

Molecular Reorientation Induced by Sunshine Suggesting the Generation of Absolute Chirality¹

Kunihiro Ichimura* and Mina Han

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-Ku, Yokohama 226-8503

(Received November 9, 1999; CL-990957)

Both azimuthal and polar directions of azobenzene chromophores tethered to liquid-crystalline polymer backbones follow the orbital motion of the sun upon exposure of a film of the polymer to sunlight. The possibility to generate absolute chirality by the orbital motion of the sun is suggested.

We reported recently that the irradiation of films embedding azobenzenes with non-polarized 436 nm light results in the reorientation of the longitudinal axis of the chromophores in parallel with the propagation direction of the light since the transition moment lies approximately in parallel with the molecular axis.²⁻⁵ These facts led us to an idea that the orientation of azobenzenes in polymer films with suitable thickness can be manipulated three-dimensionally to display different directions in depth direction. A model for controlling the direction of light propagation consists of changing both of azimuthal (α) and polar (β) angles on the basis of the Lambert-Beer rule, as illustrated in Figure 1. The larger is the polar angle β , the thinner becomes a photoactive layer into which the light can penetrate sufficiently under an appropriate choice of absorption coefficients of azobenzene at wavelengths of actinic light. Remind that sunlight is randomly polarized or simply unpolarized⁶ and changes both α and β of incidence continuously. It is anticipated consequently that the reorientational direction of azobenzenes memorizes the orbital motion of the sun in a bulk layer so that azobenzene moieties form a left-handed helical structure, as illustrated in Figure 1, though each molecular axis deviates from a coplanar orientation. Aiming at our final goal to verify the possibility of the chirality generation by the sun, we report here that the azobenzene chromophores change in fact the orientational direction in thin films to follow the incident direction of sunlight.

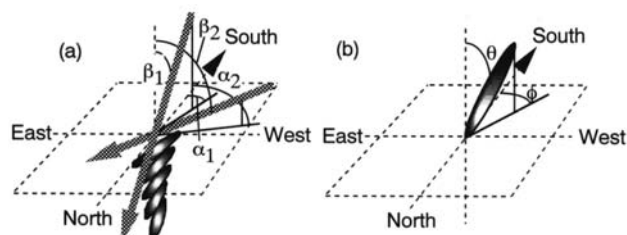


Figure 1. (a) The definition of azimuthal (α) and polar (β) angles of sunlight denoted as broad arrows at two different conditions and the hypothetical formation of helical orientation of azobenzene molecules in a solid on the basis of the Lambert-Beer rule. Refraction of light at the air/solid interface is omitted for simplicity. (b) The definition of an azimuthal (ϕ) and polar (θ) angles of a photoaligned azobenzene molecule and an incident angle (θ_m) of *p*- or *s*-polarized probe light.

Thin films of about 200 nm in thickness were prepared by spin-coating a toluene solution of liquid crystalline poly[6-{4-(4-methoxyphenyl)azophenoxy}hexyl methacrylate]⁷ on

clean fused silica plates, taking note of the efficient photogeneration of optical anisotropy of liquid crystalline polymers.^{3,8} The films were placed horizontally and exposed to sunlight passing through the combination of glass filters (Toshiba; Y-43 and V-44) to select visible light in a range of 420-520 nm for $n-\pi^*$ excitation. The intensity of direct sunshine on February 28 in 1999 in Yokohama through the filters was in a range of 2-6 mW/cm² from 10:10 a.m. to 2:30 p.m. and decreased gradually after 3 p.m. The films were illuminated with sunlight in two ways as summarized in Table 1; separated irradiation for 90 minutes (samples A, B, C and D) and continuous irradiation (samples E, F and G) from 10:10 a.m. through 4:10 p.m. For this experiment, we define α and β as an azimuthal angle confined by the southern direction and an incident plane of the sun and a polar angle of sunlight from surface normal. The directions of photoaligned azobenzenes are expressed as the azimuthal (ϕ) and polar (θ) angles which are defined in the same manner for α and β (Figure 1(b)).

Films exposed to sunlight for 90 min at different periods (samples A, B, C and D) were subjected to measurements of polarized absorption spectra as a function of azimuthal angles (α) which are the same as those defined in Figure 1(a). For the sake of the comparison of changes in $\pi-\pi^*$ absorbances at 360 nm among the samples, measured absorbances (A_t) were normalized with respect to an initial absorbance (A_0) before illumination to plot normalized values (A_t/A_0) as a function of α . The results shown in Figure 2 display that the orientational directions of the chromophores (ϕ) are shifted in fact toward the incident direction of the sun expressed as α . This fact means that the azimuthal reorientation of the azobenzene follows the solar motion to produce dichroism. ϕ values estimated from Figure 2 are listed in Table 1. Figure 2 presents also that A_t/A_0 values are markedly smaller than unity except for sample D, indicating that the molecular axis of the azobenzene tilts toward the propagation direction of sunlight, as described in our previous paper.³

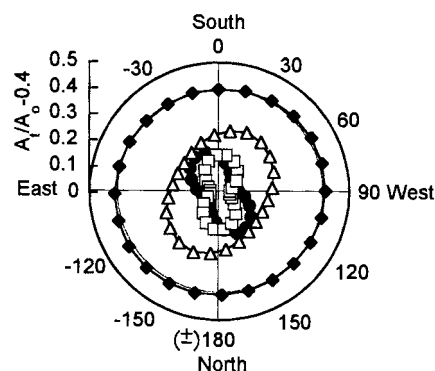


Figure 2. Circular diagrams for changes in absorbances at 360 nm as a function of the rotation angles (α) of the samples illuminated at different periods: ●, sample A; □, sample B; △, sample C; ◆, sample D.

Table 1. Photo-reorientation of the azobenzene induced by sunlight on Feb. 28, 1999

Sample	Irradiation period / h		Incident angles of sunlight / degree ^a				Directions of azobenzene / degree ^b	
	From	To	Azimuthal		Polar		Azimuthal	Polar
			α_1	α_2	β_1	β_2	ϕ	θ
A	10:10	~ 11:40	-36	~-6	54	~ 45	-26	40
B	11:40	~ 13:10	-6	~ 22	45	~ 52	4	45
C	13:10	~ 14:40	22	~ 46	52	~ 63	34	~50
D	14:40	~ 16:10	46	~ 64	63	~ 80	59	>50
E	10:10	~ 13:10	-36	~ 22	54	~ 52	-1	40
F	10:10	~ 14:40	-36	~ 46	54	~ 63	14	35
G	10:10	~ 16:10	-36	~ 64	54	~ 80	24	30

^a α_1 and β_1 denote azimuthal and polar angles when the exposure started, whereas α_2 and β_2 are for those at the times when the irradiation was stopped.

^b The definition of ϕ and θ is presented in Figure 1.

Consequently, photogenerated polar angles (θ) of the azobenzene were estimated for four samples (A, B, C and D) by measurements of polarized absorption spectra with *p*- and *s*-polarized probe light as a function of incident angles of the probe light.³ Note that *p*-polarized probe light is sensitive to a transition moment tilting in directions parallel to the plane of incidence of the light, whereas *s*-polarized probe is irrespective of the tilting state. The incident planes of the probe light were selected to be in line with the azimuthal angles of the azobenzene chromophores in each sample (ϕ), which was estimated as described above. As discussed in our previous paper, Figure 3 shows the changes of the two parameters, λ_{\max} and A_{p320}/A_{s320} , as a function of incident angle (θ_m) of the probe light from surface normal, whereas λ_{\max} , A_{p320} and A_{s320} denote the maximum wavelength of the π - π^* absorption band and π - π^* absorbances at 320 nm due to H-aggregates taken by *p*-polarized and *s*-polarized probe light, respectively.⁹ Polar angles (θ) of the photoaligned azobenzene for every sample can be evaluated from the results illustrated in Figure 3 and are listed in Table 1. For instance, sample A displayed the minimum value of A_{p320}/A_{s320} at ca. 40°, indicating that θ of the H-aggregated azobenzene is estimated to be ca. 40°.³ Consequently, it is anticipated that ϕ changes continuously in depth direction upon irradiation with sunlight from noon with the smallest β_1 through evening with the largest β_2 , as suggested in Figure 1. It is reasonably assumed that sample D may correspond to a surface layer of a thick polymer film whereas sample B represents a deeper layer.

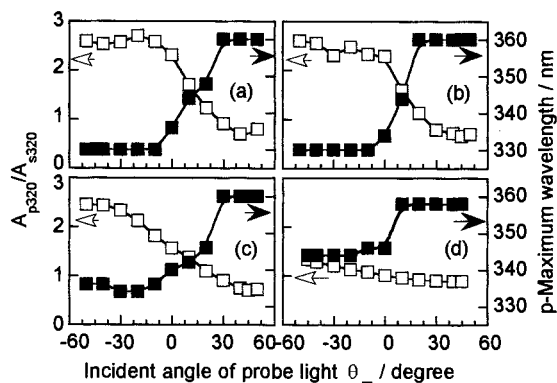


Figure 3. A_{p320}/A_{s320} and λ_{\max} of π - π^* absorption bands of films exposed to sunlight for 90 min at different periods as a function of incident angles (θ_m) of probe light: (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

It followed that the prolonged irradiation of films of the polymer was achieved on the same day. Both angles of ϕ and θ for samples (E, F, and G in Table 1) subjected to the continuous photoirradiation were estimated in the same way and listed in Table 1. All the results shown in Table 1 tell us the followings. First, azimuthal incident angles (α_2) of sunlight at the time when irradiation was stopped are not in line with the azimuthal angles (ϕ) of the azobenzene. The difference between α_2 and ϕ increases with the increase in the photoirradiation periods so that sample G displays the largest difference of 40°. Second, the ϕ values of the samples subjected to 90 min irradiation are far from those of the samples irradiated for longer than 2 h continuously even when the irradiation was stopped at the same time. For instance, the difference of ϕ between samples D and G is 35°. The results arise evidently from the suppressive effect of the photoinduced H-aggregation of the azobenzenes on the molecular photo-reorientation. This situation is in line with the fact that polar angles (θ) of samples F and G are close to each other though the irradiation was stopped at the different times. Consequently, the experimental support to verify our hypothesis for the photogeneration of absolute chirality seems not to be available at the present because prolonged exposure of films of the polymer to sunlight gives rise to the H-aggregation of the azobenzene, leading to the suppression of the continuous photo-reorientation.

In conclusion, the orientational direction of the azobenzene in polymer films is able to follow the solar motion so that it may be possible to create a left-handed helical structure of the molecular orientation in a bulk layer on the basis of the Lambert-Beer rule.

References and Notes

- 1 Photochemistry determined by light propagation. Part 4, Part 3: Ref. 5.
- 2 K. Ichimura, S. Morino, and H. Akiyama, *Appl. Phys. Lett.*, **73**, 921 (1998).
- 3 K. Ichimura, M. Han, and S. Morino, *Chem. Lett.*, **1999**, 85.
- 4 M. Han, S. Morino, and K. Ichimura, *Chem. Lett.*, **1999**, 645.
- 5 N. Yoshimoto, S. Morino, and K. Ichimura, *Chem. Lett.*, **1999**, 711.
- 6 J. Walker, in "Light from the Sky," W. H. Freeman and Company, San Francisco (1980).
- 7 A. S. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro, and M. Laus, *Liq. Cryst.*, **4**, 513 (1989).
- 8 Y. Wu, T. Ikeda, and Q. Zhang, *Adv. Mater.*, **11**, 300 (1999).
- 9 The ratio, A_{p320}/A_{s320} , is employed here instead of A_{p320} for the cancellation of changes of path length, which is a function of the incident angle of the probe light.