Successive Occurrence of Biaxial Reorientation of Azobenzene Chromophores of a Liquid Crystalline Polymer Induced by Linearly Polarized Light[1]

Mina Han, Shin'ya Morino, and Kunihiro Ichimura*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503

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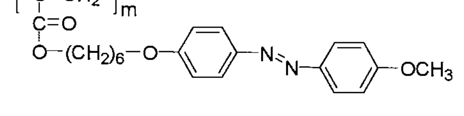
Unequivocal observation was made on the in-plane reorientation of azobenzene side chains tethered to liquid crystalline polymer backbones, followed by the out-of-plane reorientation upon irradiation with linearly polarized 436 nm light.

The photo-assisted manipulation of molecular orientation has been attracting current interest and achieved precisely by means of azobenzene photochemistry. There are two kinds of molecular reorientation modes; in-plane and out-of-plane alignment. When actinic light is linearly polarized, the chromophores display a uniaxial in-plane alignment with an orientational direction perpendicular to the electric vector of linearly polarized light.[2,3] This arises from the quantum mechanical requirements that light is absorbed specifically when the transition moment of a chromophore is in accordance with the electric vector of linearly polarized light.[4] On the other hand, we have observed recently that azobenzene residues in amorphous[5] as well as liquid crystalline polymers[6] reorient photochemically in such a way that the molecular axis becomes in parallel with the propagation direction of light, while Stumpe et al. suggested "homeotropic" reorientation of azobenzene chromophores with a LB multilayer of their liquid crystalline polymer.[7] This kind of out-of-plane alignment stems from the another selection rule that no light absorption occurs when light comes from the direction parallel to the transition moment of a chromophore, being irrespective of whether the light is linearly polarized. It has been recently discussed that the irradiation of a film of a polymer bearing azobenzene residues with linearly polarized light gives rise to the biaxial reorientation of chromophores as a result of the concurrence of in-plane and out-of-plane reorientation.[8] However, to authors' knowledge, there has been no systematic investigation on dynamic processes of the biaxial photoreorientation. We now report that the irradiation of a liquid crystalline azobenzene polymer with linearly polarized light generates both of the in-plane and out-of-plane reorientation of the chromophores successively. The former azimuthal reorientation proceeds at the early stage of photoirradiation, followed by the gradual reorientation into the direction parallel to light propagation.

A liquid crystalline polymer, poly[6-{4-(4'-methoxyphenyl)azophenyloxy}hexyl methacrylate] was employed here, taking notice of the facts that liquid crystalline azobenzene polymers display high levels of photogenerated dichroism exhibiting excellent thermal stability.[9,10] Thin films of about 70 nm in thickness were prepared by spin-coating a toluene solution of the homopolymer on fused silica plates. When a thin film was exposed to linearly polarized 436 nm light at an ambient temperature azobenzene moieties reorient perpendicularly very slowly to the electric vector of the light to give rise to dichroism. Photoirradiation with the light at 75 °C close to the glass transition temperature (T_g) of the polymer enhanced markedly the perpendicular reorientation to generate a high in-plane anisotropy at exposure doses of 1.5 J/cm^2 or more.



$M_w = 1.25 * 10^4$, $M_w/M_n = 2.8$
G 76 S 95 N 137 I
(G; glassy, S; smectic, N; nematic, I; isotropic)

The situation was changed drastically by heating the film during polarized photoirradiation at 90 °C, where the polymer displayed a smectic phase. Figure 1 shows polarized absorption spectra of the film after linearly polarized light irradiation at exposure doses of 0.05 J/cm^2 and 5 J/cm^2, respectively. The results tell us the followings. First, the π,π*-absorption band monitored by probe light with the electric vector parallel to that of the actinic light is of the monomeric chromophore and essentially not influenced by exposure doses, whereas the π,π*-absorbances ($A_{//}$) are much reduced after photoirradiation when compared with the absorbance at ca. 250 nm. Second, λ_{max} of the π,π*-absorption band is blue-shifted due to H-aggregation when measured with perpendicular probe light. Thirdly, absorbances ($A_\perp$) measured with perpendicular probe light are considerably reduced at a 5 J/cm^2 exposure, though the spectral shape is not much altered. The fact that an exposure dose required for a photostationary state is ca. 0.05 J/cm^2 suggests that the decrease in $A_\perp$ stems not from a photochemical process, but from a photophysical process.

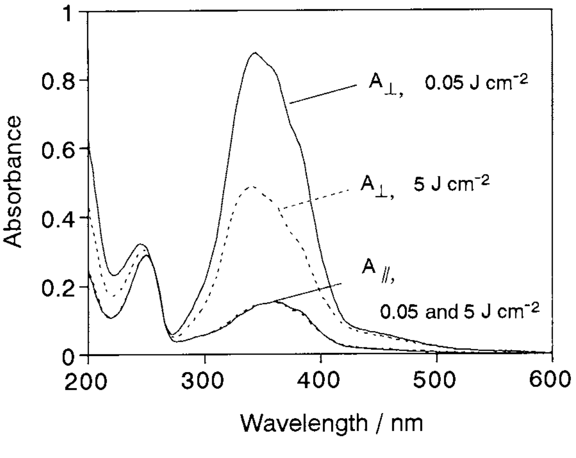


Figure 1. Polarized absorption spectra of a film of the liquid crystalline polymer with azobenzene side chains taken at room temperature after irradiation with linearly polarized 436 nm light of exposure doses of 0.05 J cm^{-2} and 5 J cm^{-2} at 90 °C, respectively.

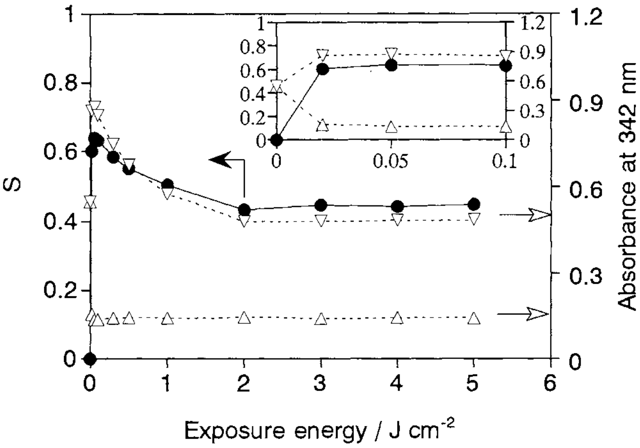


Figure 2. Polarized absorbances and order parameter S (●) of a film of the polymer at 342 nm perpendicular to ($A_{\perp}$;▽) and parallel to ($A_{//}$;△) the electric vector of linearly polarized light 436 nm as a function of exposure dose of the light.

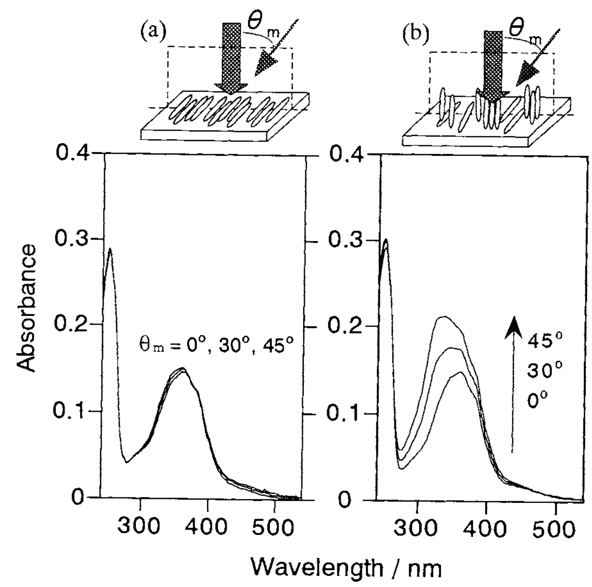


Figure 3. p-Polarized absorption spectra of a film of the liquid-crystalline polymer exposed to linearly polarized 436 nm light of exposure doses of (a) 0.05 J cm^{-2} and (b) 5 J cm^{-2}, respectively, at various incident angles (θ_m) of p-polarized probe light.

Figure 2 shows changes in $A_{\perp}$ and $A_{//}$ as a function of exposure dose of polarized 436 nm light. An exposure dose of 0.05 J/cm^2 results in a maximum value in $A_{\perp}$ (see the inset in Figure 2) and simultaneously in an abrupt decline of $A_{//}$ which becomes throughly constant afterwards. Changes in order parameter (S) defined as $S = (A_{\perp} - A_{//})/(A_{\perp} + 2A_{//})$ is also shown in Figure 2. Because of the predominant contribution of $A_{\perp}$values, S displays a rapid increase, followed by a gradual decrease through a maximum value of 0.64 to give a saturated value of S = 0.44. This observation can be reasonably interpreted in terms of the involvement of two reorientational processes.

In order to gain further insight into the spatial orientation of azobenzene chromophores in films, measurements of their electronic absorption spectra with s- and p-polarized probe light was performed at various incident angles (θ_m). θ_m is defined as an angle confined by the surface normal and the propagation direction of the probe light. Since the long axis of azobenzene molecules is approximately in consistence with the π,π^*-transition moment[11,12] so that it possible to determine their spatial orientation by measuring the polarized π,π^*-absorption band as a function of θ_m.[6] In particular, measurements with p-polarized probe light gives significant information about out-of-plane aligned molecules.[13,14] Figure 3 shows p-polarized absorption spectra of a film exposed to linearly polarized 436 nm light of 0.05 J/cm^2 and 5 J/cm^2 doses at 90 °C, respectively, as a function of θ_m. The electric vector of probe light is parallel to that of actinic light. As seen in Figure 3a, p-polarized spectra of a film illuminated at a 0.05 J/cm^2 dose are similar to that of monomeric azobenzene and not influenced by θ_m at all. This means that there is essentially no H-aggregated azobenzene with a molecular axis in parallel with the electric vector of actinic light.

On the other hand, p-polarized spectra of a film exposed to a 5 J/cm^2 dose display contrastive dependence on θ_m, as shown in Figure 3b. The larger θ_m is, the more λ_{max} is blue-shifted, accompanied by the increment of absorbances. This dependence on θ_m arises evidently from the reorientation to the surface normal and the concurrent self-assemblage of the azobenzene residues. In other words, prolonged irradiation with linearly polarized light brings about the out-of-plane reorientation of the azobenzene, which is determined by the propagation direction of actinic light, leading to the formation of H-aggregates because of the liquid crystallinity. The slow process of the subsequent out-of-plane reorientation stems unequivocally from small absorbances of perpendicularly oriented chromophores.

In summary, exposure of a spin-coated film of the liquid crystalline azobenzene polymer to linearly polarized 436 nm light gives rise to in-plane reorientation in the early stage to form H-aggregates, followed by gradual out-of-plane reorientation upon prolonged photoirradiation.

References and Notes

1 Photochemistry Determined by Light Propagation. Part 2, Part of this series; Ref. 6.

2 M. Eich and J. H. Wendorff, *Makromol. Chem. Rapid Commun.*, **8** 467 (1987).

3 A. Natansohn, P. Rochon, J. Gosselin, and S. Xie, *Macromolecules*, **25**, 2268 (1992).

4 N. J. Turro, "Modern Molecular Photochemistry," University Science Books, California (1991).

5 K. Ichimura, S. Morino, and H. Akiyama, *Appl. Phys. Lett.*, **73**, 921 (1998).

6 K. Ichimura, M. Han, and S. Morino, *Chem. Lett.*, **1999**, 85.

7 Th. Gune, A. Ziegler, and J. Stumpe, *Macromolecules*, **30**, 5729 (1997).

8 T. Buffeteau and M. Pézolet, *Macromolecules*, **31**, 2631 (1998).

9 L. Läsker, T. Fischer, J. Stumpe, S. Kostromin, S. Ivanov, V. Shibaev, and R. Ruhmann, *Mol. Cryst. Liq. Cryst.*, **253**, 1 (1994).

10 T. Fischer, L. Läsker, S. Czapla, J. Rübner, and J. Stumpe, *Mol. Cryst. Liq. Cryst.*, **298**, 213 (1997).

11 M. B. Robin and W. T. Simpson, *J. Chem. Phys.*, **36**, 580 (1962).

12 P. Uznanski, M. Kryszewski, and E. W. Thulstrup, *Spectrochem. Acta*, **46A**, 23 (1990).

13 J. Sagiv, *J. Am. Chem. Soc.*, **102**, 92 (1980).

14 J. Sagiv, *Isr. J. Chem.*, **18**, 346 (1979).