

## Photoinduced Supramolecular Chirality in Amorphous Azobenzene Polymer Films

Mi-Jeong Kim, Bu-Gon Shin, Jang-Joo Kim, and Dong-Yu Kim\*

Center for Frontier Materials, Department of Materials Science and Engineering, Kwang-Ju Institute of Science and Technology, Kwang-Ju 500-712, Republic of Korea

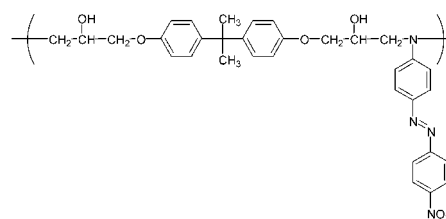
Received November 2, 2001

Fundamental questions concerning chiroptical polymers arise from the characteristics of natural polymers, which have a one-handed helical conformation and show characteristic functionality in living systems.<sup>1</sup> Conformational chirality can be optically induced by the irradiation of photochromic molecules and polymers.<sup>2–10</sup> This phenomenon has been investigated for cases of many kinds of photochromophores, for example, azobenzenes,<sup>2–4</sup> overcrossed alkenes,<sup>5,6</sup> diarylethens,<sup>7</sup> binaphthalenes,<sup>8</sup> and spiroopyranes.<sup>9</sup>

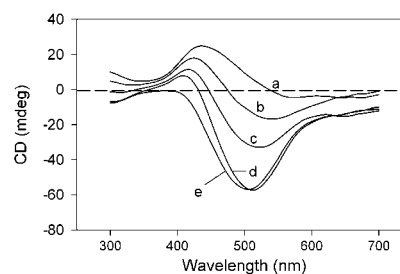
Since the pioneering studies by Goodman,<sup>10</sup> the optical induction of supramolecular chirality has been widely studied using azobenzene-containing polymers. Azobenzenes are well-known chromophores for their photoinduced linear orientation via trans–cis–trans photoisomerization.<sup>11</sup> Photoinduced chirality changes in azopolymers have been reported for polymethacrylates,<sup>2</sup> polypeptides,<sup>3</sup> and polyisocyanates.<sup>4</sup> These azobenzene polymers contain chiral centers, and the chiral properties were investigated in solution using two different wavelengths as the light source.

The use of circularly polarized light (CPL) has been demonstrated as a method for partially resolving a racemic mixture.<sup>6,12</sup> Recently, Nikolova et al. reported on the photoinduced chirality of amorphous and liquid crystalline azobenzene polymers by irradiation with CPL.<sup>13,14</sup> The induced chirality of the azobenzene polymers was investigated as a function of the ellipticity of incident light. However, Iftime et al. reported that circular dichroism (CD) is not induced in an amorphous azopolymer film by irradiation with CPL and proposed that liquid crystalline alignment represents one of the key factors in the creation of a chiral superstructure.<sup>15</sup> Therefore, the issue of the origin of the photoinduced chirality of azobenzene polymer films irradiated by light with handedness is not clear. In this research, we report on an investigation of chirality photoinduction from amorphous and achiral azobenzene polymer films. The findings show that liquid crystallinity is not a necessary condition for a material to exhibit photoinduced chiral properties.

To attain an amorphous polymeric property, epoxy-based azobenzene polymer PDO3 that contains no chiral centers was used in this study. PDO3 was synthesized via the reaction of 2,2-bis(4-glycidyloxyphenyl)propane with disperse orange 3.<sup>16</sup> The chemical structure is shown in Figure 1. Optically transparent films were prepared by spin-casting a solution of 10 wt % PDO3 in cyclohexanone on glass slides. The glass transition temperature of the polymer was 110 °C, and the films were baked at 160 °C to give 0.4- $\mu$ m thick films. A UV absorption maximum was observed at 477 nm. The light source for chirality induction was an argon ion laser (Coherent) at 488 nm with an intensity of 100 mW/cm<sup>2</sup>. Handedness and ellipticity of the incident laser beams were controlled using a  $\lambda/4$  waveplate. The beam was expanded and collimated to obtain a homogeneous light intensity over the entire area to be exposed. After the film was exposed for 10 s to 70 min,



**Figure 1.** Chemical structure of epoxy-based amorphous polymer PDO3 containing azobenzene chromophores and no chiral groups.

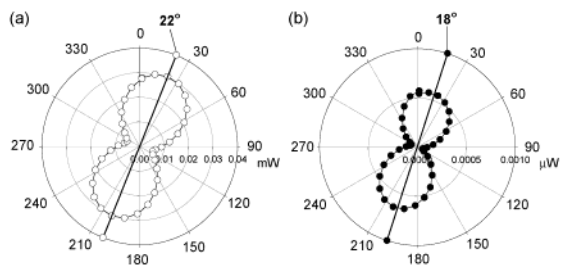


**Figure 2.** Induced CD spectra of the PDO3 films, which were irradiated by left-handed Ar<sup>+</sup> laser beam (488 nm, 100 mW/cm<sup>2</sup>,  $\psi = 14.8^\circ$ ). Exposure time was (a) 10 s, (b) 30 s, (c) 1 min, (d) 10 min, (e) 70 min.

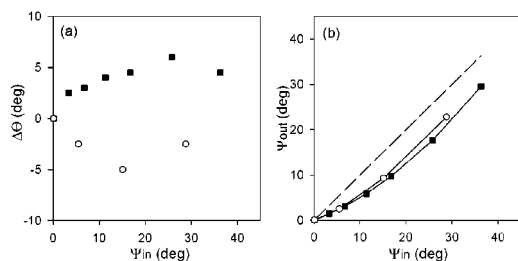
CD was measured from 300 to 700 nm using a JASCO 720 CD spectrometer.

No circular dichroism was detected from unirradiated PDO3 films, indicating that the materials initially were achiral. When the films were exposed to right- or left-handed CPL, no CD was observed as well. However, when we introduced the linear polarized portion to the incident CPL, that is, elliptically polarized light (EPL), a large CD signal was detected. Herein, light ellipticity ( $\psi$ ) is defined by the angle  $\psi = \arctan(b/a)$ , where  $b/a$  is the ratio of light intensity at the minor (b) and major axis (a).<sup>1</sup> Figure 2 shows photoinduced CD spectra of the film that was exposed to left-handed EPL with a 14.8° ellipticity. The variation in CD spectra was monitored as a function of exposure time. A positive CD peak centered at 435 nm (Figure 2a) became split into two oppositely signed peaks (Figure 2b–d) with increasing the exposure time, that is, negative exciton coupling. As the exposure was continued further, the intensity of the negative CD increased and that of the positive CD decreased. After 70 min of irradiation, only a single negative CD peak at 505 nm with an intensity of –57 mdeg was evident. Under all these conditions, CD signals appeared in the region of corresponding  $\pi \rightarrow \pi^*$  transition of the azobenzenes. Therefore, the CD spectrum might have been generated from the photoinduced chiral orientation of azobenzene chromophores. Exciton coupling arises from interactions between neighbor chromophores through their locally excited states. The negative exciton coupling represents an anticlockwise orientation of azobenzene chromophores. According to exciton coupling theory<sup>1</sup>, blue-shifted exciton excitation

\* To whom correspondence should be addressed. E-mail: kimdy@kjist.ac.kr.



**Figure 3.** Intensity profile of (a) the left-handed incident  $\text{Ar}^+$  laser beam ( $\theta_{\text{in}} = 22^\circ$ ,  $\mu_{\text{in}} = 11.4^\circ$ ) and (b) the transmitting beam after the irradiated film ( $\theta_{\text{out}} = 18^\circ$ ,  $\psi_{\text{out}} = 5.9^\circ$ ). The major axis of the transmittal light was rotated in a counterclockwise direction.

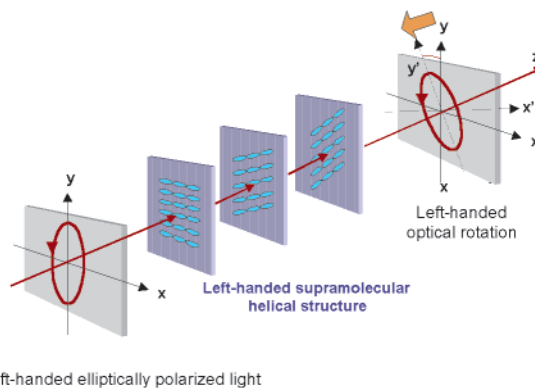


**Figure 4.** (a) Optical rotation angle ( $\Delta\theta$ ) and (b) ellipticity change of the principal axis as a function of the incident light ellipticity ( $\psi_{\text{in}}$ ) for the amorphous PDO3 film exposed to left ( $\blacksquare$ )/right ( $\square$ )-handed elliptically polarized  $\text{Ar}^+$  laser beams. Exposure time was 10 min.

occurs in the case of the parallel orientation of chromophores, but a red-shift occurs in the case of the in-line orientation. Therefore, the induction of azobenzene chiral orientation might progress from a parallel to an in-line orientation of azobenzene chromophores.

Other evidence of a photoinduced chiral suprastructure of the amorphous PDO3 polymer was the optical rotation of the principal axis. Figure 3a shows an intensity profile of an incident laser beam with left-handedness. The ellipticity ( $\psi_{\text{in}}$ ) was  $11.4^\circ$ , and the principal axis ( $\theta_{\text{in}}$ ) is located at  $+22^\circ$ . Figure 3b shows an intensity profile of the beam passing through the irradiated polymer film. The principal axis was rotated  $4^\circ$  in a counterclockwise direction. The ellipticity of transmitted light becomes smaller ( $\Delta\psi = -5.5^\circ$ ). Considering the film thickness of  $0.4 \mu\text{m}$ ,  $4^\circ$  represents a huge amount of optical rotation. This clearly shows that the film became optically active. Figure 4 shows the optical rotation angle and the ellipticity change of the films after exposure to left-/right-handed EPL with various ellipticities. If the polymer film was exposed to right-handed EPL, the major axis was rotated in a clockwise direction. However, the angle of optical rotation was not exactly the same as the case of left-handed EPL. This might be due to a different activation energy or conformational stability between left- and right-handed supramolecular helical orientations.<sup>15,17</sup>

The chirality photoinduction of an azobenzene polymer might be a combination process of linear polarization and circular polarization of incident light. Figure 5 illustrates one of the possible mechanisms for the chirality photoinduction, based on our CD spectra and optical rotation experiments. It is supposed that the film of the amorphous azopolymer consists of several sublayers. If the first layer was exposed to left-handed EPL, the linear polarized portion of the incident beam would cause the azobenzenes to orient perpendicularly to the major axis of the incident light. The major axis of light passing through the first layer would rotate in a counterclockwise direction. In the case of the second layer, the orientation plane of the azobenzenes would rotate by the same extent as that of the optical rotation angle. This stepwise optical rotation would be extended along the successive layers of the film. Therefore, a left-handed supramolecular helical structure might be



**Figure 5.** Schematic diagram of a proposed mechanism for the optical induced chiral suprastructure of an amorphous azopolymer film. Left-handed elliptical light might induce a left-handed helix orientation of azobenzene chromophores.

generated. If the film was exposed to complete CPL, the preferred axis of azobenzene orientation could not be generated on amorphous azopolymer films. In the case of the liquid crystalline azopolymer film, the intrinsic birefringence would change the incident circular polarization to the elliptical state after the first layer. Optical rotation through further layers would be generated in the same manner as for the amorphous film. This is consistent with the explanation proposed previously.<sup>14,15</sup> Consequently, a key factor for photoinduced chirality of an azopolymer film is believed to be the linear orientation. Chirality photoinduction using CPL in liquid crystalline polymers represents a special case.

In summary, chiral orientation of azobenzene chromophores on the amorphous polymer films was optically induced by irradiation with  $\text{Ar}^+$  laser light with elliptical polarization. The chiral structures were strongly dependent on exposure energy. The induction of chirality might arise from the stepwise rotation of a linear orientation of the azobenzene groups through propagation of the light. We are currently investigating the detailed mechanism of optically induced chiral suprastructures and potential chirality amplification by taking advantage of this extraordinarily high optical rotation.

**Acknowledgment.** This work was supported by IITA and NRL program of the Ministry of Science and Technology of Korea.

## References

- (1) *Circular Dichroism Principles and Applications*, 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH, Inc.: New York, 2000.
- (2) Angiolini, L.; Caretti, D.; Giardini, L.; Salatelli, E. *Macromol. Chem. Phys.* **2000**, *201*, 533.
- (3) Pieroni, O.; Fissi, A.; Ciardelli, F. *React. Funct. Polym.* **1995**, *6*, 185.
- (4) Muller, M.; Zentel, R. *Macromolecules* **1996**, *29*, 1609.
- (5) Feringa, B. L.; Jager, W. F.; Lange, B. d. *J. Am. Chem. Soc.* **1991**, *113*, 5468.
- (6) Huck, N. P. M.; Jager, W. F.; Lange, B. d.; Feringa, B. L. *Science* **1996**, *273*, 1686.
- (7) Yamaguchi, T.; Uchida, K.; Irie, M. *J. Am. Chem. Soc.* **1997**, *119*, 6066.
- (8) Janicki, S. Z.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 8485.
- (9) Eggers, L.; Bush, V. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 881.
- (10) Goodman, M.; Falxa, M. L. *J. Am. Chem. Soc.* **1967**, *89*, 3863.
- (11) Xie, S.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1993**, *5*, 403.
- (12) Li, J.; Schuster, G. B.; Cheon, K.-S.; Green, M. M.; Selinger, J. V. *J. Am. Chem. Soc.* **2000**, *122*, 2603.
- (13) Nikolova, L.; Todorov, T.; Ivanov, M.; Andruzzi, F.; Hvilsted, S.; Ramanujam, P. S. *Opt. Mater.* **1997**, *8*, 255.
- (14) Nikolova, L.; Nedelchev, L.; Todorov, T.; Petrova, T.; Tomova, N.; Dragostinova, V.; Ramanujam, P. S.; Hvilsted, S. *Appl. Phys. Lett.* **2000**, *77*, 657.
- (15) Iftime, G.; Labarthe F. L.; Natansohn, A.; Rochon, P. *J. Am. Chem. Soc.* **2000**, *122*, 12646.
- (16) Wang, X.; Kumar, J.; Tripathy, S. K.; Li, L.; Chen, J.-I.; Marturankakul, S. *Macromolecules* **1997**, *30*, 219.
- (17) Urata, H.; Miyagoshi, H.; Kumashiro, T.; Mori, K.; Shoji, K.; Akagi, M. *J. Am. Chem. Soc.* **2001**, *123*, 4845.

JA017454W