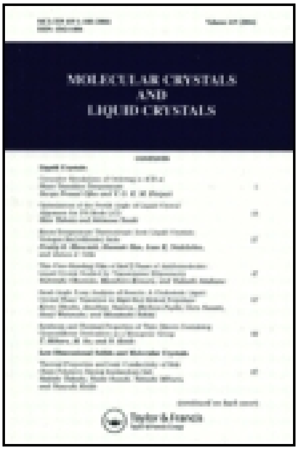

Molecular Crystals and Liquid Crystals

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

Influence of Molecular Weight on Photoinduced Reorientation of 4-Methoxyazobenzene-Containing Polymethacrylate Films Using 633 nm He-Ne Laser

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Version of record first published: 17 Oct 2011

To cite this article: Nobuhiro Kawatsuki, Tomoko Shiraku & Emi Uchida (2005): Influence of Molecular Weight on Photoinduced Reorientation of 4-Methoxyazobenzene-Containing Polymethacrylate Films Using 633 nm He-Ne Laser, Molecular Crystals and Liquid Crystals, 441:1, 163-171

To link to this article: http://dx.doi.org/10.1080/154214091009680

Mol. Cryst. Liq. Cryst., Vol. 441, pp. 163–171, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214091009680

Influence of Molecular Weight on Photoinduced Reorientation of 4-Methoxyazobenzene-Containing Polymethacrylate Films Using 633 nm He-Ne Laser

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*This paper describes influence of the molecular weight on thermally enhanced photoinduced reorientation of polymethacrylate films comprising 4-methoxyazobenzene side groups, generated by an axis-selective Z-to-E photoisomerization using linearly polarized (LP) 633 nm He-Ne laser light and subsequent annealing. The polymers with number average molecular weight (M_n) between 4800–27 000 were synthesized by the atom transfer radical polymerization (ATRP) method. Regardless of the molecular weight, high in-plane reorientation order parallel to polarization direction (**E**) of LP 633 nm light was accomplished when the exposed films were annealed in the smectic temperature range of the polymer films. However, degree of the thermal amplification of the photoinduced optical anisotropy depended on the molecular weight when the annealing temperature increased in the nematic temperature range.*

Keywords: azobenzene polymer liquid crystal; optical anisotropy; photoinduced reorientation

INTRODUCTION

Because of its attractive applications in holographic and optical data storage devices, photoinduced orientation in azobenzene-containing polymeric films has received a lot of attention [1–3]. A versatile molecular orientation can be triggered by *E*-to-*Z* photoisomerization of the azobenzene groups due to the different thermodynamic stabilities

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This work was partly supported by Iketani Science and Technology Foundation.

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of the *E* and *Z* isomers [3–5]. Many kinds of liquid crystalline (LC) and amorphous azobenzene-containing polymers are synthesized, and their reorientation behavior is investigated by irradiating with linearly polarized (LP) light [4–6]. This reorientation mechanism is based on an axis-selective *E*-to-*Z* photoisomerization. The simultaneous *Z*-to-*E* back-reaction of azobenzene groups causes reorientation perpendicular to the polarization (**E**) of the **LP** light. Additionally, thermal amplification of the photoinduced optical anisotropy is often observed in certain types of LC polymers [7,8].

Alternatively, a new reorientation technique for azobenzene-containing polymers has been proposed using a He-Ne 633 nm light, based on an axis-selective photoreaction of the *Z*-isomers, where the azobenzene groups are almost off-resonant [9–12]. Reorientation is achieved by pre-exposing a film to nonpolarized ultraviolet (NPUV) light to create a photostationary state of the *Z*-isomers prior to irradiating with LP He-Ne 633 nm light. The axis-selective *Z*-to-*E* photoisomerization leads to a reorientation of the azobenzene groups parallel to **E**. The photoinduced optical anisotropy is thermally enhanced when the exposed film is annealed in its LC temperature range [10–12]. We reported the thermally enhanced reorientation of polymethacrylate films with 4-methoxyazobenzene (4MAz) side groups using LP 633 nm light, and clarified the influence of the alkylene spacer length and the reorientation mechanism [11,12]. Since photogenerated *Z*-isomers are relatively stable for several hours, *Z*-to-*E* photoisomerization of 4MAz groups was clearly observed. The in-plane order parameter greater than +0.8 was achieved regardless of the alkylene spacer length between 4MAz groups and the polymethacrylate backbone.

In this paper, to investigate an influence of the molecular weight on thermally enhanced photoinduced reorientation, polymethacrylates comprising 4MAz side groups (PMAz6, Fig. 1) with various molecular weights and narrow molecular weight distribution were synthesized by the atom transfer radical polymerization (ATRP) method. The photoinduced optical anisotropy and thermal enhancement of the molecular reorientation of the films were measured by polarization UV-visible (vis) spectroscopy and polarization optical microscope (POM) observation.

EXPERIMENTAL SECTION

Materials and Polymer Synthesis

All starting materials from Tokyo Kasei Chemicals were used as received. The methacrylate monomers with 4MAz side groups were obtained according to the literature [13].

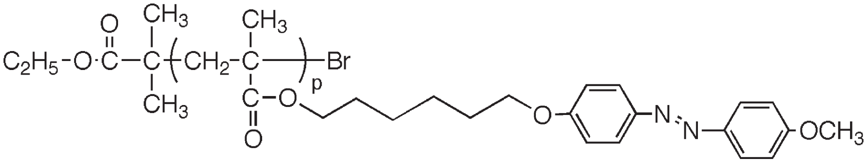

FIGURE 1 Chemical structure of PMAz6 used in this study.

The 4MAz containing polymers were synthesized using the ATRP method using 2-bromoisobutyrate, HMTETA and Cu(I)Cl as initiators [14]. Adjusting the ratio of methacrylate monomer and initiators controls molecular weight of the polymers. Table 1 summarizes molecular weight and thermal properties of synthesized polymers.

Photoreaction and Characterization

The polymer was spin-coated on a quartz substrate from a methylene chloride solution, resulting in a 200 nm-thick film. Photoreactions were conducted by irradiating with a 250 W high-pressure mercury lamp attached with interference filters at 365 nm (FWHM = 10 nm, 25 mWcm^{-2}) and a 13 mW LP 633 nm He-Ne laser expanded to 4 mm diameter (average intensity of 40 mWcm^{-2}). To irradiate with LPUV light, Glan-Taylor polarizing prisms were used. The optical anisotropy of the film was estimated by POM (Olympus BX-51) and polarization UV-vis spectra (Hitachi U-3030 spectrometer equipped with Glan-Taylor polarizing prisms). Birefringence was measured using LP He-Ne 633 nm light.

TABLE 1 Molecular Weight and Thermal Properties of PMAz6

	Molecular weight[a]		Thermal property/°C[b]		
PMAz6	$M_n \times 10^{-3}$	M_w/M_n	Tg	Tsn	Tni
a	4.8	1.10	60	82	124
b	7.2	1.09	63	85	126
c	10.5	1.08	66	91	132
d	15.0	1.09	65	95	136
e	20.7	1.07	67	96	135
f	27.0	1.08	69	96	135

[a] Measured by GPC with polystyrene standards.

[b] Measured by DSC. 2nd heating data.

The in-plane order parameter, S, is expressed in Eq. (1);

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{(\mathrm{large})} + 2A_{(\mathrm{small})}} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to $\mathbf{E}$, respectively, while $A_{(\mathrm{large})}$ is the larger of $A_{\parallel}$ and $A_{\perp}$, while $A_{(\mathrm{small})}$ is the smaller. These values were calculated by polarized UV-vis spectroscopy at a wavelength of 345 nm.

RESULTS AND DISCUSSION

Polymer Synthesis and Photoreaction with NP 365 nm Light

All synthesized PMAz6 polymers show liquid crystalline nature and exhibit very narrow M_w/M_n ratio less than 1.1 because the polymerization was carried out by the ATRP method [14]. All polymers display glass transition, and smectic and nematic LC phases as summarized in Table 1. Transition temperatures decreased as molecular weight of the polymer decreases but the temperatures becomes almost the same when the molecular weight is greater than 15 000 as plotted in Figure 2.

Irradiating PMAz6 film with NP 365 nm light induces the E-to-Z photoisomerization reaction of 4MAz groups. Figure 3a plot the formed Z-isomer fraction as a function of NP 365 nm light exposure energy. Exposing to 1 Jcm^{-2} or more reached approximately 70–75 mol% of the Z-isomer for all the films. The photoreaction rate did not depend

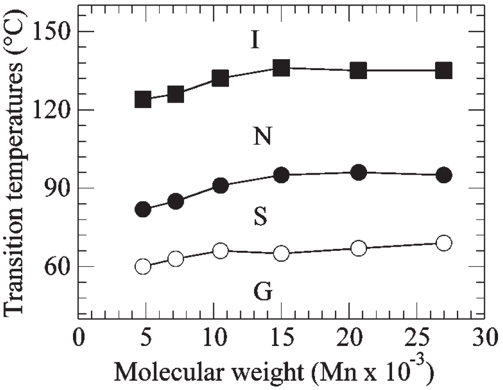

FIGURE 2 Transition temperatures PMAz6 as a function of molecular weight (Mn).

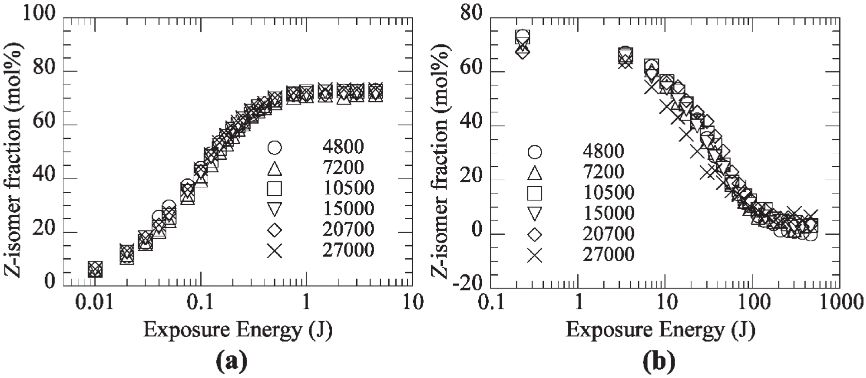

FIGURE 3 (a) Photoisomerized *Z*-isomer fraction as a function of 365 nm light exposure energy. (b) Fraction of *Z*-isomer as a function of exposure energy of He-Ne 633 nm light for films that initially contained about 70–75 mol% of Z-isomer.

on the molecular weight. It is known that *Z*-isomers thermally return to the *E*-isomer although *Z*-isomer of donor-donor type azobenzene is relatively stable at room temperature. It took more than 5 hours for half of the *Z*-isomers to thermally relax to the *E*-isomers. The *Z*-to-*E* reaction is accelerated by irradiating with 633 nm light [11]. Figure 3b plots the fraction of *Z*-isomer as a function of exposure energy to films that initially contained 75 mol% of *Z*-isomers. It shows the *Z*-to-*E* photoreaction rate also did not depend on the molecular weight.

Thermally Enhanced Photoinduced Reorientation by Exposing to NP 365 nm Light Followed by Irradiating with LP 633 nm and Annealing

We reported irradiating with LP 633 nm light to *Z*-isomers of PMAz6 film and subsequent annealing generated parallel reorientation with an in-plane reorientational order greater than +0.8 [11,12]. Typical spectral change is shown in Figure 4 [12]. It shows that an axis-selective *Z*-to-*E* photo-isomerization generates optical anisotropy parallel to **E** and subsequent annealing enhances it. A similar reorientation behavior was investigated in polymer films with 4-cyanoazobenzene groups [9,10].

Figure 5 plot photoinduced and thermally enhanced in-plane order parameter, as a function of exposure doses of LP 633 nm light. For all cases, films initially contain 75 mol% of *Z*-isomers, which were created by pre-exposing to NP 365 nm light. Irradiating with LP 633 nm light

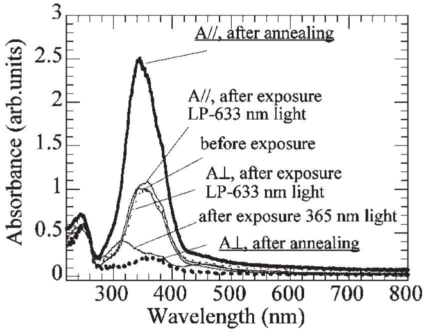

FIGURE 4 UV polarization spectrum of PMAz6 (Mn = 25 000) film before photoirradiating, after exposing to NP 365 nm light for 1.5 Jcm^2 doses followed by irradiating with LP 633 nm light for 185 Jcm^2 doses (thin lines), and after subsequent annealing (thick lines) at 90°C for 10 min. $A_{//}$ is the solid lines and $A_{\perp}$ is the dotted lines [12].

generates axis-selective *Z*-to-*E* photoreaction and a small positive optical anisotropy ($\Delta A > 0$) appears. Annealing temperatures were in the smectic temperature range of each PMAz6. It reveals that order parameter larger than +0.8 is obtained when the exposure doses is larger than 70–80 Jcm^{-2}, where more than 90 mol% of the 4MAz groups returned to *E*-isomers. These results indicate that the thermal

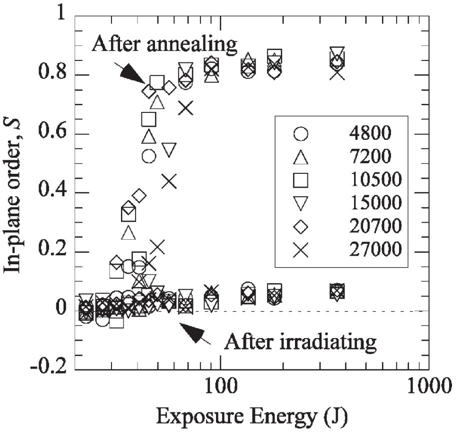

FIGURE 5 Photoinduced and thermally enhanced in-plane order parameter of PMAz6 films as a function of exposure doses of LP 633 nm light. All films were annealed in the smectic temperature range for 10 min after irradiation with LP 633 nm light.

amplification of the photoinduced optical anisotropy annealed in the smectic temperature range is not influenced by the molecular weight of the PMAz6.

Effect of Annealing Temperature

Finally, we examined an influence of the annealing temperature on the thermal enhancement of the photoinduced optical anisotropy. Films containing 75 mol% of *Z*-isomers were exposed to LP 633 nm light for 100 Jcm^{-2} doses. This process creates most of the 4MAz groups returned to *E*-isomers, and the photoinduced in-plane order parameter about $+0.04$ is generated for all cases.

Figure 6a–f plots photoinduced and thermally enhanced order parameters of the films as a function of annealing temperatures. For all cases, thermal amplification is achieved when the annealing temperature is higher than Tg of the polymer, and generated order parameter is greater than $+0.8$. However, for PMAz6a, b and c, when the annealing temperature increased to be in the nematic temperature range, enhanced order parameter decreased as the temperature increased. This phenomena is obviously observed for PMAs6a (Figure 6a). In contrast, other polymers generate large in-plane order in the whole LC temperature range. Additionally, thermal amplification does not occur when the annealing temperature is higher than Ti for all cases.

PMAz6a and PMAz6b are composed of approximately 12 and 18 monomer units, respectively. In general, when the polymer melts, viscosity of a polymer liquid with lower molecular weight is lower than that with higher molecular weight. Since mobility of the mesogenic groups in the nematic temperature range for PMAz6a, b and c will be larger than that of others, annealing in the higher nematic temperature range increases a molecular motion to reduce the self-organization of the mesogenic groups. Namely, lower viscosity near Ti resulted in decreasing the thermal enhancement of the photoinduced optical anisotropy.

CONCLUSION

The influence of the molecular weight on thermally enhanced photoinduced reorientation of 4-methoxyazobenzene containing polymethacrylate films, which were synthesized by ATRP method, was investigated. The axis-selective *Z*-to-*E* photoisomerization was caused by LP 633 nm light and thermal enhancement of the photoinduced optical anisotropy led to high order molecular orientation parallel to **E** in all the PLC films, when the annealing temperature was in the

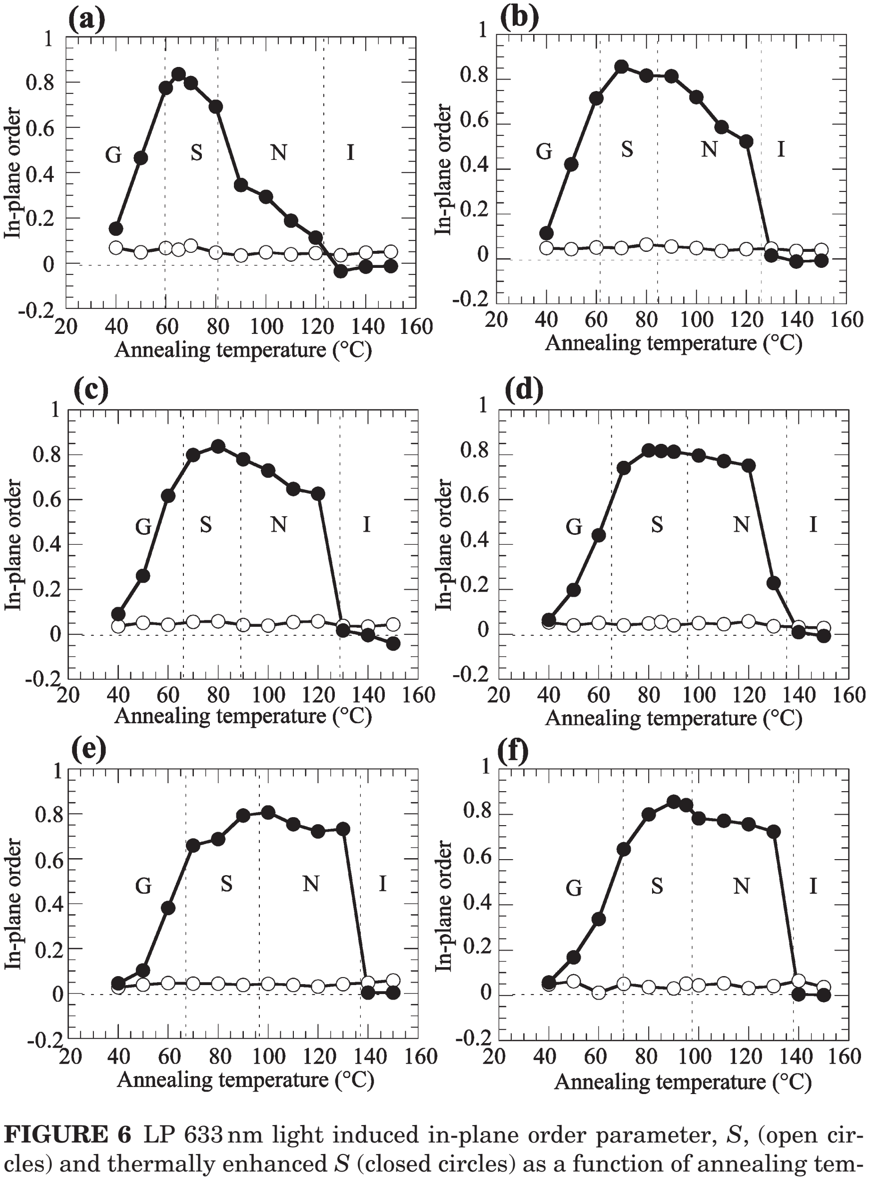

FIGURE 6 LP 633 nm light induced in-plane order parameter, *S*, (open circles) and thermally enhanced *S* (closed circles) as a function of annealing temperature. (a) Mn = 4800, (b) Mn = 7200, (c) Mn = 10500, (d) Mn = 15000, (e) Mn = 20700, and (f) Mn = 27000.

smectic temperature range of the polymer. In contrast, the degree of the thermal amplification of the photoinduced anisotropy decreased for polymers with low molecular weight when the annealing temperature increased in the nematic temperature range.

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