

## Photoinduced Reorientation of Polymethacrylate Film with 4-Methoxyazobenzene Side Groups Using Linearly Polarized He-Ne Laser and Annealing

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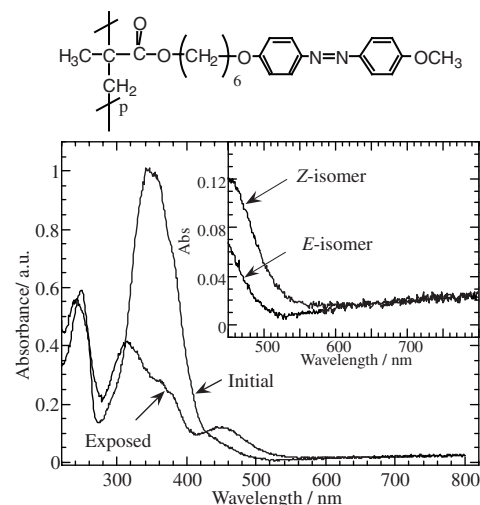
This letter describes thermally enhanced reorientation of azobenzene-containing polymer films by linearly polarized (LP) 633 nm He-Ne laser light. Axis-selective photoreaction of the *Z*-isomers and subsequent annealing generated parallel reorientation with a reorientational order larger than +0.8 although the film was almost off-resonant at 633 nm.

Numerous studies on the photoinduced reorientation of azobenzene-containing polymer films have been investigated for applications such as optical data storage and birefringent devices.<sup>1</sup> The axis-selective *E*-to-*Z* photoisomerization reaction of azobenzene groups using linearly polarized (LP) light leads to reorientation perpendicular to the polarization (**E**) of the LP light.<sup>2-4</sup> Thermal enhancement of the photoinduced optical anisotropy occasionally occurs for donor-donor substituted azobenzene groups since the photogenerated *Z*-isomer is relatively stable at room temperature.<sup>5,6</sup> In contrast, different techniques using non-polarized (NP) UV light and longer wavelength LP light, at which the azobenzene groups is almost off-resonant, have recently been reported for the photoinduced reorientation of azobenzene groups.<sup>7,8</sup> In this case, parallel reorientation of the azobenzene groups was generated, but the prolonged exposure resulted in normal reorientation perpendicular to **E**.<sup>8</sup>

This study aimed to fabricate a birefringent film of a polymethacrylate with 4-methoxyazobenzene side groups (PMAz6M, Figure 1) using LP-633-nm He-Ne laser light and to clarify the reorientation mechanism. When a thin PMAz6M film is exposed to LP-365-nm light and subsequently annealed, thermally enhanced photoinduced reorientation is generated perpendicular to **E**.<sup>5,9</sup> However, the reorientation of a 1 μm-thick film was difficult because of the large absorbance of the material. In this letter, we found that only the *Z*-isomers of the PMAz6M showed the axis-selective photoreactivity with LP-633-nm light, where the *E*-isomers are off-resonant. The efficient reorientation parallel to **E** was achieved and a large birefringence,  $\Delta n$ , of 0.31 was obtained after annealing the resultant film even when the film was 1.1 μm thick.

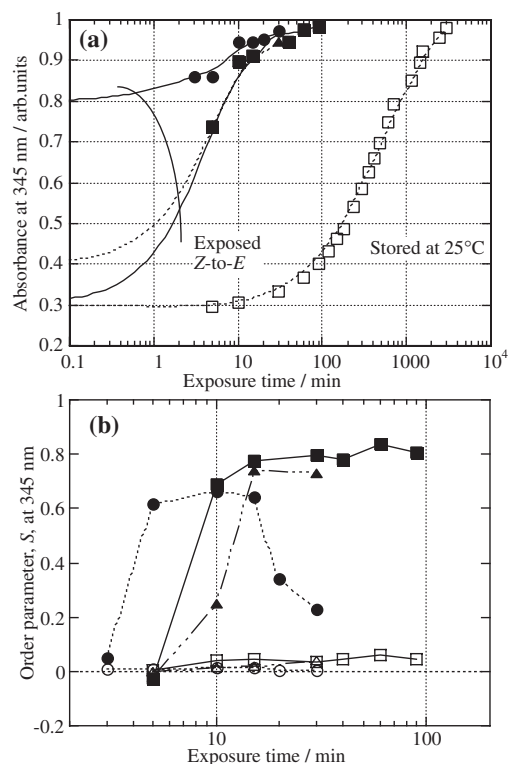
PMAz6M was synthesized according to the literatures.<sup>5,9</sup> Films were prepared by a spin-coating method from a methylene chloride solution onto quartz substrates. A high-pressure Hg lamp with a 365-nm interference filter (FWHM = 10 nm, 30 mW cm<sup>-2</sup>) and a 13 mW LP-633-nm He-Ne laser expanded to 5 mm diameter (average intensity of 65 mW cm<sup>-2</sup>) were used. After forming the *Z*-isomers of PMAz6M using NP-365-nm light, the axis-selective photoreaction was achieved by irradiating with LP-633-nm light. A conventional photoinduced reorientation using LP-365-nm light was conducted according to a method previously described.<sup>5,9</sup> After exposure in all cases, the

films were annealed at 90 °C for 10 min to reorient the MAz groups. Photoinduced dichroism,  $\Delta A$ , was determined by  $\Delta A = A_{\parallel} - A_{\perp}$ , where  $A_{\parallel}$  and  $A_{\perp}$  were absorption parallel and perpendicular to **E**, respectively, and the orientational order of the film,  $S$ , was estimated by  $S = \Delta A / (A_{(\text{larger})} + 2A_{(\text{smaller})})$ , where  $A_{(\text{large})}$  was the larger value of  $A_{\parallel}$  and  $A_{\perp}$ , and  $A_{(\text{small})}$  was the smaller one. The  $\Delta n$  of the film was measured at 633 nm.



**Figure 1.** Chemical structure of PMAz6M and changes in the absorption spectrum for 0.2 μm-thick film before and after exposure to 365-nm light.

Figure 1 shows the changes in absorption spectrum of a 0.2 μm thick film before and after exposure to 1.5 J cm<sup>-2</sup> doses of NP-365-nm light. After exposure, the absorption bands at 350 nm decreased and at 450 nm increased, indicating the formation of 73 mol % of the *Z*-isomer of the azobenzene groups. The *Z*-isomers thermally returned to *E*-isomers after storing at room temperature for 1 day. Surprisingly, irradiating with LP-633 nm He-Ne laser light accelerated the *Z*-to-*E* isomerization, even though the film was virtually off-resonant (inset of Figure 1). Figure 2a plots the changes in absorbance at 345 nm of the films, which initially contained 73, 57, and 23 mol % of *Z*-isomer, as a function of the exposure time to LP-633-nm light. It reveals that irradiating with LP-633-nm light facilitates the *Z*-to-*E* isomerization. Additionally, spectrum changes were not observed for the as-coated film (100% of *E*-isomers) upon LP-633-nm light exposure for two days. These phenomena were also present in solution. Figure 3 shows absorption spectrum of a concentrated PMAz6M solution (3.8 mol/L in chloroform) before and after exposure to 365-nm light. It shows that after exposure a small  $n\pi^*$  absorption tail to 633 nm appeared. The thermal *Z*-to-*E* isomerization occurred when the solution was stored for 2 days at

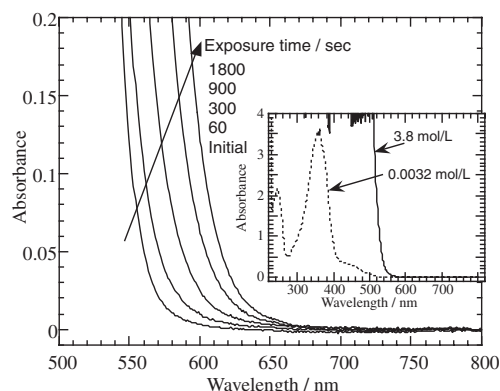


**Figure 2.** (a) Change in the absorbance at 345 nm of PMAz6M films with varying amounts of Z-isomers as a function of irradiation time with LP-633-nm light (closed points) and stored at room temperature (open square). (b) Order parameter,  $S$ , at 345 nm of the irradiated films with LP-633-nm light (open points) and after subsequent annealing (closed points) as a function of irradiation time of LP-633-nm light. Initial content of the Z-isomers were 73 mol % (squares), 57 mol % (triangles), and 23 mol % (circles).

25 °C. Like the films, irradiating with LP-633-nm He-Ne laser light accelerated this isomerization. These results suggest that the Z-isomers exclusively exhibit photoreactivity at 633 nm. Furthermore, irradiating generated a positive  $\Delta A$  and  $S$  as plotted in Figure 2b, which indicates the axis-selective photoreaction of Z-isomers.

The photoinduced  $S$  was thermally amplified parallel to  $\mathbf{E}$  as plotted in Figure 2b. When the film initially contained 73 mol % of Z-isomers and the exposure time was longer than 10 min, which left less than 10 mol % of the Z-isomers, a large  $S$  of +0.8 was obtained. Additionally, the amplified  $S$  values did not decrease even when most of MAz groups returned to E-isomers by LP-633-nm light exposure. In these cases, the positive photoinduced  $\Delta A$  was still observed. This means that a small amount of reorientation parallel to  $\mathbf{E}$  and the annealing amplified the  $\Delta A$  that accompanied the Z-to-E photoisomerization. The conventional method using LP-365-nm light generated a negative  $\Delta A$  due to the axis-selective E-to-Z photoisomerization and was thermally enhanced perpendicular to  $\mathbf{E}$  with the thermal Z-to-E isomerization when the content of the Z-isomer was less than 15 mol %.<sup>5,9</sup> However, forming more Z-isomer did not thermally enhance the optical anisotropy because liquid crystalline nature of the film was too small.<sup>10</sup>

Table 1 summarizes the generated  $\Delta n$  for the reoriented films with various thicknesses fabricated under the different conditions. The technique used in this study fabricated transparent



**Figure 3.** Changes in absorption spectrum of 3.8 mol/L PMAz6M in chloroform solution upon 365-nm light exposure. Inset compares the spectrum to a normal concentration before exposure.

birefringent films, in which  $\Delta n$  decreased as the film thickness increased. This means that the axis-selective Z-to-E photoisomerization reaction occurred in the entire film, but the efficient uniaxial in-plane reorientation is more difficult for thick films. On the other hand, films that were thicker than 0.8  $\mu\text{m}$  fabricated by LP-365-nm light exposure became turbid after annealing and photoisomerization for efficient molecular reorientation at the opposite side of the light propagation was difficult due to the large absorbance at 365 nm. Thus, the annealing process formed multi-domain formations.

In summary, parallel molecular orientation in a PMAz6M film was accomplished based on an axis-selective Z-to-E photoisomerization using LP-633-nm light and annealing. The resultant films were transparent and high orientational orders greater than +0.8 and  $\Delta n$  of 0.31 were obtained for a 1.1  $\mu\text{m}$  thick film. Further studies on the 3-D reorientation using oblique LP-633-nm light exposure and fabricating holographic optical devices are currently in progress.

**Table 1.** Fabrication conditions and generated  $\Delta n$  of the oriented PMAz6M film

Thickness / $\mu\text{m}$	Exposure Condition <sup>a</sup>		Reorientation Direction	$\Delta n^b$
	365 nm/ $\text{J cm}^{-2}$	633 nm/ $\text{J cm}^{-2}$		
0.2	NP (1.5)	LP (23)	parallel	0.39
0.8	NP (1.5)	LP (28)	parallel	0.33
1.1	NP (1.5)	LP (23)	parallel	0.31
1.5	NP (1.5)	LP (55)	parallel	0.19
0.2	LP (0.05)	None	perpendicular	0.36
0.8	LP (0.05)	None	-	Turbid
1.1	LP (0.05)	None	-	Turbid

<sup>a</sup> All films were annealed at 90 °C for 10 min after exposure. <sup>b</sup> Measured at 633 nm.

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