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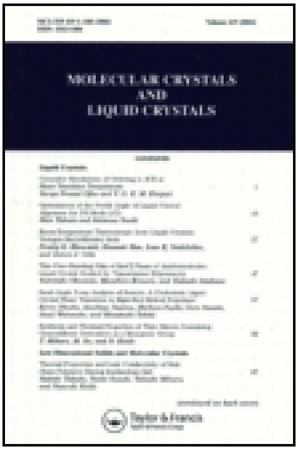

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Photoinduced Molecular Re-orientation and Supramolecular Helical Structure Formation in Azobenzene Materials

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Version of record first published: 16 Aug 2006

To cite this article: Takashi Fukuda, Jun Young Kim, Hiroshi Sumimura, Masahide Itoh & Toyohiko Yatagai (2006): Photoinduced Molecular Re-orientation and Supramolecular Helical Structure Formation in Azobenzene Materials, Molecular Crystals and Liquid Crystals, 446:1, 61-70

To link to this article: http://dx.doi.org/10.1080/15421400500383188

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Mol. Cryst. Liq. Cryst., Vol. 446, pp. 61–70, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500383188

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Photoinduced chirality in azobenzenes has been investigated. Even in low-molecular weight azobenzenes, photoinduced optical rotation could be observed and the characteristics were similar to that of ever reported in azobenzene side-chain-type polymer. Any relationship between molecular chirality and photoinduced chirality could not be observed in low-molecular weight azobenzenes. Further, very large optical rotation of 41 deg./μm could be observed in an azobenzene copolymer containing large birefringent unit. Dependence of optical rotation on intensity, wavelength and ellipticity of excitation beam were examined. The phenomenon was discussed based on the assumption that photoinduced helical structure was formed by elliptically polarized beam irradiation.

Keywords: Achiral azobenzene polymer; low-molecular weight azobenzene; photoinduced birefringence; photoinduced chirality; photoinduced molecular re-orientation; photoinduced optical rotation; photoinduced supramolecular helical structure formation

INTRODUCTION

In this decade, many new findings on azobenzene materials have been brought about one after another from both basic and application

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viewpoint, for example, photo-induced surface relief formation [1,2], photo-induced chirality [3–5], photo-driven actuator [6] and development of re-writable holographic memory using azopolymer as a media [7,8]. All of those are attributed to unique photo-responsible properties of azobenzene such as photo-induced mass transport, molecular re-orientation and volume contraction.

Especially photoinduced molecular reorientation is unique and useful characteristics for various optical applications. This is attributed dynamic response of azobenzene molecules that preferably re-orient to the direction perpendicular to the electric field of excitation beam via continuous trans-cis-trans photoisomerization cycle. On evolving these characteristics, the observation of optical rotation and circular dichroism in achiral azobenzene materials under irradiation with elliptically polarized light (EPL) has been recently reported [9,10]. Usually, optical rotation is a phenomenon that occurs in materials with a three dimensional distinction called chirality that never coincide with their mirror image. Alternatively, it can be achieved by forming three dimensional asymmetric structure such as a helix. One of the hypothesis on the generation of photoinduced chirality in achiral material is that it is attributed to the photofabrication of helical structure in a long-range (or short-range) order. As reported so far, the photoinduced optical rotation and circular dichroism depend on the condition of the excitation beam such as ellipticity, beam intensity and irradiation time [3–5]. The photoinduced chirality is expected to realize many unique optical components such as tunable optical rotator and circular dichroic filter.

Nikolova *et al.* has explained photoinduced chirality by the formation of a helical structure in a long-range order, layering azobenzene material as shown in Figure 1 [4,9,10]. Here it is considered the case where a sample is excited by right-handed EPL. Azobenzene molecules align to the direction perpendicular to principal axis of EPL because they re-orient to a direction that is less likely to get excited. This generates a birefringence in azobenzene material. Due to this birefringence, right-handed EPL propagates to the second layer accompanied by a clockwise tilt of principal axis. Azobenzene molecules on the second layer align in the direction perpendicular to principal axis of EPL similar to the first layer. This operation continuing and a right-handed helical structure is formed in the case of right-handed EPL irradiation. Thus, light induces a gradual rotation of the optical axis along the propagating light path, so the light pass through the film will be affected a right-handed rotation along the rotating optical axis. Theoretical calculation of the propagation of light in a helical structure was done by Nedelechev *et al.* [11]. Based on these facts, the

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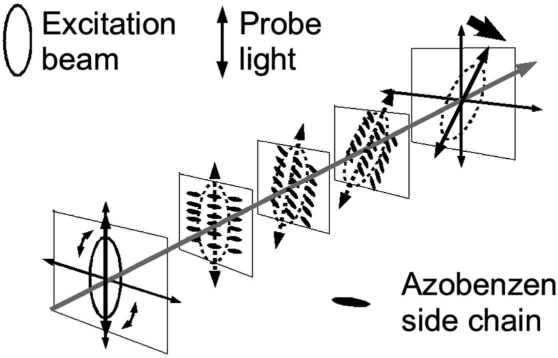

FIGURE 1 Formation of helical structure in achiral azobenzene materials. The arrows illustrate the rotation of principal axis of input elliptic beam along the light propagation.

formation of a helical structure is considered to be one of the explanation for photoinduced chirality in achiral azobenzene polymer.

In this paper, photoinduced chirality in three azobenzene materials has been investigated. Two of them are low-molecular weight azobenzens. These have molecular chirality due to binaphtyl-based atropisomers. Firstly, we have investigated whether this kind of molecular chirality affects to (or enhance) the photoinduced chirality or not. And remaining one of three samples is an achiral azobenzene copolymer that consists of cyanoazobenzene and the moiety with extended π-conjugation. This polymer has been developed to increase linear birefringence of the material. Since the linear birefringence get larger, the difference between the orthogonal component of incident electric field becomes large and it is easily conceived that a larger rotation can be generated. Using this large birefringent achiral polymer, photoinduced chirality has been investigated and dependence of optical rotation on intensity, wavelength and ellipticity of excitation beam have been examined.

EXPERIMENT

The chemical structures of azobenzene materials employed in this study are shown in Figure 2. Binaphtyl-based bisazobenzenes have been synthesized from S-(–)-1,1′-2-naphthol and R-(+)-1,1′-2-naphthol that have atropisomeric chirality. One is amorphous (BNAC) and the other is liquid crystalline material (BNAOC), but both gave amorphous films when we spin-coat onto the glass substrate from dichloromethane solutions at the ambient conditions. The copolymer consists

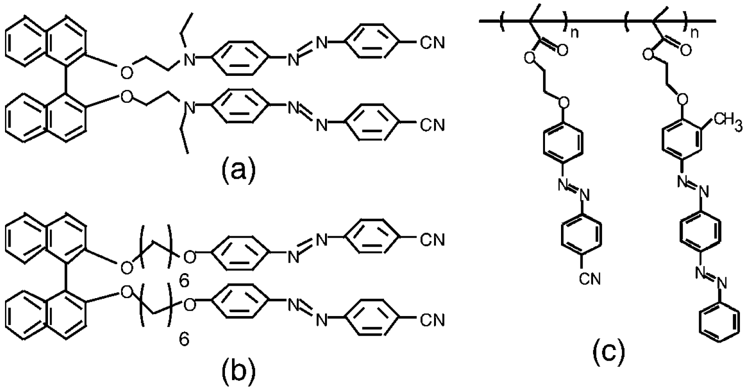

FIGURE 2 Molecular structures of (a) BNAC, (b) BNAOC, and (c) PCDY50.

of cyanoazobenzene and 4-[4-(phenylazo)phenylazo]-*o*-cresol at the molar ratio of 1:1 (PCDY50). This is soluble in common organic solvent such as chloroform, dichloromethane, THF and so on. Thin films of these azobenzenes were obtained from 5 wt% of dichloromethane solution by spin-coating technique at the conditions of 700 r.p.m for 30 sec. Amorphous thin films of about 1 μm-thick with good optical quality were obtained. From our preliminary experiments, it was pointed out that the optical quality of the film strongly affects to the absolute value of photoinduced rotation. Therefore, we have paid great attention to the spin coating procedure in order to obtain clear, homogeneous, smooth and non-scattering high quality thin film. Namely, the sample solution was filtered by membrane with 0.2 micron ϕ pore, and the substrate temperature was kept to approximately 25°C and the atmospheric gas exchanged by dried nitrogen in order to eliminate moisture.

In order to measure photoinduced chirality, we used Ar^+ laser as an excitation beam with 3 mm of diameter. The beam was irradiated to the sample films for 5 min at normal incidence. The light was adjusted to be left-handed EPL with desirable ellipticity whose principal axis was set to the vertical by a linear polarizer and a variable waveplate. The ellipticity change and azimuthal rotation of the light transmitted through the azobenzene was measured by a polarimeter, which can measure four Stokes parameters of the light simultaneously. He-Ne laser whose wavelength is out of the absorption band of the azobenzenes was also employed as the probe beam. The diameter of the He-Ne laser beam was 1 mm and small enough than that of excitation beam. The He-Ne laser beam was incident on the sample at small angle with respect to the Ar^+ laser beam.

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RESULTS AND DISCUSSION

Figure 3 shows the results on ellipticity change between excitation beam and transmitted Ar^+ beam. Although a slight difference was observed in BNAC, proportional relationships have been observed in general that means there were not significant change on the ellipticity in the transmission of Ar^+ laser beam. Next, photoinduced optical rotation was measured for each sample and confirmed that all of the samples exhibit photoinduced chirality. However, contrary to our expectation, the photoinduced chirality for BNAC and BNAOC was generated regardless of the initial molecular chirality. This result implies that the molecular chirality does not affect to (or enhance) the photoinduced chirality as far as in our low-molecular weight examples.

The observed optical rotation characteristics for each sample are shown in Figure 4 as a function of ellipticity of the excitation beam. Regarding BNAC and BNAOC, the similar tendency to the Nikolova's result [4] was observed even in non-polymeric low-molecular weight azobenzene materials. Namely, a convex curve and a sigmoidal curve were observed for BNAC and BNAOC, respectively, that corresponds to the feature of amorphous and liquid crystalline azobenzene polymer. Even more, though the PCDY50 copolymer is not liquid crystalline, it was observed a sigmoidal feature that is typical for liquid crystalline materials and found the absolute value is quite large. This result may be attributed to the anisotropic shape and the large birefringence of copolymer segment (4-[4-(phenylazo)phenylazo]-*o*-cresolyl moiety). Since we could observed very large photoinduced

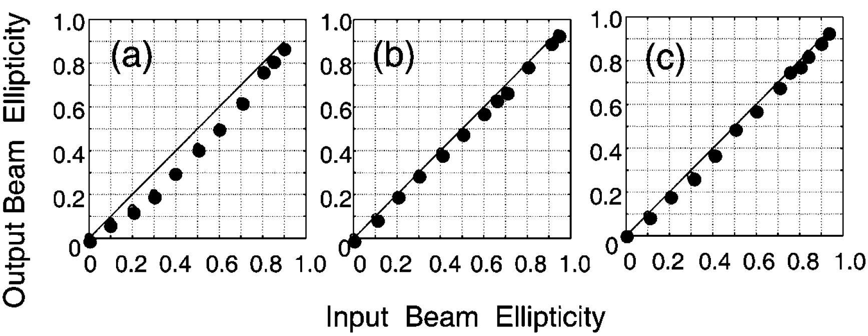

FIGURE 3 Ellipticity change between excitation Ar^+ beam (488 nm) and transmitted beam. (a)–(c) correspond to BNAC, BNAOC, and PCDY50, respectively. Irradiance ~800 mW/cm^2, irradiation time = 5 min.

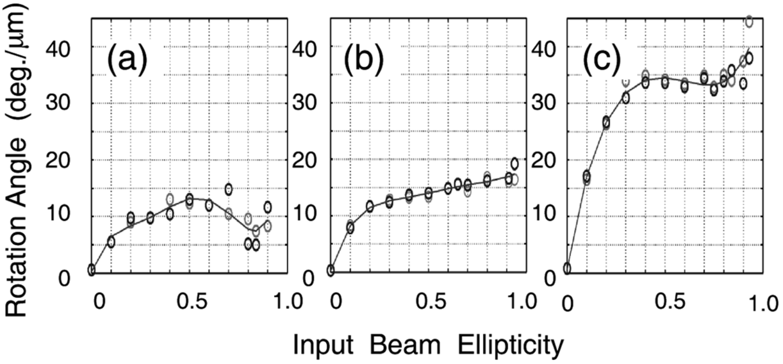

FIGURE 4 Relationship between optical rotation angle and ellipticity of the excitation Ar^+ beam (488 nm). (a), (b), and (c) correspond to BNAC, BNAOC and PCDY50, respectively. Irradiance ~800 mW/cm^2, irradiation time = 5 min.

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rotation in PCDY50, succeeding more detailed experiments were performed on this polymer.

Figure 5 shows the results of dependence on beam intensity and wavelength of the excitation beam observed in PCDY50. The ellipticity of excitation beam was fixed to −0.5 in this experiment. In the vertical axis of the figures, the data of observed rotation angle were normalized to correspond to the film with 1 μm thickness. As shown in the Figure 5(a), it was found that the practical rotation angle was

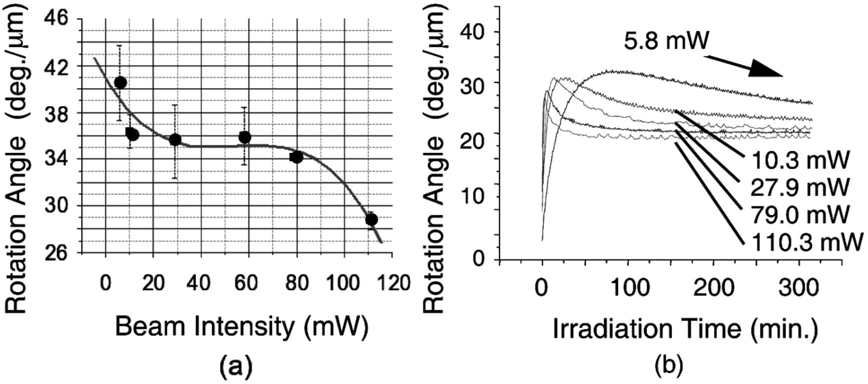

FIGURE 5 Dependence of rotation angle on irradiation beam intensity (a) and on irradiation time (b). Circles, bars, solid line in the figure (a) show averaged data of five-times experiment, error bar and polynominal curve fitting (order = 3), respectively.

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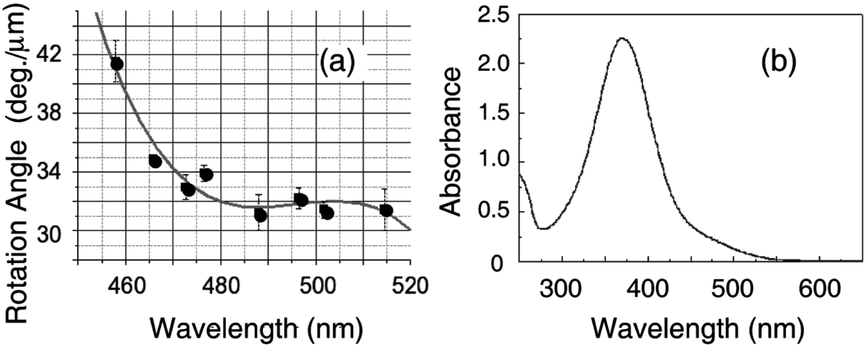

FIGURE 6 Wavelength dependence of rotation angle (a) and absorption spectrum of PCDY50 (b). Circles, bars, solid line in the figure (a) show averaged data of five-times experiment, error bar and polynominal curve fitting (order = 3), respectively.

increased with decreasing the intensity of excitation beam. However, as shown in Figure 5(b), the absolute value of optical rotation decayed gradually and not reached to the constant even if we wait for long time in case the beam intensity was lower than 30 mW. Therefore, the intensity of the excitation beam was fixed to 30 mW in the following experiment.

The results on wavelength dependence is shown in Figure 6. It was measured at eight different wavelengths within Ar^+ laser emission, i.e., 457.9, 465.8, 472.7, 476.5, 488.0, 496.5, 501.7, and 514.5 nm. Then, it was found that the value of rotation angle was increased with decreasing the wavelength of excitation beam. It is considered this feature is closely related to the absorption dispersion of PCDY50. (The absorption maximum locates at around 370 nm and a broad tail continues to 550 nm.)

As a result, the optimized condition for PCDY50 could be determined as 30 mW and 457.9 nm for the excitation beam as far as in our experimental apparatus. On this condition, we could get quite large rotatory power of 41 deg./μm compared to those previously reported so far. Such large rotatory power of the achiral azobenzene polymer strongly suggests that our initial concept to increase the absolute value by introducing large linear birefringence moiety was positively confirmed. Of course, this is not unique solution to increase the value of photoinduced rotatory power. It should be noticed that Pagès *et al.*, recently reported that a sample with even smaller linear birefringence than ours could exhibit large rotation angle comparable to ours [12].

So it is conceivable that the chemical modification not only in degree of linear birefringence but that taking into a consideration of liquid crystallinity is effective to develop the desirable material function.

Assuming that the photoinduced optical rotation originates in a formation of supramolecular helical structure of the azobenzene moieties in a long-range (this assumption is the same as Nikolova's interpretation [3,4]), the pitch of the helical structure (P) can be calculated by the following equation:

$$P = \frac{2\pi(1 - e_0^2)}{2e_0\delta} \tag{1}$$

where e_0 is input ellipticity of the excitation light and δ is an anisotropic phase difference, which is calculated by

$$\delta = 2\pi\frac{\theta}{360} \tag{2}$$

with total twist angle per unit thickness θ. According to these equations, θ was 41deg in our case then the pitch was estimated to be 8.78 μm.

Finally, we can show the results on photoinduced optical rotation of PCDY50 measured by using He-Ne laser. The sample has been previously irradiated by Ar^+ laser beam at the optimum condition to introduce photoinduced chirality into the film. The relationships between the ellipticity of input probe beam (633 nm) and the rotation angle of the transmitted beam are shown in Figure 7. The value of the vertical axes were normalized to that of the 1 μ-thick film. Figure 7 (a) and (b) are corresponds to the different elliptic condition of Ar^+ excitation beam, i.e., -0.5 and -0.2, respectively. As a result, extremely large photoinduced optical rotation (more than 60 deg./μm) could be achieved with our newly developed polymer at the optimized condition.

The solid circles and the open circles in the figure correspond to the data for the conditions that the input probe beam has the same azimuthal angle (lies in vertical axis) and the azimuthal angle with $\pi/2$ difference (in horizontal axis). Nedelchev *et al.*, have already reported [11] that they could explain the photoinduced optical rotation in achiral amorphous azobenzene by their analytical model. However, that was based on the assumption (or approximation) that the principal axis of the input probe beam does not change on passing through the sample film. As far as in our sample, this assumption was not valid so that we analyzed our data based on general ellipsometry [13] by means of solving a transformation matrix of the sample which exhibits photoinduced chirality after the light irradiation. (Details of the

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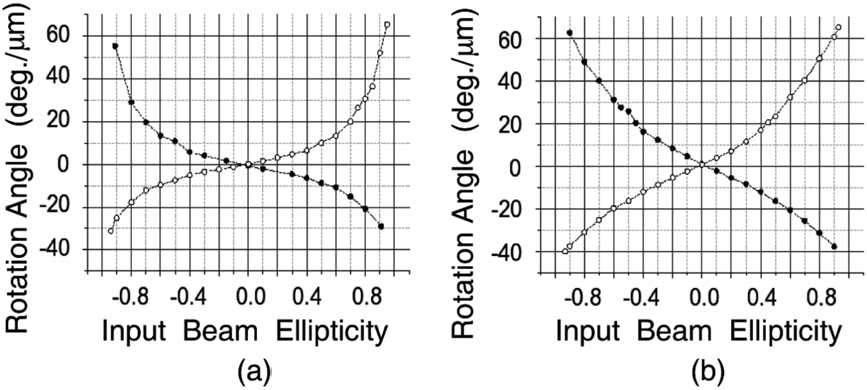

FIGURE 7 Relationship between the ellipticity of input probe beam and transmitted beam (633 nm). (a) and (b) are the results obtained for the beam with the ellipticity of −0.5 and −0.2, respectively. Solid and open circle show the results that in the case the probe light with the same azimuthal angle and with difference in azimuthal angle of $\pi/2$ to the excitation light, respectively.

theoretical procedure of our analytical model will be reported in elsewhere.) It was confirmed that the theoretical curves (solid lines) reproduced with the elements of transformation matrix for this polymer explained well about the experimental data.

CONCLUSION

The photoinduced chirality was observed in our azobenzene materials, even in the non-polymeric low-molecular weight materials. However, any relationship between molecular chirality and photoinduced chirality could not be observed in low-molecular weight azobenzenes that we have expected. On the other hand, significant photoinduced optical rotation has been observed in newly developed azobenzene copolymer having large linear birefringent moiety. The dependence of photoinduced optical rotation on intensity, wavelength and ellipticity of the excitation beam have been examined and the optimum conditions have been determined. At this optimum condition, quite large rotatory power of 41 deg./µm @ 458 nm for transmitting beam has been observed. The absolute value is fairly large by comparing to those previously reported so far. Thus, it was confirmed that the introduction of large linear birefringence moiety to the azopolymer is effective to increase the photoinduced optical rotatory power. It could be confirmed that our analytical method based on the conventional ellipsometry explains the photoinduced optical rotation occurs on

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achiral amorphous polymer very well. However, the mechanism of this phenomenon has not fully elucidated yet. There are another possibilities on the essential physical picture for the generation of photoinduced chirality in molecular level. Further study on this phenomenon is necessary for better understanding.

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