was reduced after the laser beam was switched off. Moreover, the modulation of refractive index ($\Delta n'$) between the bright and dark fringes with the interference pattern increased in the **P2** film, while in the **P1** film $\Delta n'$ decreased immediately after the actinic light was switched off. The changes in Δn and $\Delta n'$ strongly suggest that the oxyethylene spacers effectively decouple the azobenzene moieties from the main chain. It was found that the Δn and $\Delta n'$ in both block copolymer films were reduced with an increase in temperature. Rapid change in molecular alignment can be induced in **P1** during photoirradiation at high temperatures, which suggests its potential applications as dynamic holographic materials.

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