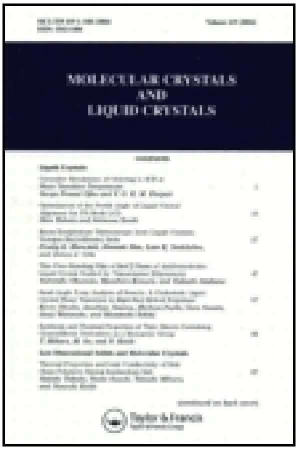

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoinduced Alignment Behavior of Poly(alkyl methacrylate)s Containing an Azobenzene Moiety in the Side Chain

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Version of record first published: 31 Jan 2007

To cite this article: Hyo-Bok Cha, Atsushi Shishido, Tomiki Ikeda & Takeshi Shiono (2005): Photoinduced Alignment Behavior of Poly(alkyl methacrylate)s Containing an Azobenzene Moiety in the Side Chain, Molecular Crystals and Liquid Crystals, 443:1, 201-209

To link to this article: http://dx.doi.org/10.1080/15421400500253712

Mol. Cryst. Liq. Cryst., Vol. 443, pp. 201–209, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500253712

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A series of poly(alkyl methacrylate)s having azobenzene and cyanobiphenyl moieties were synthesized and their optical properties were characterized. The effect of content of the photosensitive unit and the length of alkyl chain of a transparent unit on the photoresponsive alignment behavior was investigated. The azobenzene monomer (photoresponsive unit), the cyanobiphenyl monomer (mesogenic unit), and the alkyl methacrylate monomers with methyl, ethyl, n-butyl, hexyl or lauryl group (transparent unit) were copolymerized to yield transparent polymer films. Upon irradiation of LPL at 488 nm, a uniaxial optical anisotropy was generated due to the molecular alignment. The photoinduced alignment behavior was strongly dependent on the alkyl chain length and the intensity of the actinic light.

Keywords: azobenzene; change in birefringence

INTRODUCTION

Recently, much attention has been paid to photoresponsive materials for rewritable holographic recording. Various recording materials such as photorefractive materials [1–5], thermoplastics [6,7], photochromic compounds [8–10] were proposed as candidates for the hologram. Among them, the photochromic compounds are capable of repeated recording due to relatively high and reversible sensitivity. A number

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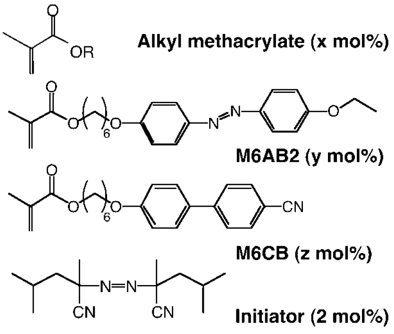
of specific characteristics need to meet the requirements in terms of diffraction efficiency, spatial resolution, and photosensitivity simultaneously. In particular, the diffraction efficiency is the key factor in holography since it can be an indicator of brightness in the hologram. In the recording process of phase-type holograms, a periodic modulation in refractive index is formed. The diffraction efficiency induced in the film is determined by the photoinduced change in refractive index and the film thickness: high diffraction efficiency is obtained with a large modulation of refractive index in a thick film.

Liquid-crystalline polymers having an azobenzene moiety in the side chain have been extensively studied for photonic applications since a large change in refractive index is induced due to *trans-cis* photoisomerization and the resultant change in molecular alignment of the azobenzene moiety [11]. Upon photoirradiation, a photochemical phase transition or a three-dimensional change in molecular alignment is induced, by which optical switching and data storage are successfully achieved [12–14]. Furthermore, holographic recording in the azobenzene polymers has been explored by these phenomena [15–17]. Using thin films, Raman-Nath holograms, whose theoretically maximum diffraction efficiency is 34%, could be formed at the efficiency of 32%. To raise the diffraction efficiency, a Bragg hologram, which allows 100% diffraction efficiency theoretically, is necessary. However, liquid-crystalline polymers generally exhibit considerable scattering, which prevents the formation of regular grating, giving rise to low diffraction efficiency. We might expect to realize the rewritable Bragg hologram when transparent polymer films incorporated with a photoresponsive part and a mesogenic part are employed. Poly (methyl methacrylate) is one of the suitable polymers for optical applications due to its optical transparency. In addition, an introduction of methyl methacrylate unit to the liquid-crystalline polymers could destabilize the liquid-crystalline nature, leading to the disappearance of scattering. In this paper, we synthesized the copolymers containing an azobenzene monomer, a cyanobiphenyl monomer, and an alkyl methacrylate monomer, which could cease the liquid-crystalline nature, and investigated their photoresponsive behavior that would provide the basic information for the holographic grating formation.

EXPERIMENTAL

Materials

The chemical structures and abbreviation of these poly(alkyl methacrylate)s containing an azobenzene moiety are shown in Figure 1.



Abbreviation of polymers

Polymer	R
PMMA-Azo y	CH_3
PEMA-Azo y	CH_2CH_3
PBMA-Azo y	$CH_2(CH_2)_2CH_3$
PHMA-Azo y	$CH_2(CH_2)_4CH_3$
PLMA-Azo y	$CH_2(CH_2)_{10}CH_3$

y: mol% of M6AB2 (azobenzene unit)

FIGURE 1 Chemical structure and abbreviation of the polymers used in this study.

Alkyl methacrylate monomers were purified by washing successively with 5% aq. sodium hydroxide solution followed by distilled water, and dried with anhydrous magnesium sulfate and finally distilled at reduced pressure. Other monomers, 6-[4-(4-ethoxyphenyl)azophenyloxy]hexylmethacrylate (M6AB2) and 4-[6-(methacryloyloxy)-hexyloxy]-4-cyanobiphenyl (M6CB) were prepared by using a procedure similar to the literature [18].

Sample Preparation

The composition ratio and glass transition temperature (T_g) of the prepared polymers are listed in Table 1. The polymers were obtained by

TABLE 1 Phase Transition Temperature and Molecular Weight of Copolymer Used in this Study[a]

Sample	Content (x:y:z)	M_n ($\times 10^4$)	M_w/M_n	Phase transition temperature (°C)
PMMA-Azo5	65:5:30	6.7	2.1	G 55 I
PEMA-Azo5	65:5:30	5.8	8.6	G 53 I
PBMA-Azo5	65:5:30	11.4	4.3	G 40 I
PHMA-Azo5	65:5:30	11.6	5.2	G 32 I
PLMA-Azo5	65:5:30	13.1	6.5	G 22 I
PMMA-Azo10	60:10:30	11.8	5.8	G 61 I
PEMA-Azo10	60:10:30	5.6	5.9	G 58 I
PBMA-Azo10	60:10:30	14.1	6.7	G 44 I
PHMA-Azo10	60:10:30	13.7	6.4	G 34 I
PLMA-Azo10	60:10:30	15.3	6.2	G 26 I

[a] G, Glass; I, Isotropic; M_n, number-average molecular weight; M_w, weight-average molecular weight.

copolymerization of alkyl methacrylate, M6AB2 and M6CB containing 2 mol% of a radical initiator 2,2-azobis(2,4-dimethylvaleronitrile). Polymerization was carried out at 61°C for 24 h after filling the monomer mixture into a homemade glass cell with a thickness of 100 μm, taking advantage of capillary forces. Thickness of the cell was adjusted to be 100 μm using glass spacers. Thermotropic property of the polymers was measured with a DSC (Seiko I&E SSC-5200 and DSC220C) at a heating and cooling rate of 10°C/min. At least three scans were performed to check reproducibility. The molecular weight of the polymer was determined by GPC (JASCO DG-980-50; column, Shodex GPC K802 + K803 + K804 + K805; eluent, chloroform). Conversion was around 90% in all polymers, and a good agreement between the initial monomer ratio and the composition of the copolymer was obtained.

Measurement

The optical setup for the photoinduced alignment change is shown in Figure 2. When the polymer film was irradiated with linearly polarized light from an Ar^+ laser (488 nm), the intensity of the probe light at 633 nm from a He–Ne laser transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode.

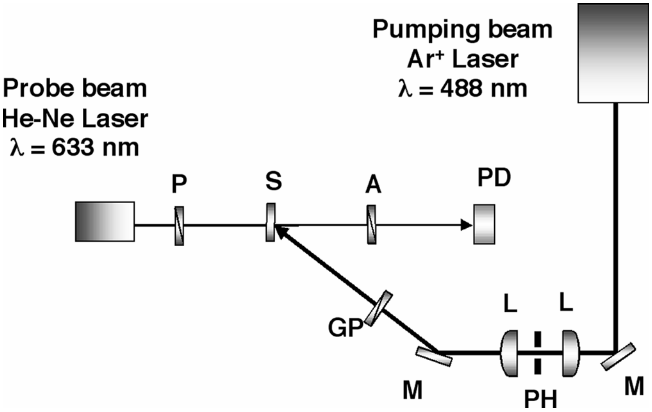


FIGURE 2 Optical setup for evaluation of photoinduced alignment change. A, analyzer; GP, Glan-Thomson prisms; L, lens; M, mirror; P, polarizer; PD, photodiode; PH, pinhole; S, sample.

RESULTS AND DISCUSSION

As shown in Table 1, T_g of the obtained polymers varied from 22°C to 61°C depending on the length of the alkyl chain. As the length increases, T_g decreased despite of the content of the azobenzene moiety. The photoinduced alignment behavior in these films was examined at room temperature.

Effect of Length of Alkyl Chain on Photoinduced Alignment Behavior

Figure 3 shows the change in transmittance upon irradiation of a linearly polarized beam at 40 mW/cm^2. In the initial state, the transmittance of the probe beam was not observed, indicating that the film shows no birefringence. Upon photoirradiation, the transmittance gradually increased, reached 100%, and then decayed by successive irradiation in all samples. The generation of transmittance represents that birefringence is induced due to molecular alignment of the azobenzene and cyanobiphenyl moieties by photoirradiation.

In the case of the polymer films containing 5-mol% azobenzenes in Figure 3 (A), we observed the faster response in **PBMA** having the butyl group in the side chain compared to **PMMA**, **PEMA**, and **PHMA**. No change was induced in **PLMA** with the lauryl group. In the polymer films with 10-mol% azobenzenes, **PBMA** showed the fastest rise as observed in the polymer with 5-mol% azobenzenes, while we

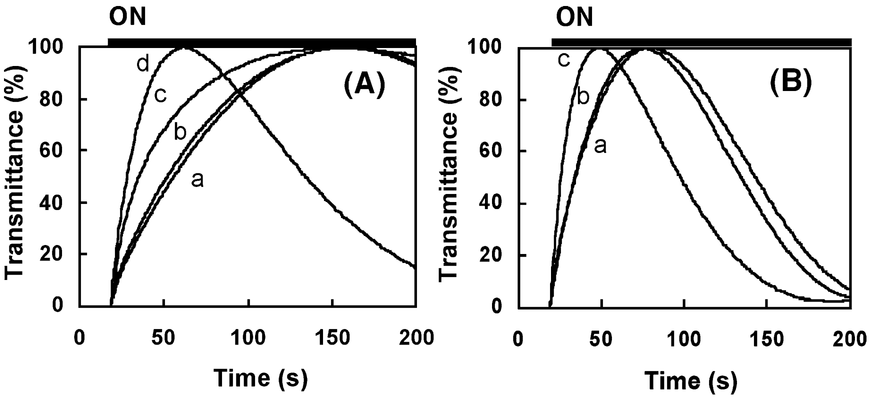


FIGURE 3 Change in transmittance upon irradiation of a linearly polarized beam at 40 mW/cm^2. (A) a, **PMMA-Azo5**; b, **PEMA-Azo5**; c, **PHMA-Azo5**; d, **PBMA-Azo5**. (B) a, **PMMA-Azo10**; b, **PEMA-Azo10**; c, **PBMA-Azo10**.

obtained no change in **PHMA** and **PLMA**. The polymers with shorter alkyl chain possess higher T_g, which lowers the mobility for the molecular alignment on photoirradiation. On the other hand, the long alkyl chain disturbs the cooperative effect of mesogenic group. In other words, the molecular alignment of the azobenzene moieties causes a cooperative motion of neighboring cyanobiphenyl moieties when the alkyl chain is short. We assume that these two effects mainly contribute to the photoresponsive behavior of the copolymer films, leading to the fastest response in **PBMA** with a butyl group.

Next, we evaluated photoinduced birefringence in the films to discuss the photoresponsive behavior more quantitatively. The transmittance (T) can be related to birefringence by the following equation [19]:

$$T = \sin^2(\pi d\Delta n/\lambda)$$

where d is the sample thickness (100 μm), Δn is birefringence of sample and λ is the wavelength of the probe light (633 nm).

Figure 4 shows the photoinduced change in transmittance and the estimated change in birefringence in **PBMA-Azo10** and **PMMA-Azo10**.

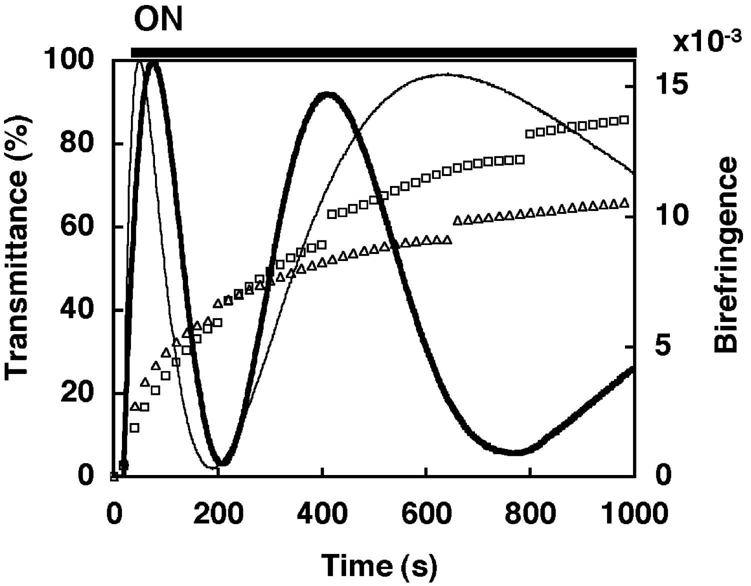


FIGURE 4 Change in transmittance and the estimated birefringence in the **PMMA-Azo10** (thick line and square) and **PBMA-Azo10** (thin line and triangle), respectively. The irradiation of a linearly polarized beam was performed at 40 mW/cm^2.

In **PBMA** having the butyl group, Δn built up faster than those of **PMMA** until 200 s, and then finally reached a lower value. We assume that the alignment of the azobenzene moiety is efficiently induced due to the larger free volume of the butyl group, while the induced alignment tends to relax at the same, resulting in the faster rise and lower birefringence.

Effect of Light Intensity of Pumping Beam on Photoinduced Alignment Behavior

Next, we explored the effect of light intensity of the pumping beam on the photoresponsive behavior. Figure 5 shows the change in transmittance in **PBMA-Azo10** at various intensities of the pumping light. It was found that the transmittance rose up faster with an increase in the light intensity. At high intensities, the molecular alignment of the azobenzene and cyanobiphenyl moieties is efficiently induced according to fast trans-cis-trans isomerization cycles of the azobenzene, which accounts for the fast response.

Figure 6 shows the effect of light intensity of the pumping beam on the photoinduced birefringence after 1000 s exposure. In the films with

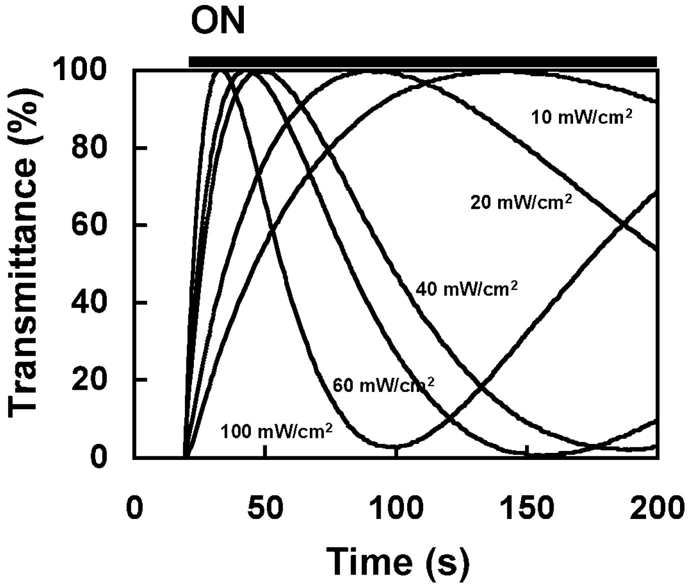


FIGURE 5 Effect of light intensity of the pumping beam on photoinduced alignment behavior in the **PBMA-Azo10**. Photoirradiation was carried out at room temperature.

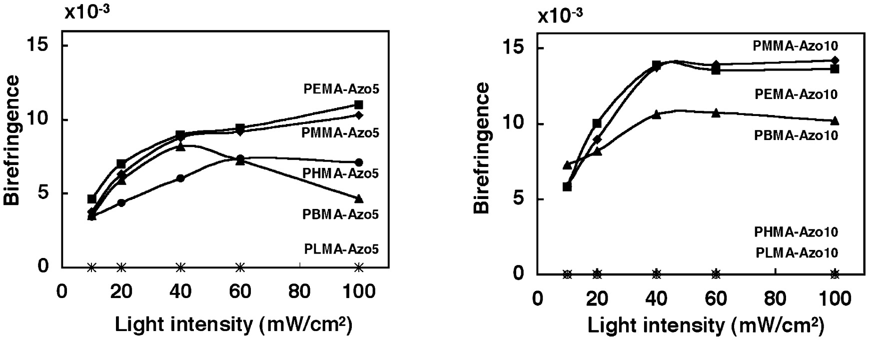


FIGURE 6 Photoinduced birefringence after exposure for 1,000 s in the polymer films.

higher concentration of the azobenzene moiety, which is 10%, we obtained slightly higher birefringence compared to the polymers with 5% azobenzenes, which can be interpreted in terms of more photoisomerization.

In terms of the alkyl chain length, **PEMA** and **PMMA** showed higher birefringence than **PBMA** unlike the response in the early stage. This result can also be explained by the relaxation of the alignment in **PBMA** with the longer alkyl chain and lower T_g. We revealed that the polymer films prepared show both high optical transparency and high photoresponsiveness, and can be expected as a candidate for new holographic materials.

CONCLUSION

A series of poly(alkyl methacrylate)s containing azobenzene moiety in the side chain have been synthesized and their photoresponsive behavior was explored. Upon photoirradiation of the pumping beam, birefringence was generated in the polymer films except **PLMA** with a lauryl group as the alkyl chain. It was found that the length of the alkyl chain incorporated to the copolymer with azobenzene and cyanobiphenyl moieties affected the glass transition temperature, photoresponse and induced birefringence. In **PBMA** having a butyl group in the side chain, the birefringence rose up fastest. We found that, in the early stage, the change in alignment of azobenzene moiety is efficiently induced. The polymer films prepared with both high optical transparency and high photoresponsiveness can be applied to new holographic materials.

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