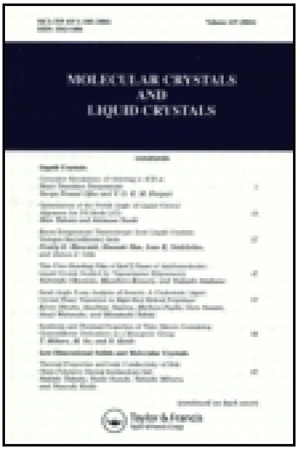

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromic Behavior in Thin Films of Polymethacrylates Substituted with Side-on and Head-on Type Azobenzenes

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To cite this article: Haruhisa Akiyama & Kunihiro Ichimura (1998): Photochromic Behavior in Thin Films of Polymethacrylates Substituted with Side-on and Head-on Type Azobenzenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 315:1, 47-52

To link to this article: http://dx.doi.org/10.1080/10587259808044309

Mol. Cryst. Liq. Cryst., 1998, Vol. 315, pp. 47–52
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Photochromic Behavior in Thin Films of Polymethacrylates Substituted with Side-on and Head-on Type Azobenzenes

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The photochemical behavior of two kinds of side-chain type azobenzene-polymers, poly[2-(2-methacryloyloxyethoxy)-4-methoxyazobenzene] (**pMAzS2**) and poly[4-(2-methacryloyloxyethoxy)azobenzene] (**pMAz2**), was investigated in order to obtain information about effect of molecular structures on photoreorientation process. Irradiation of polymer films with linearly polarized visible light (488 nm) brought about reorientation of azobenzene moieties. Trans isomers in both polymers were aligned in the perpendicular direction to the electric vector of the actinic polarized light.

Keywords: polarized light; photoisomerization; photoreorientation; azobenzene; polymethacrylates

INTRODUCTION

Many reports have been published on the reorientation of azobenzenes in polymer matrices upon irradiation with linearly polarized light (LPL).[1-7] This phenomenon has potential value for practical applications such as display and memory devices because the molecular reorientation induces the optical modulation of the matrices. Recently, films of polymers containing photochemicaly alined azobenzene have been used for surface-assisted photocontrol of liquid crystal (LC) alignment.[9-11] In this case, a high degree of alignment of azobenzenes is not necessary to control LC alignment, because film surfaces that have only slight anisotropy make LC molecules align homogeneously. This study deals with photochemicaly induced dichroism of azobenzene chromophores linked to amorphous polymethacrylates, **pMAz2** and **pMAzS2** (Figure 1). **pMAz2** and **pMAzS2** are called head-on type and side-on type, respectively, since they have structures as side chain azobenzenes are attached linearly and laterally to the main chains. It is expected that such a drastic difference in a molecular structure will be affect on efficiency of photoreorientation.

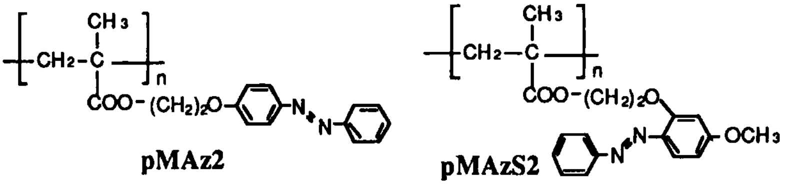

FIGURE 1 Chemical structures of polymer

TABLE 1 Characterization of polymers

Polymer	$Mw \times 10^{-5}$	Mw/Mn	Tg (°C)
pMAz2	1.5	2.5	88
pMAzS2	1.3	2.6	72

EXPERIMENTAL

pMAzS2 and the monomer, [2-(2-methacryloyloxyethoxy)-4-methoxyazobenzene] (**MAzS2**), were synthesized as described in the previous paper[11]. poly[4-(2-methacryloyloxyethoxy)azobenzene] (**pMAz2**) was given by polymerization of 4-(2-methacryloyloxyethoxy) azobenzene (**MAz2**) under a similar condition to the polymerization of **pMAzS2**. Characterizations of polymers are summerized in Table 1.

A 3 wt% toluene solution of **pMAz2** or **pMAzS2** was spin-coated on 1 × 3 cm^2 quartz plates to give thin polymer films of 60-80 nm thickness. Films were irradiated with 488 nm light from Jasco CRM-FD diffraction irradiator. Linearly polarized light was obtained by passing through a polarizer. The light intensity of actinic LPL was 1 mW cm^{-2}. UV and visible absorption spectra were measured with a Hewlett-Packard diode array spectrometer 8452Ax.

RESULTS and DISCUSSION

Figure 2 shows extinction coefficients of trans and cis isomers of the monomers . The maxima in spectra of trans-**MAz2** observed at 342 nm and 445 nm are attributed to π-π* and n-π* transition, respectively. In the spectrum of trans-**MAzS2**, a maximum attributed to π-π* transition was observed at 364 nm, but an absorption band correspond to n-π* transition was not clear since it overlapped with the band of π–π* transition. The red shift of the π-π* absorption band compared to that of **MAz2** (λmax=342 nm) is owing to the alkoxy substituent at the *o*-position of the azobenzene. Isosbestic points were observed at 296 nm for **MAzS2** and at 294 nm for **MAz2**.

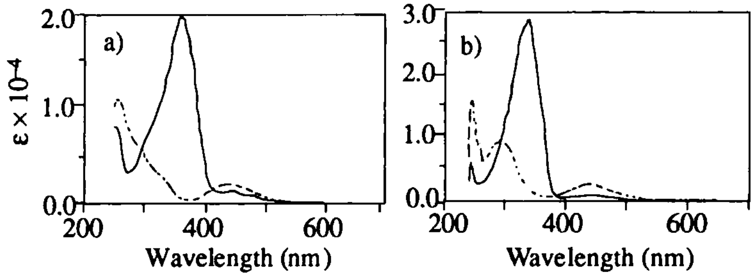

FIGURE 2 Extinction coefficients of trans (solid line) and cis-isomer (dash line) of a) **MAzS2** and b) **MAz2**.

Films of **pMAz2** and **pMAzS2** were irradiated with LPL at 488 nm, and subjected to polarized absorption spectrum measurement. Then dichroic ratios were measured as a function of exposure energy of LPL. A dichroic ratio (DR) is defined as follows:

$$DR = (A_{\perp}-A_{//})/A_0 \qquad (1)$$

where $A_{\perp}$ and $A_{//}$ denote absorbencies at 370 nm measured with two kinds of polarized monitoring light with polarization perpendicular to and in parallel with that of the actinic LPL, respectively, and A_0 is absorbance measured before irradiation (irradiation time=0). The extinction coefficients of trans-isomer at 370 nm were much larger than those of cis-isomer both in **pMAz2** and **pMAzS2** films. This fact indicates that the difference between $A_{//}$ and $A_{\perp}$ at 370 nm corresponded predominantly to the extent of orientation of trans-isomer. As shown in Figure 3, the dichroic ratio of a **pMAzS2** film leveled off at an exposure energy of about 200 mJ cm^{-2}. It should be noticed here that a maximum of the dichroism was observed at about 250 mJ cm^{-2} in a **pMAzS2** film. On the contrary, LPL-irradiation of a **pMAz2** film gave no such a maximum. The dichroism increased monotonously and reached at a saturated value after irradiation with light of exposure energy of 1 J cm^{-2} or more. The presence of a maximum observed in a **pMAzS2** film is explained in terms of involvement of two photochemical processes; photoselective isomerization and photoreorientation. The photoreorientation results from repeated isomerization of azobenzene chromophores. Another process referred to here as the photoselection is an axial-selective photon absorption and consequent photoisomerization, leading to "destructive" photodichroism which requires no repetition of the isomerization. If photodichroism generated via only photoselection process, it might be lost upon prolonged LPL-irradiation, because trans-azobenzenes with transition moments, which are almost perpendiculr to the actinic polarization plane, absorb photons more or less to result in the gradual photoisomerization to cis form.

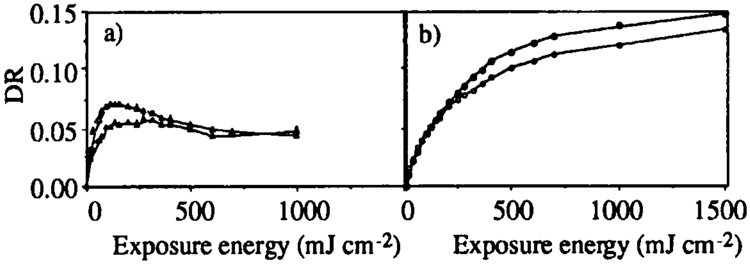

FIGURE 3 Exposure energy dependence of dichroic ratios (DR) of a) **pMAzS2** and b) **pMAz2** films irradiated with actinic LPL at 488 nm. DRs are calculated according to equation (1) from absorbancies at 370 nm (open marks) and at isosbestic points (black marks).

Dichroic ratios were evaluated from absorbancies at 294 nm for **pMAz2** and 296 nm for **pMAzS2**. Then, the difference between dichroic ratios at 370 nm and those at the isosbestic points are plotted in Figure 4. Dichroic ratios evaluated from absorbancies at 370 nm reflect the orientational state of only trans isomers, while those evaluated at the isosbestic points represent the orientational state of total azobenzene moieties including cis- and trans-isomers. Therefore, the difference of dichroic ratios should represent the extent of the alignment of cis isomers. The differences were negative on the short irradiation as shown in Figure 4. This fact obviously indicates that the alignment of cis-isomers in a parallel direction with the electric vector of the actinic LPL is dominant. The parallel alignment suggests that cis-isomers generated from trans isomers with the polarization matched to the electric vector of the actinic light, without large molecular rotation. Although, in the case of a **pMAz2** film, the degree of the parallel alignment of cis-isomers was very low. It is attribute to a larger amount of trans-isomers of **pMAz2** (77 %) remained after irradiation with 488 nm light than that of **pMAzS2** (65 %).

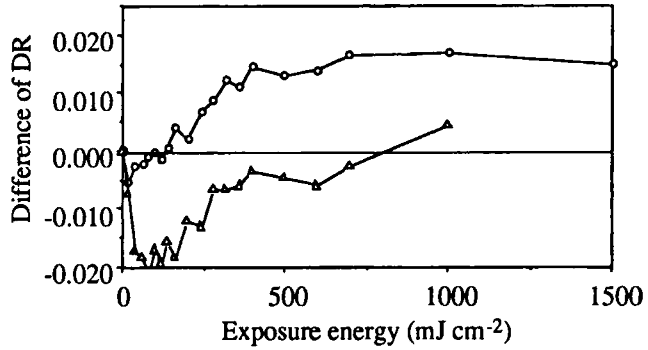

FIGURE 4 Differences between dichroic ratios calculated from absorbancies at 370nm and those at isosbestic points for **pMAz2** (○) and **pMAzS2** (△) films against exposure energy.

Upon further irradiation, the photoalignment of cis isomers in a **pMAzS2** film disappeared, whereas cis-azobenzenes in a **pMAz2** film were reoriented to perpendicular direction to polarization of the actinic light. No photoalignment of cis isomer in a **pMAzS2** film after the long irradiation suggest the possibility that volume required for the molecular rotation is small compared to the free volume of a polymer matrix. In order to confirm this consideration, more information about kinetics of the photoreaction of azobenzene moieties will be needed.

CONCLUSION

Dichroism of azobenzenes is induced by the irradiation of polymer films with linearly polarized visible light due to the reorientation of both trans-isomers and cis-isomers. The orientational direction of trans-isomers is perpendicular to the polarization plane of actinic light. Whereas, cis-isomers aligned in a parallel direction with the polarization of the actinic light on the short irradiation, and gradually changed in their orientational direction.

Acknowledgments

This work was conducted when the first author was a research fellow of the Japan Society for the Promotion Science (JSPS). The authors would like to thank JSPS Fellowships for the support.

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