Macromol. Symp. 137, 129–136 (1999)

Thermally Stable Photoaligned *p*-Cyanoazobenzene Moieties in Polymer Thin Films

Kunihiro Ichimura,* Masatoshi Kidowaki, Takenori Fujiwara

Research Laboratory of Resources Utilization, Tokyo Institute of
Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

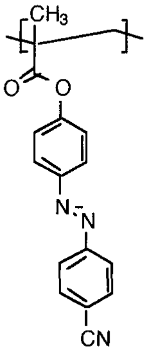
SUMMARY: Poly(4-cyano-4'-methacryloyloxyazobenzene) displayed a slow *E*-to-*Z* photoisomerization rate and a low *Z*-isomer content at a photostationary state in a film. Linearly polarized 436 nm light irradiation resulted in the gradual generation of dichroism due to the reorientation of the azobenzene chromophores. The photodichroism was enhanced markedly by heating the film and not deteriorated even at 240 °C. Discussion was made on the thermally enhanced photodichroism of the polymer with *p*-cyanoazobenzene side chains in respect to its semi-crystallinity.

Introduction

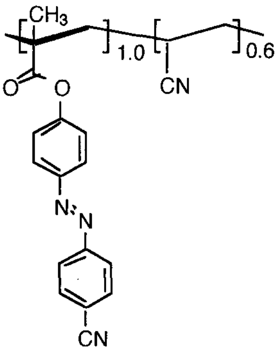
Linearly-polarized-light-induced generation of optical anisotropy of thin films of amorphous as well as liquid crystalline polymers with azobenzene side chains has been extensively investigated.[1] Our recent efforts have been concentrated to reveal the photoreorientation behavior of azobenzene moieties in polymeric as well as molecular films in conjunction with surface-assisted photocontrol of orientation of liquid crystal (LC) systems to give azimuthally homogeneous alignment as an extension of our systematic studies on command surfaces.[2] We reported that the irradiation of thin films of amorphous poly(methacrylates) with azobenzene side chains with linearly polarized light induces the reorientation of the photoisomerizable units to give rise to homogeneous alignment of nematic LCs.[3,4] An optical axis of the photogenerated homogeneous LC alignment is determined reversibly by

CCC 1022-1360/98/$ 17.50

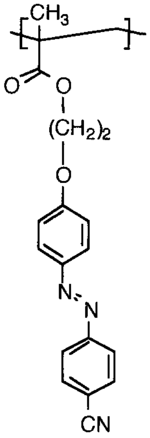
the electric vector of actinic polarized light so that this system provides the working principle for light-addressed LC devices as a photonics application. On the other hand, the photoinduced LC alignment has being attracting practical interest recently because this technique gives rise to produce LC-aligning films, which are inevitable materials for the fabrication of advanced LC display devices.[5] For this purpose, a photogenerated oriented state of a polymer thin film leading to a homogeneous LC alignment should display extraordinary stability toward external stimulation. We described previously that the thermal stability of homogeneous LC alignment is enhanced when photoaligned azobenzene polymers are subsequently photo-crosslinked with aid of azide moieties, though the thermal relaxation of a photoaligned state of azobenzenes was not thoroughly suppressed.[6] We report here that the photogenerated optical anisotropy of thin films of polymethacrylates with *p*-cyanoazobenzenes side chains displays anomalously high stability toward heat and practical applicability to LC-aligning films.



CNAz



CN-AN



Azh

Experimental part

Materials. 4-cyano-4'-hydroxyazobenzene of mp. 203-205 °C was prepared by diazo-coupling of 4-cyanoaniline with phenol according to a conventional procedure and converted into 4-cyano-4'-methacryloyloxyazobenzene (**1**) of mp 145-147 °C by the reaction with methacryl chloride in the presence of triethylamine in a 81% yield. A solution of 1.0 g of **1** and 5 mg of AIBN in 4 g of THF was filled in an ampoule, subjected to freeze-thaw cycles for degassing and sealed, followed by shaking at 65 °C for 8 hr. The product was diluted with THF to be filtered to remove an insoluble substance and poured into methanol to isolate poly(4-cyano-4'-methacryloyloxyazobenzene) (CNAzh) (Mw = 3.8×10^4, Mw/Mn = 1.7, Tg = 171 °C) in a 34 % yield. Dissolution/precipitation procedure was carried out five times for the purification of the homopolymer. A 1 : 0.6 copolymer (CNAz-AN) of **1** with acrylonitrile was prepared in a similar way from a mixture of 1.2 g of **1** and 0.85 g of acrylonitrile in 4 g of THF.

Poly[2-(4-phenylazophenyloxy)ethyl methacrylate) (Azh) (Mw = 3.2×10^4, Mw/Mn = 3.2, Tg = 114 °C) was prepared according to our previous work.[3]

Results and discussion

E/Z photoisomerization. It was observed that prolonged irradiation with 365 nm light is required to give photostationary states in films of CNAzh and CN-AN and that the level of *E-to-Z* photoisomerization is markedly suppressed. This situation can be visualized more clearly in first order plots for the photoisomerization of both of CNAzh and the copolymer (CNAz-AN), as shown in **Fig. 1**. Polar *p*-cyanoazobenzene residues are tethered directly to polymer backbones so that the suppression of the photoisomerization arises from both of steric hindrance and strong dipole-dipole interactions between the azobenzene moieties. It should be mentioned here that *E-to-Z* photoisomerization in films of both polymers deviates from first order plots more or less even in THF solutions, reflecting the dense packing of the chromophores.

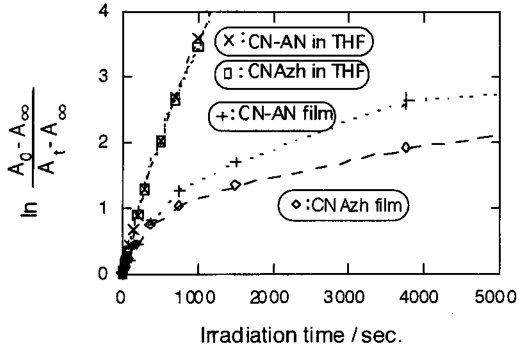


Fig. 1 First order plots for *E-to-Z* photoisomerization of azobenzenes in polymer films upon irradiation with 365 nm light.

Photoreorientation. It has been well established that the photoreorientation of azobenzene chromophores takes place in polymer films upon irradiation with linearly polarized light as a result of repetition of axis-selective *E/Z* photoisomerization. This was also the case for CNAzh; the π,π^*-transition moment of the azobenzene units reoriented particularly to the electric vector of polarized 436 nm light. The order parameter, defined as $S = (A_\perp - A_{//}) / (A_\perp - 2A_{//})$, was 0.06 at an exposure dose of polarized 436 nm light of 5 J cm^{-2}. $A_\perp$ and $A_{//}$ stand for absorbances with monitoring light with electric vectors perpendicular to and in parallel with that of the actinic light. The photoinduced dichroic nature of the film was further confirmed by measurements of polarized FT-IR spectra. Both of absorption bands due to ν_{CN} at 2228 cm^{-1} and to benzene ring at 1593 cm^{-1} supports the orientation of the azobenzene perpendicular to the electric vector of the light. On the basis of $A_\perp$ and $A_{//}$ values in the FT-IR spectra, S was calculated to be 0.07, being in line with that stated above. The FT-IR spectra reveal also that $A_{//}$ of ν_{CO} due to the ester carbonyl at 1710 cm^{-2} is larger than $A_\perp$, indicating that the C=O groups directly attached to polymer backbones align in parallel with the electric vector of the light. This is reasonable because all atoms between the C=O and CN groups are in sp^2 so that no flexibility exists in the molecular framework.

Fig. 2 shows photogenerated *S* values as a function of exposure doses of polarized 436 nm light. For comparison, the results for Azh with unsubstituted azobenzene side chains are shown here since this polymer displays photodichroism and is active for LC alignment photocontrol, as reported in our previous paper. The results are remarkable. Whereas *S* values leveled off at exposure energies of few hundreds mJ cm^{-2} for an Azh thin film, *S* values of *p*-cyanoazobenzene residues increase gradually even after illumination of exposure doses of 10 J cm^{-2} or more for both of the homopolymer and the copolymer. The prominent difference in photodichroic behavior may arise from whether azobenzene polymer is amorphous or semi-crystalline. Though a precipitated solid of CNAzh from a solution shows Tg in the first heating process, polarized microscopic observation revealed that the cooled polymer solid demonstrates optical anisotropy, indicating the polymer possesses crystallinity. Because of the densely packed structures in a film, the molecular mobility of *p*-cyanoazobenzene residues is highly suppressed to give rise to the results shown in **Fig. 2**.

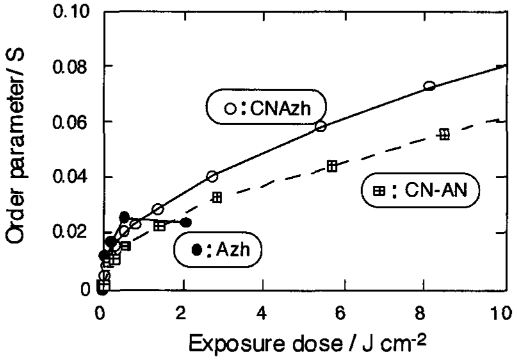


Fig. 2 Order parameters (*S*) of the azobenzenes in polymer films as a function of exposure doses of polarized 436 nm light.

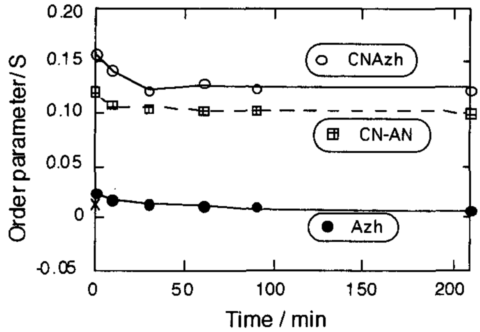


Fig. 3 Changes of order parameters (S) of the azobenzenes in photoirradiated films stored at 60 °C.

Thermal stability of photodichroism. Encouraged by the observation mentioned above, the thermal stability of photoorientation of the azobenzene chromophores was investigated. **Fig. 3** shows changes in S values of films of the azobenzene polymers stored at 60 °C after linearly polarized light irradiation. After a slight decrease in S at the early stage of the heating, no observable decline of the photodichroism occurred for both of the polymers with *p*-cyanoazobenzene side chains, maintaining relatively large S values, whereas Azh showed gradual decrease in S upon prolonged storage. The photodichroism of Azh disappeared completely at temperatures above Tg. This kind of thermal relaxation has been reported occasionally. In a keen contrast to the cases, quite an interesting phenomenon was found for CNAzh. When a photoirradiated film of the polymer was heated, S values increased as the increase in heating temperatures. One of the typical examples is shown in **Fig. 4**. While $S = 0.12$ at an exposure dose of 20 J cm^{-2}, prominent enhancement of dichroism was observed after heating at 240 °C for 1 hr to give $S = 0.46$, exhibiting that the photoaligned state becomes anomalously thermally stable. This event may result from the preferable formation of supramolecular structures of polar and rigid *p*-cyanoazobenzene units and is closely related with the observation that the photodichroism of spin-cast films

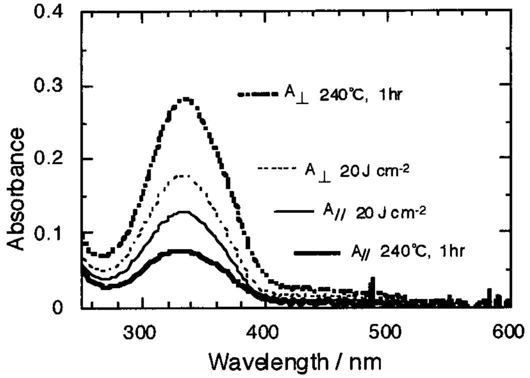


Fig. 4 Polarized absorption spectra of a CNAzh film irradiated with linearly polarized 436 nm light of an exposure dose of 20 J cm^{-2} before and after heating at 240 °C for 1 hr.

of liquid crystalline[7] as well as semi-crystalline[8] polymers with azobenzene side chains is enhanced thermally.

Conclusion

CNAzh and the related copolymer with *p*-cyanoazobenzene residues tethered directly to polymer backbones demonstrate remarkable photoorientation behavior when compared with a counterpart polymer with unsubstituted azobenzene side chains (Azh). Optical anisotropy of a thin film of CNAzh displayed anomalously high thermal stability probably owing to effective cooperative works among the polar and rigid p-cyanoazobenzene moieties. This type of thin films are of practical significance to apply to produce LC aligning films for LC display devices.

References

1) S. Xie, A. Natansohn, P. Rochon, *Chem. Mater.* **5**, 403 (1993).

2) K. Ichimura, in "*Polymers as Electrooptical and Photooptical Active Media*", Ed. V. Shibaev, Springer, Berlin 1996, p.138.

3) K. Ichimura, H. Akiyama, N. Ishizuki, Y. Kawanishi, *Makromol. Chem., Rapid. Commun.* **14**, 813 (1993).

4) H. Akiyama, K. Kudo, K. Ichimura, *Makromol. Chem., Rapid. Commun.* **16**, 35 (1995).

5) M. Schadt, H. Seiberle, A. Schuster, *Nature* **381**, 212 (1996).

6) H. Akiyama, K. Kudo, Y. Hayashi, K. Ichimura, *J. Photopolym. Sci. Technol.* **9**, 49 (1996).

7) J. Stumpe, L. Läsker, Th. Fischer, M. Rutloh, S. Kostromin, R. Ruhmann, *Thin Solid Films* **284/285**, 252 (1996).

8) A.Natansohn, P. Rochon, M. Pezolet, P. Audet, D. Brown, S. To, *Macromolecules* **27**, 2580 (1994).