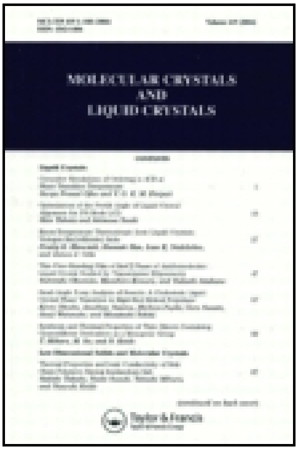


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromic Behavior of Thin Films of Polymehacrylate Substituted with Laterally Attached Azobenzenes Displaying Liquid Crystal Alignment Photocontrol

H. Akiyama [a] , Y. Akita [a] , K. Kudo [a] & K. Ichimura [a]
[a] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokohama, Japan

To cite this article: H. Akiyama , Y. Akita , K. Kudo & K. Ichimura (1996): Photochromic Behavior of Thin Films of Polymehacrylate Substituted with Laterally Attached Azobenzenes Displaying Liquid Crystal Alignment Photocontrol, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 91-96

To link to this article: http://dx.doi.org/10.1080/10587259608040315

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 91–96
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTOCHROMIC BEHAVIOR OF THIN FILMS OF POLYMETHACRYLATE SUBSTITUTED WITH LATERALLY ATTACHED AZOBENZENES DISPLAYING LIQUID CRYSTAL ALIGNMENT PHOTOCONTROL

H. AKIYAMA, Y. AKITA, K. KUDO and K. ICHIMURA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Yokohama, Japan

Abstract Photo- and thermal isomerization of poly[2-(2-methacryloyoxy)azobenzene] derivatives was investigated both in solution and in film state. In the photo-induced trans-cis isomerization, the rate in film state was smaller than that in solution. The kinetics of the thermal back reaction was proved to depend on the copolymerization ratio of the polymer. Linearly polarized light (LPL) irradiation of a thin film of the polymer induced dichroism of the film. The degree of the dichroism was related to the Tg of the polymers. In-plane alignment of nematic liquid crystals (LCs) was regulated by photodichroic thin films. Heat treatment of a film before irradiation was a important factor for the photoregulation.

INTRODUCTION

Recently new materials for optical data storage and display devices using linearly polarized light (LPL) as an external stimulus have been attracting intensive interest.[1-4] In many cases, azobenzenes were employed as photoreactive molecules. In these systems, optical modulation was due to the molecular reorientation through the photoisomerization of azobenzene induced by irradiation with LPL. However, the relationship between the photoreaction inducing LPL and the molecular structure of azobenzenes have not been thoroughly investigated.

These materials fall into three main groups; 1) an azo-dye-dispersed polymer or an amorphous polymer bearing azobenzene in the side chain,[1] 2) liquid crystalline polymer films including mesogenic azobenzene moiety in the side chain,[2] 3) surface-assisted alignment control of nematic liquid crystals by the surface of azobenzene-containing polymer films.[3] These systems are of practical significance because optical information could be repeatedly written-in and erased simply by rotating an electric vector of LPL from a single light source.

Concerning the third category, we have demonstrated that the reversible regulation of in-plane alignment of LC could be achieved by the photoisomerization of azobenzenes which were covalently introduced through their 2-positions to surfaces of silica glass plate[5] or poly(vinyl alcohol) film[6]. Considering the shape of these laterally attached azobenzenes, such system have advantages for the effective induction of a planar alignment of LC, hence they are useful for the in-plane alignment control. In order to obtain more information on the photoreaction and LC alignment regulation, we synthesized poly(methacrylate) having laterally attached azobenzenes in the side chain. In this paper, the photoreaction of poly[2-(2-methacryloyoxylethoxy)azobenzene] derivatives was investigated with respect to 1) a rate of trans-cis photoisomerization, 2) a rate of the thermal cis-trans isomerization, and 3) the dichroism induced by reorientation of azobenzene (Az) units.

EXPERIMENTAL

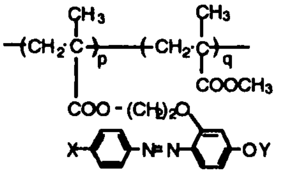
Materials

The synthesis of 2-hydroxy-4′-hexyl-(4-hexyloxy) azobenzene have been described previously.[7]

2-(Hydroxy)-4-methoxyazobenzene were prepared according to the same method. mp: 45-46°C. Found: C,72.90; H, 8.47; N, 5.64. Calcd: C,72.84; H, 8.56; N, 5.64. ^{1}H-NMR ($CDCl_3$): 0.89(6H, d, CH_3), 1.10-2.00(2H, m, $-CH_2-$), 1.93(3H, s, $CH_2=C-CH_3$), 2.61(2H, t, $Ar-CH_2-$), 4.00(2H, m, $ArO-CH_2-$), 4.50(4H, m, $COO-CH_2-$, $ArO-CH_2-$), 5.52(1H, s, C=C-H), 6.61(1H, s, C=C-H), 6.55(2H, d, Ar-H), 7.26(2H, d, Ar-H), 7.71(3H, t, Ar-H).

A degassed 33 wt% solution of a monomer containing 0.5 wt% 2,2′-azobis(isobutyronitrile) in dry benzene in an ampoule was heated at 65°C for 12 h, and resulting viscous solution was poured into methanol to precipitate polymeric materials. Purification was carried out by repeated precipitation using benzene/methanol system. The product was finally dissolved in benzene and lyophilized. The results of polymerization and the structure of polymers are summarized in Table 1.

TABLE 1. Characterization of polymers



	X	Y	(p:q)	yield(%)	Mw x10^{-4}	Mw/Mn	Tg (°C)
pMaz-10	H	CH_3	1:0	85	13.1	2.6	72
pMaz-19			1:9.2	66	3.9	3.5	84
pMaz-199			1:119	74	4.0	2.0	112
pMazhex-10	C_6H_{13}	C_6H_{13}	1:0	86	7.7	2.3	<r.t.
pMazhex-19			1:9.8	69	18.8	2.3	84

A 3 wt% solution of the polymer in toluene was spin-coated on a quartz plate (1x3 cm). After baking at an appropriate temperature, the film was subjected to photoirradiation with light from an ultra high pressure mercury arc through glass filters.

Measurement

19) was lower than those in solution. It might be due to the steric hindrance between the vicinal azobenzenes. In homopolymer films, the cis fraction of pMazhex-10 was larger than that of pMaz-10 in spite of large steric hindrance for hexyl and hexyloxy groups. This behavior might be explainable by considering the Tg of polymers; pMazhex-10 has low Tg (<r.t.), therefore, it was liquid-like at room temperature. The heat treatment before irradiation did not affect the value.

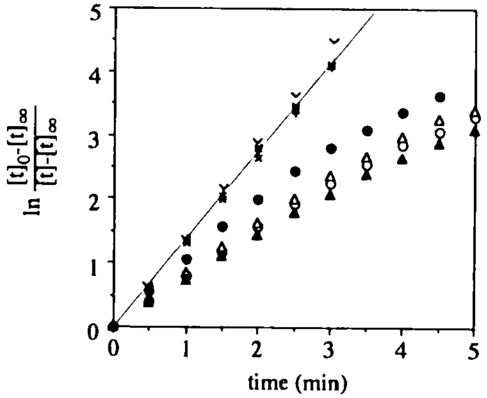


FIGURE 2. First order plots for the trans-cis photoisomerization of pMaz-10 (○), pMaz-19 (●), pMazhex-10 (△) and pMazhex-19 (▲) in film state (annealed at 120°C for 12h) and pMaz-10 (×), pMaz-19 (+), pMazhex-10 (v) and pMazhex-19(⁎) in toluene.

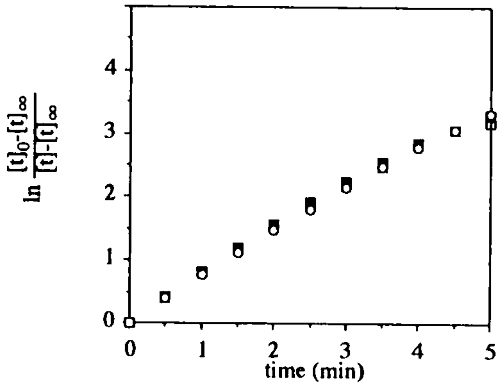


FIGURE 3. First order plots for the trans-cis photoisomerization of pMaz-10 films annealed at 120° C for 0 h (□), 1h (■) and 12h (○) before irradiation.

Kinetic analysis on the trans-cis photoisomerization was carried out in terms of the following equation (1),[9]

$$\ln\frac{[t]_0-[t]_\infty}{[t]-[t]_\infty}=Kt \quad \cdots(1)$$

where [t] is the trans azobenzene concentration, $[t]_\infty$ and $[t]_0$ are concentration of the trans isomer in a photostationary state and before UV-irradiation, respectively. Figure 2 shows first order plots of the photoisomerization of azobenzenes of polymers. The reaction of the polymers obeyed first order kinetics in solution, whereas it deviated from first order kinetics in film state. The decrease of the reaction rate in film could be explicable by assuming that the mobility of Az is limited in the polymer matrix. Heat treatment of the films at 120 °C before irradiation did not affect the rate of the photoisomerization.

Thermal backward reaction

Differential scanning calorimetry was conducted on a DSC200 of Seiko Electronics Co., Ltd., at a heating rate of 10°C/min. Gel permeation chromatography was carried out on an instrument of Jasco systems, a 860-CO column oven equipped with 875 UV detector at a flow rate of 1.0 mL/min with chloroform as an eluent. Molecular weights of the polymers were determined according to a polystyrene calibration curve. Copolymerization ratios were estimated by ^{1}H-NMR spectra measured on a JEOL FX90Q. The thermal backward reaction of azobenzene was monitored by absorbance at 365 nm using a Hitachi 320 spectrometer equipped with a thermoregulated cell holder. The azobenzene photoisomerization was followed by measuring UV and visible absorption spectra with a Hewlett-Packard diode array spectrometer 8452A.

RESULTS AND DISCUSSION

Photoisomerization

The photoisomerization of the azobenzenes attached to a polymethacrylate backbone was investigated both in solution and in a thin film. Figure 1 shows a spectral change of pMaz-10 (Table 1) in film state upon irradiation with 365 nm light. The top curve corresponds to the spectrum before irradiation, reflecting the spectrum of the trans isomer of the azobenzene. The absorption maximum observed at 365 nm was attributed to the π–π* transition of trans azobenzenes. The red shift of π–π* absorption band compared to non-substituted azobenzene (λmax=312 nm) was owing to the alkoxy substituent at the o- and p- position of azo-group. The absorbance decreased with increasing the irradiation time which indicates the photoisomerization of azobenzene moieties.

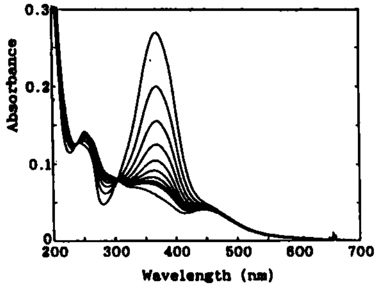


FIGURE 1. Change in UV-Vis spectra of pMaz-10 in film state during 365nm light irradiation.

TABLE 2. Cis Fractions (%) at photostationary states in solution

Solvent	pMaz-10	pMaz-19	pMazhex-10	pMazhex-19
toluene	90	96	95	95
THF	95	97	-	-

TABLE 3. Cis Fractions (%) at photostationary states in film state

Baking time (h)	pMaz-10	pMaz-19	pMazhex-10	pMazhex-19
0	78	95	87	90
1	79	96	88	93
12	79	97	87	94

From the absorbance of 365nm, the cis fraction could be calculated[8]. The contents of the cis isomer at the photostationary states are summarized in Table 2 and 3. In film state, the cis fraction of copolymer (pMaz-19 and pMazhex-19) was similar to that in solution. In contrast, the cis fractions of the homopolymers (pMaz-10 and pMazhex-

Kinetic analysis of the thermal cis-trans isomerization of a pMaz-10 film at 60°C was analyzed using the equation (2),

$$\ln \frac{[t]^{H}_{\infty}-[t]^{H}_{0}}{[t]^{H}_{\infty}-[t]} = Kt \quad \cdots(2)$$

where $[t]^{H}_{0}$ and $[t]^{H}_{\infty}$ are concentration of the trans isomer of the azobenzene in photostationary state and before irradiation, respectively. As shown in Figure 3, it followed first order kinetics. Therefore, the mobility and the free volume around azobenzene units in the film at 60°C might be analogous to those in solution. On the other hand, the thermal backward reaction rate of the copolymers in film state was initially larger and finally lower than that in solution. The phenomenon was more apparent with the polymer of lower azobenzene content. Such a rate enhancement in the beginning of the thermal isomerization is usually explained in terms of residual strain in the cis azobenzene produced by UV irradiation.[9]

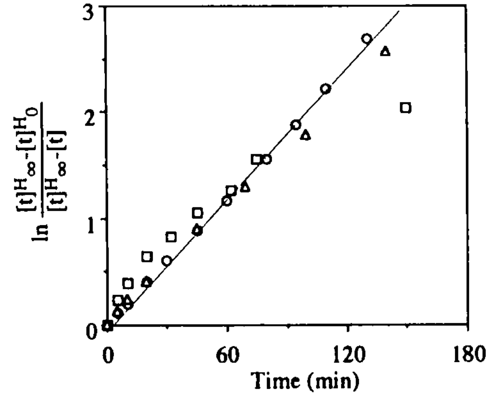


FIGURE 4. First order plots for the thermal cis-trans isomerization of films of pMaz-10 (○), pMaz-19 (△), pMaz-199 (□). The solid line was drawn on the basis of the isomerization behavior of pMaz-10 in toluene.

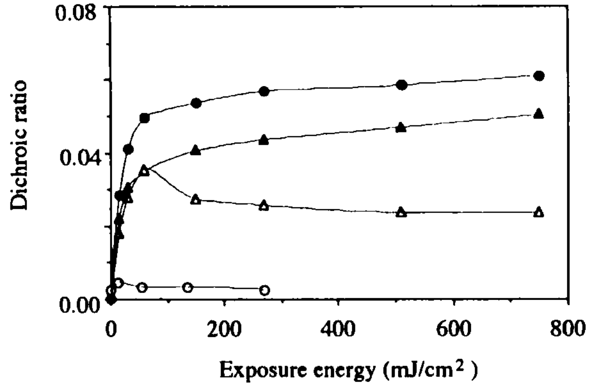


FIGURE 5. Polarized light exposure energy dependence of dichroic ratios of pMaz-10(○), pMaz-19 (●), pMazhex-10 (□) and pMazhex-19(■).

Photoinduced dichroism

Polymer films were irradiated with linearly polarized visible light (436 nm) and subjected to polarized absorption spectra measurement to reveal the occurrence of dichroism. Dichroic ratio was defined as shown in the equation (3),

$$\text{dichroic ratio} = \frac{A_{\perp}-A_{//}}{A_{\perp}+A_{//}} \quad \cdots(3)$$

where $A_{\perp}$ and $A_{//}$ denotes for the absorbances at 365 nm, of which the direction of an electric vector of polarized probe light is perpendicular and parallel to that of the actinic LPL, respectively. As shown in Figure 5, the exposure energy required for a saturation of dichroic ratio was 50 mJ/cm^2, and the maximum value for a pMaz-10 film was observed at about 50 mJ/cm^2. These results had been discussed previously.[7] The dichroic ratio was dependent on glass transition temperature (Tg) of the polymers rather than the structure of azobenzene or the copolymerization ratio. A film of a polymer having a higher glass transition temperature displayed larger dichroic ratio. The dichroic ratio of all polymers were below 0.08. This low value seems to be attributable to a portion of the rapid thermal relaxation of the photo-induced dichroism. Especially dichroic ratio of a film of pMazhex-10 was very low, compared to those of other polymers. With this polymers of low Tg (<r.t.), the orientation was more easily randomized thermally.

Liquid crystal photoalignment

We have already reported that the photocontrol of LC alignment on the films of pMaz-10 and pMaz-19.[7] The alignment regulation had been observed when the polymer film was pre-heated at 120°C before irradiation. A rate of the photoreaction of azobenzene units for actinic LPL was not seemed to vary with annealing because of no effect of the heat treatment of the film on the photoisomerization. It was suggested that conformational change at a topmost surface takes place in order to minimize a surface energy during the heat treatment. The hydrophobic chromophores might been located at an uppermost surface of the film after the annealing.

Photoalignment regulation experiment was performed by preparing polymeric films under the following condition. Spin-coated films of pMaz-10, pMaz-19 and pMazhex-19 were heated at 100°C for 6 h. A film of pMazhex-10 was heated at 40°C for 12 h. The temperature was set slightly higher than Tg of the polymer. Then they were irradiated with actinic LPL (436 nm). The exposure energy of actinic LPL was 200 mJ/cm^2. This value was sufficiently larger than an exposure energy of 50 mJ/cm^2, which resulted in the saturation of the dichroic ratio. A nematic LC, NPC-02 of T_{NI}=35.0°C, was put between two polymer films. The results were summarized in Table 4. Homogeneous alignment of LCs was brought about except an LC-cell using the pMazhex-10 films. In this case, homogeneous alignment was not observed. This result parallels with the degree of dichroic ratio.

TABLE 4. Photoregulation of LC alignment

Polymer	In-plane orientation
pMaz-10	+
pMaz-19	+
pMazhex-10	-
pMazhex-19	+

+: Homogeneous alignment.
-: Schlieren texture was observed.

REFERENCES

1. P. Rochon, J. Gosselin, A. Natansohn, S. Xie, Appl. Phys. Lett., 60, 4(1992)
2. K. Anderle, R. Birenheide, M. J. A. Werner, J. H. Wendroff, Liq. Cryst., 9, 691 (1991)
3. W. M. Gibbons, P. J. Shannon, S. T. Sun, B. J. Swelin, Nature, 351, 49(1991)
4. M. Schadt, K. Schmitt, V. Kozinov, V. Chigrinov, Jpn. J. Appl. Phys., 31, 2155(1992)
5. K. Ichimura, Y. Hayashi, H. Akiyama, N. Ishizuki, Langmuir, 9, 3298(1993)
6. H. Akiyama, K. Kudo, K. Ichimura, Macromol. Rapid Commun., 16, 35(1995)
7. H. Akiyama, M. Momose, K. Ichimura, S. Yamamura, Macromolecules, 28, 288(1995)
8. J. G. Victor, J. M. Tokelson, Macromolecules, 20, 2241 (1987)
9. I. Mita, K. Horie, K. Hirano, Macromolecules, 22, 558(1989)