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A Supramolecular Chiroptical Switch Using an Amorphous Azobenzene Polymer**

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Supramolecular chirality has been optically induced in an achiral epoxy-based polymer containing photoresponsive azobenzene groups. The origin of this effect is the long-range helical arrangement of the azobenzenes, which extends through the entire thickness of the film. The helicity induced by the handedness of the laser can be reversibly switched by alternately exposing the film to a 488 nm laser with right- and left-handed elliptical polarization. The chiral properties of these films have been characterized by circular dichroism spectroscopy and optical rotation. After five switching cycles, the fatigue resistance is seen to depend on the absorption wavelength of the film, probably due to differences in the photoresponsive speed of the azobenzenes and the polymeric segments.

1. Introduction

The reversible photochemical isomerization of bistable organic molecules has been widely studied with the goal of producing novel molecular photonic devices, such as optical memory devices, displays, and switches.^[1] Chiral molecules are promising candidates for these applications because the different enantiomers, mirror-image stereoisomers, have the same energy and intrinsic interactions with light polarized in opposite directions.^[2–8] To produce a reversible chiroptical switch, chiral functionalities have been combined with photoisomerizable molecules such as diarylethene,^[2] fulgide,^[3] spiroindolino-pyran,^[4] and azobenzene.^[5] The switching component is the photoisomerizable molecule and not the chiral group, and therefore chiroptical switching can be categorized as diastereomeric switching operated by alternating irradiation at two different wavelengths.

To design photoswitchable chiral molecules, we make use of the classification of chirality shown in Figure 1. Three different types of chirality are depicted: configurational chirality, conformational chirality, and supramolecular chirality. Configura-

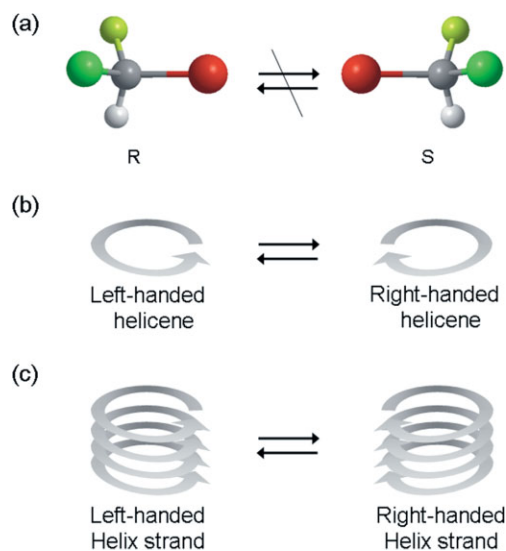


Figure 1. Schematic representation of chiroptical switching between two enantiomers possessing a) configurational chirality, b) conformational chirality, and c) supramolecular chirality.

tional chirality arises from the binding of different atoms (Fig. 1a). Isomerization between configurational enantiomers is difficult in practice due to the need to break bonds and form new bonds on the opposite side. For conformational enantiomers, isomerization can occur either by rotation or inversion (Fig. 1b). Feringa and co-workers have reported a novel conformational chiral unit consisting of overcrowded ethylene, which exhibits novel chiroptical switching behavior upon being alternately irradiated with right- and left-handed circularly polarized light (r-CPL and l-CPL, respectively).^[6] When these chiral molecules are incorporated into a liquid crystal or amorphous polymeric material, the molecular chirality influences the structure of the adjacent matrix molecules, thereby imparting chiral properties.^[7] In addition, the self-assembly of conformational chiral molecules can lead to long-range ordering of

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the conformational chirality; this phenomenon is called supramolecular chirality (Fig. 1c).^[8] A supramolecular chiral switch operated by irradiation with light of alternate handedness requires the presence of conformational chiral molecules undergoing polarization-sensitive photoisomerization in the matrix.^[6]

Azobenzene is a well-known polarization-sensitive photoisomerizable molecule.^[9] When a donor–acceptor-substituted azobenzene polymer is exposed to linearly polarized light (LPL) at the appropriate absorption wavelength, trans–cis–trans photoisomerization cycles occur continuously until the trans-isomers are located perpendicular to the polarization axis.^[10] This approach has been used to obtain photoinduced molecular alignment in various systems, such as for optical data storage^[11] and nonlinear optics.^[12] By selecting the polarization state, the direction of alignment can be controlled; moreover, the alignment can be erased by heating above the glass-transition temperature (T_g) or by irradiating with CPL. Nikolova and co-workers^[13] and Iftime et al.^[14] have recently reported that CPL can induce a helical orientation of azobenzenes inside an amorphous or liquid-crystalline azobenzene polymer film. Our group has previously reported that the photoinduced chirality of amorphous azobenzene polymers requires some amount of linear polarization in the CPL, which essentially means that elliptically polarized light (EPL) is required.^[15] Hore et al. have measured circular Bragg reflections from a liquid-crystalline azopolymer that exhibits photoinduced chiral alignment.^[16] Recently, a very large optical rotation has been reported for an amorphous azopolymer,^[17] and the influence of liquid-crystalline structures has been discussed.^[18]

In this work, we have investigated the details of photoinduced supramolecular chirality in ‘achiral’ and ‘amorphous’ azobenzene polymer films as a function of the handedness and ellipticity of light. In addition, we demonstrate chiroptical switching mediated by the reversible conversion of the helical sense of the supramolecular structures upon changing the handedness of the incident light. Fatigue resistance of the chiroptical switching behavior is discussed as a function of the absorption wavelength of the azobenzene polymer.

2. Results and Discussion

2.1. Photoinduced Supramolecular Chirality

The molecular structure of azobenzene consists of a N=N double bond bridging two aromatic benzenes; the corresponding absorption band is located in the UV-vis region of the electromagnetic spectrum. An achiral polymer, poly(disperse orange 3) (PDO3) has been used in this study because of the amorphous nature of its epoxy-based main chain. Figure 2 shows the chemical structure of this polymer. The weight-average molecular weight (M_w) of the polymer is 8791 g mol⁻¹, the polydispersity is 2.4, and the T_g is 110 °C.^[19] Figure 3 (broken line) shows the UV-vis absorption spectrum of the PDO3 film measured at room temperature without any irradiation. The maximum absorption wavelength (λ_{max}) is 477 nm and the absorbance is 1.9 for a film with a thickness of 0.45 μ m. The

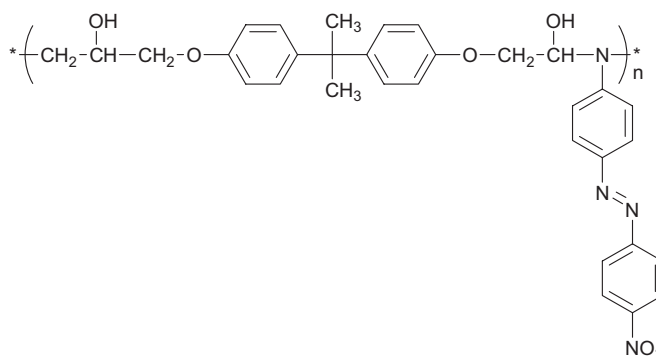


Figure 2. Chemical structure of achiral PDO3.

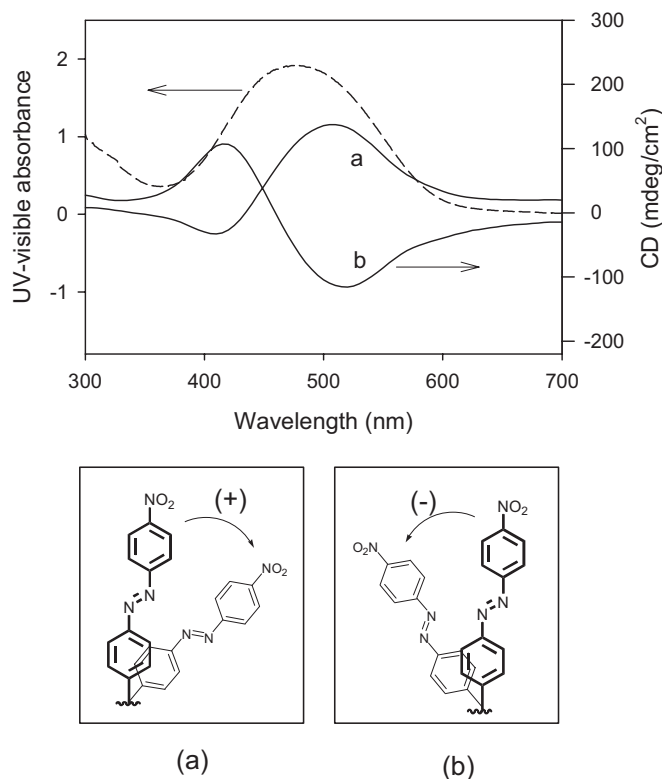


Figure 3. UV-vis spectrum of the unirradiated PDO3 film (λ_{max} = 477 nm) and circular dichroism (CD) spectra of PDO3 films irradiated with a) r-EPL and b) l-EPL for 10 min (ellipticity, ψ = 11°).

strong π – π^* and weak n – π^* transitions are overlapped. The trans isomer is thermodynamically more stable than the cis isomer, and thus dominates the absorption spectrum. The lifetime of *cis*-aminoazobenzene is on the order of microseconds, and therefore most of the cis isomer is thermally converted to the trans isomer at room temperature.^[20]

After irradiating the PDO3 films with right- and left-handed EPL (r-EPL and l-EPL) possessing an ellipticity ψ (see definition in Experimental and Fig. 4b) of 11° for 10 min, circular dichroism (CD) spectra have been acquired, as shown in Figure 3a and b. The definition of CD is the differential absorption for l-CPL with respect to r-CPL. Strong CD signals are ob-

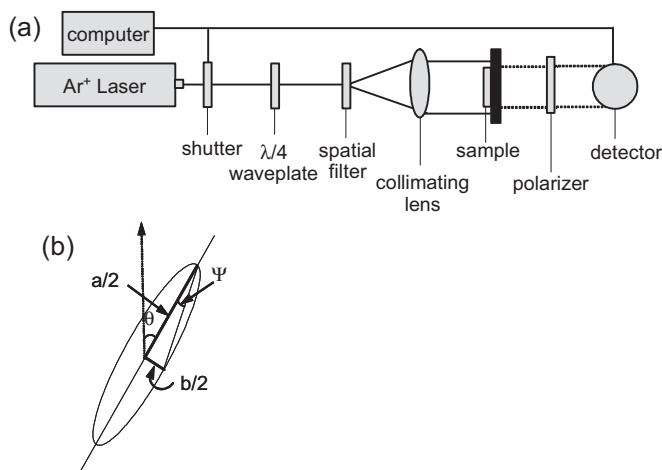


Figure 4. a) Optical setup for the induction of supramolecular chirality in the PDO3 film. b) Illustration of the definition of ψ and optical axis (θ).

served in the region corresponding to the absorption maximum of the *trans*-azobenzene. This indicates that the *trans*-azobenzene has an induced chiral orientation in the film. Individual azobenzene molecules do not contain a chiral functionality, and thus this induced chirality arises from a kind of conformational chirality of the azobenzene groups, specifically supramolecular chirality. From the literature, exciton coupling arises from intermolecular interactions between neighboring chromophores through their locally excited states.^[21] According to exciton coupling theory, when the relevant induced electric dipoles are oriented to form a positive (right-handed or clockwise) chiral array, the long-wavelength component of the associated exciton couplet can be expected to exhibit a positive Cotton effect.^[21,22] From the positive exciton coupling observed in Figure 3a, we can conclude that r-EPL induces a right-handed chiral orientation of the photochromic azobenzenes. The negative Cotton effect shown in Figure 3b implies that a left-handed chiral orientation is induced in the film by l-EPL. Thus, the handedness of the chiral orientation is governed by the handedness of light.

To investigate the effect of ψ on the photoinduction of supramolecular chirality, the PDO3 films have been exposed to l-EPL for 30 min while varying ψ in the range 0.59–40.05°. Figure 5 shows the corresponding CD spectra. The film exposed to $\psi = 0.59^\circ$ has a positive CD peak centered at 430 nm (Fig. 5a). When ψ is increased to 5.06°, negative exciton-coupled CD peaks appear at 420 and 530 nm (Fig. 5b). The positive peak (40.2 mdeg) has a higher intensity than the negative peak (–24.5 mdeg). At $\psi = 14.08^\circ$, the intensity of the positive peak decreases to 17.8 mdeg, and that of the negative peak increases to –39.9 mdeg (Fig. 5c). Upon further increasing ψ to 30.24°, the intensities of both peaks decrease to 6.5 and –20.3 mdeg, respectively (Fig. 5d). From the sign of the negative exciton-coupled peak, the azobenzenes appear to have a left-handed orientation. Finally, when the film is exposed to nearly CPL with $\psi = 40.05^\circ$, no CD peaks are detected in the

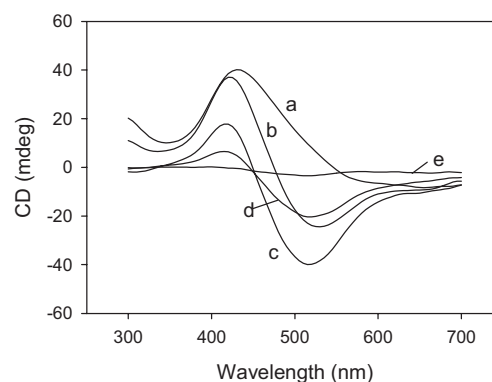


Figure 5. Induced CD spectra of PDO3 films irradiated by a left-handed Ar^+ laser beam for 30 min. The ellipticity is a) 0.59°, b) 5.06°, c) 14.08°, d) 30.24°, and e) 40.05°.

300–800 nm range (Fig. 5e). This indicates that CPL cannot induce a supramolecular chiral structure in the amorphous PDO3 film. This behavior is quite different from that of the liquid-crystalline azobenzene polymer. According to measurements made by Iftime et al., a CD spectrum is observed for a liquid-crystalline p4MAM (p4MAM: poly{4'–[(4-methacryloxy-alkyl)methylamino]–4-nitroazobenzene}) film after irradiation with CPL.^[14] The origin of this chirality may be the intrinsic molecular alignment of the liquid crystal, which enables the polarization state to change from CPL to EPL. The extent of this change depends on the film thickness, the extent of liquid crystallinity, and the phase. If a cholesteric liquid-crystal phase is used, chiroptical interactions between the intrinsic supramolecular chiral structure and the incident light may affect the photoinduced chirality. In the case of our amorphous film, the absence of a CD signal under CPL irradiation is reasonable due to the absence of a preferential direction of polarization and the initial lack of any intrinsic chirality in the randomly aligned polymeric structure. Based on the above discussion, we conclude that EPL, an intermediate state between linear polarization and circular polarization, is required for the photoinduction of supramolecular chirality in amorphous and achiral azobenzene polymer films.

The most essential property of a chiral material is the optical rotation of polarized light due to different interactions with r-CPL and l-CPL. By measuring the polarization states before and after the beam passes through the film, the direction and extent of the optical rotation can be examined. The measured intensity profiles of the laser beam are shown in Figure 6. When l-EPL with $\psi = 0.15^\circ$ and $\theta = 5^\circ$, close to LPL (Fig. 6a), is used as the incident beam, the transmitted beam has a smaller ψ and left-handed optical rotation (Fig. 6b). The values of $\Delta\psi$ and $\Delta\theta$ are -0.09° and -0.8° , respectively. When an incident laser beam with $\psi = 36.3^\circ$ is used (Fig. 6c), the transmitted beam exhibits a much smaller ψ and higher optical rotation as compared to the values shown in Figure 6a and b. The values of $\Delta\psi$ and $\Delta\theta$ are -6.8° and -4.5° , respectively (Fig. 6d). This indicates that EPL with a high degree of circular polarization can induce relatively more chirality in the film. However, when ψ is over

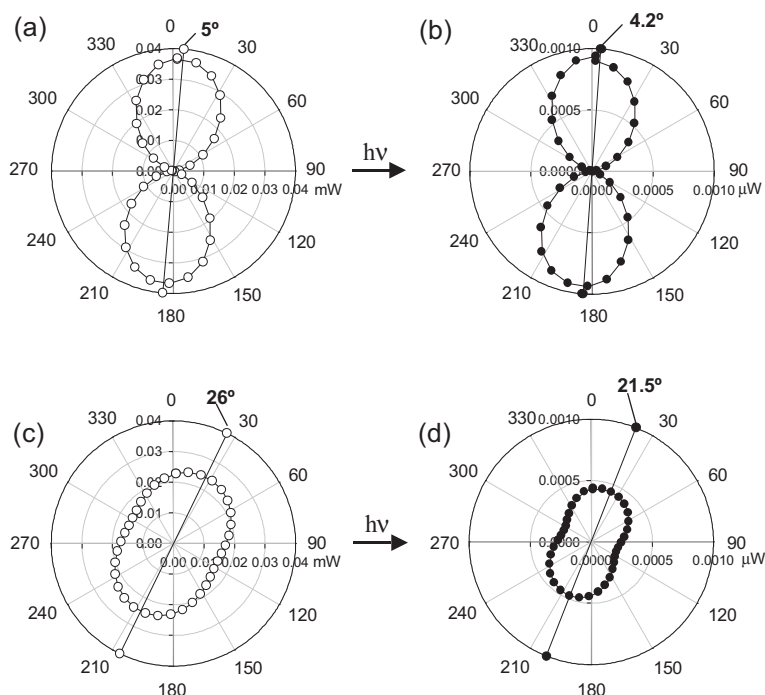


Figure 6. Intensity profiles of a,c) the incident l-EPL and b,d) the transmitted beam passing through the PDO3 film. (ψ, θ) is a) (0.15°, 5°), b) (0.06°, 4.2°), c) (36.3°, 26°), and d) (29.5°, 21.5°).

40°, the degree of optical rotation decreases, which is consistent with the result obtained from the CD spectra (Fig. 5). The l-EPL used in Figure 6a and c produces left-handed optical rotation. This confirms that the handedness of the supramolecular chiral structures is governed by the handedness of the incident laser beam. From the negative signal of the exciton coupling in the CD spectrum (Fig. 2), the left-handed supramolecular chiral film gives left-handed optical rotation. From the above results, the supramolecular chirality might originate from the stepwise rotation of the linearly oriented azobenzene groups perpendicular to the major axis of the EPL through the propagation of light.^[15] This is the reason why EPL is essential for photoinduced chirality: linear orientation is induced by a portion of the LPL and rotation of the orientation axis is induced by a part of the CPL.

2.2. Chiroptical Switching of the Helical Sense of the Supramolecular Structure

An important requirement for chiroptical switching is the reversible conversion of the helical sense of the supramolecular structure. In order to investigate the reversible generation of CD signals, the PDO3 film has been alternately irradiated with r- and l-EPL with $\psi = 14^\circ$. The switching cycle starts with l-EPL, designated as 1L. After measuring the CD spectrum, the film is exposed to r-EPL, designated as 2R. Five switching cycles are performed and the CD spectra are as shown in Figure 7a. The length of time for each switching sequence is

10 min. During five cycles, the helicity of the supramolecular structure is reversibly converted with respect to the handedness of the incident laser. The fatigue resistance of the CD intensity is observed to vary with the wavelength. Figure 7b shows the switching of the CD intensity at 410, 510, and 700 nm. After five cycles of switching, the CD intensity at 510 nm slightly decreases to 98 % of the 1L intensity. In contrast, after five switching cycles, the CD signal at 410 nm rapidly decreases to 37 % of the 1L intensity, which is indicative of very low fatigue resistance. This variation of the fatigue with the absorption wavelength in the same system is caused by the inhomogeneous conformations of azobenzenes in the entangled polymeric matrix. When the azobenzene groups helically arrange in response to the handedness of the incident light, the optically insensitive polymeric main chains should change their conformations to follow the azobenzenes. This may generate a local inhomogeneous perturbation force against the chiral orientation of the azobenzenes. A more detailed investigation is required to produce materials with highly reproducible properties.

Using a wavelength of 488 nm as the light source, the chiroptical property of the material is modulated over a much broader range of wavelengths than the absorption wavelength of the azobenzene chromophore. The CD intensity at 700 nm is plotted in Figure 7b. CD spectroscopy is not only sensitive to the local chirality of the chromophore unit, but also reflects the global chirality, i.e., the way the chiral units are arranged in space. For example, CD spectroscopy has been used to distinguish secondary structures (α helix, β sheet, β turn, and random coil) within polypeptide chains of proteins.^[22] In our current context, the band broadening of the CD peak may originate from a change in the macroscopic structure when the azobenzenes are chirally aligned.

The reversible helix inversion process has been monitored by measuring the CD spectrum as a function of the irradiation time. The PDO3 film is first irradiated with l-EPL ($\psi = 13^\circ$) for 10 min (1L, Fig. 8a), and then irradiated with r-EPL of the same ψ (2R, Fig. 8b–e). Helicity inversion from right- to left-handedness occurs within 10 s of irradiation with 2R. A strong exciton coupling is visible for up to 2 min after irradiation. The CD intensity gradually decreases after 30 s. From these results, it appears that the azobenzene molecules respond instantly to polarized light. The main chains of the polymer may slowly change from a distorted conformation to a more thermodynamically stable conformation. The supramolecular chirality is maintained for periods of several months.

3. Conclusions

Photoinduced supramolecular chiral structures are optically generated in amorphous PDO3 azopolymer films by treatment with EPL at a wavelength of 488 nm using an Ar⁺ laser. The

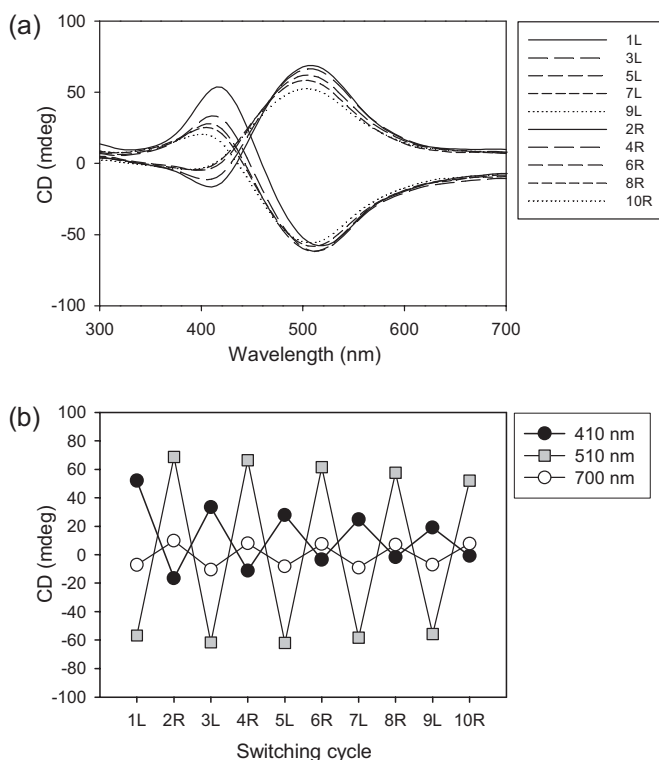


Figure 7. a) Chiroptical switching of the CD spectra by alternating irradiation with r- and l-EPL ($\psi = 14^\circ$). The switching cycle starts with l-EPL, designated as L1. After the CD measurement, the same film is irradiated with r-EPL, designated as R1. b) The intensity of the CD signal at 410, 510, and 700 nm.

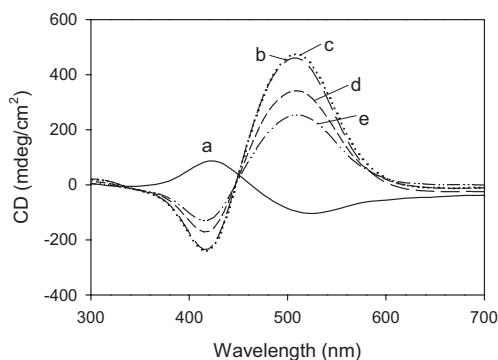


Figure 8. Induced CD spectrum of a PDO3 film irradiated with a) r-EPL for 10 min. After this irradiation, the film is irradiated with l-EPL ($\psi = 13^\circ$). The CD spectra are monitored as a function of the exposure time: b) 10 s, c) 30 s, d) 1 min, and e) 2 min.

helicity is controlled by the handedness, and the degree of helicity is controlled by the ellipticity of the incident light. By alternating irradiation with a right- and left-handed laser, the reversible switching of the helical sense of the supramolecular structure can be tuned in a range exceeding the absorption wavelength of the material. The fatigue resistance of the chiroptical switching varies with the absorption wavelength. This research may be useful for applications in photoswitchable functional materials and polymeric optical devices operated by polarization states at a single wavelength.

4. Experimental

4.1. Azobenzene Polymer

The chemical structure of PDO3 is shown in Fig. 2. PDO3 was synthesized by the reaction of bisphenol A diglycidyl ether (5.8 mmol, TCI) with disperse orange 3 (5.8 mmol, Aldrich). The polymerization reaction was carried out at 110°C for 24 h. After cooling, the mixture was dissolved in 50 mL tetrahydrofuran (THF) and added dropwise to 500 mL of methanol with stirring. The precipitate was filtered and dried in vacuum. The detailed synthetic procedures have been published previously [23]. A glass slide was used as the substrate for the polymer film. The slide was cleaned by sonication in a surfactant solution, acetone, and water. Optically transparent films were prepared by spin-casting a 10 wt % cyclohexanone solution of PDO3 onto the glass slides. The films were baked at 160°C to obtain $0.45\ \mu\text{m}$ thick films.

4.2. Optical Experiments

The optical setup for inducing supramolecular chirality is illustrated in Figure 4 [15]. The light source was an Ar⁺ laser (Coherent, Innova 305C) at 488 nm with an intensity of $100\ \text{mW cm}^{-2}$. The beam was expanded and collimated in order to obtain a homogeneous intensity of the laser over the entire exposed area. The irradiation time was varied between 10 and 30 min. The handedness and ellipticity (ψ) of the incident laser beams were controlled using a $\lambda/4$ waveplate. ψ is defined as the angle between the major and minor axes, as illustrated in Fig. 4b [21]. This value was calculated using the equation, $\psi = \arctan(b/a)$ (where a is the intensity along the major axis and b is the intensity along the minor axis). The polarization states were verified by using a polarizer with and without inserting the sample.

4.3. Characterization

The molecular weight of the polymer was determined by size exclusion chromatography (SEC) (Waters model 515) in THF solution and was calibrated against polystyrene standards. The T_g was measured by differential scanning calorimetry (DSC2100, TA Instruments) with a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen. The film thickness was measured by an α -step surface profiler. UV-vis spectra were recorded using a Perkin Elmer spectrometer (Lambda 12). The CD spectrum was measured using a CD spectrometer (JASCO720, Jasco Inc.). A piezoelectric modulator in the CD spectrometer alternated the phase of the analysis beam between r-CPL and l-CPL by oscillating in the horizontal direction with a frequency of 50 kHz. To prevent the thermal relaxation of CD signals, the CD spectra were carefully obtained in the dark exactly 10 min after the irradiation.

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- [1] a) *Molecular Switches* (Ed: B. L. Feringa), Wiley-VCH, Weinheim, Germany **2001**. b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685. c) Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717. d) G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.* **2000**, *100*, 1741. e) P. Belser, L. D. Cola, F. Hartl, V. Adamo, B. Bozic, Y. Chriqui, V. M. Iyer, R. T. F. Jukes, J. Kühni, M. Querol, S. Roma, N. Salluce, *Adv. Funct. Mater.* **2006**, *16*, 195.
- [2] T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **1997**, *119*, 6066.
- [3] S. Z. Janicki, G. B. Schuster, *J. Am. Chem. Soc.* **1995**, *117*, 8524.
- [4] L. Eggers, V. Buss, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 881.
- [5] a) M. Müller, R. Zentel, *Macromolecules* **1994**, *27*, 4404. b) S. Mayer, R. Zentel, *Macromol. Rapid Commun.* **2000**, *21*, 927. c) S. R. Lustig, G. J. Everlof, G. D. Jaycox, *Macromolecules* **2001**, *34*, 2364. d) P. Guo,

- L. Zhang, M. Liu, *Adv. Mater.* **2006**, *18*, 177. e) M. C. Carreño, I. García, M. Ribagorda, E. Merino, S. Pieraccini, G. P. Spada, *Org. Lett.* **2005**, *7*, 2869. f) S. Pieraccini, S. Masiero, G. P. Spada, G. Gottarelli, *Chem. Commun.* **2003**, 598. g) S. Pieraccini, G. Gottarelli, R. Labruto, S. Masiero, O. Pandoli, G. P. Spada, *Chem. Eur. J.* **2004**, *10*, 5632. h) R. A. Delden, T. Mecca, C. Rosini, B. L. Feringa, *Chem. Eur. J.* **2004**, *10*, 61. i) E. Yashima, J. Noguchi, Y. Okamoto, *Macromolecules* **1995**, *28*, 8368.
- [6] a) B. L. Feringa, R. A. Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789. b) N. P. M. Huck, W. F. Jager, B. Lange, B. L. Feringa, *Science* **1996**, *273*, 1686.
- [7] a) E. Yashima, K. Maeda, Y. Okamoto, *Nature* **1999**, *399*, 449. b) H. Nakashima, J. R. Koe, K. Torimitsu, M. Fujiki, *J. Am. Chem. Soc.* **2001**, *123*, 4847.
- [8] a) T. Verbiest, S. V. Elshocht, M. Kauranen, L. Helleman, J. Snauwaert, C. Nuckolls, T. J. Katz, A. Persoons, *Science* **1998**, *282*, 913. b) N. Higashi, T. Koga, N. Niwa, M. Niwa, *Chem. Commun.* **2000**, 361.
- [9] A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139.
- [10] a) T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.* **1984**, *23*, 4309. b) M. J. Kim, C. Chun, T. Nakayama, D. Y. Kim, *Jpn. J. Appl. Phys., Part 2* **2006**, *45*, L169.
- [11] S. Kawata, Y. Kawata, *Chem. Rev.* **2000**, *100*, 1777.
- [12] J. A. Delaire, K. Nakatani, *Chem. Rev.* **2000**, *100*, 1817.
- [13] a) L. Nikolova, T. Todorov, M. Ivanov, F. Andruzzi, S. Hvilsted, P. S. Ramanujam, *Opt. Mater.* **1997**, *8*, 255. b) I. Naydenova, L. Nikolova, P. S. Ramanujam, S. J. Hvilsted, *Opt. A: Pure Appl. Opt.* **1999**, *1*, 438. c) L. Nikolova, L. Nedelchev, T. Todorov, Tz. Petrova, N. Tomova, V. Dragostinova, P. S. Ramanujam, S. Hvilsted, *Appl. Phys. Lett.* **2000**, *77*, 657.
- [14] G. Iftime, F. L. Labarthe, A. Natansohn, P. Rochon, *J. Am. Chem. Soc.* **2000**, *122*, 12646.
- [15] a) M. J. Kim, B. G. Shin, J. J. Kim, D. Y. Kim, *J. Am. Chem. Soc.* **2002**, *124*, 3504. b) M. J. Kim, J. Kumar, D. Y. Kim, *Adv. Mater.* **2003**, *15*, 2005.
- [16] D. Hore, Y. Wu, A. Natansohn, P. Rochon, *J. Appl. Phys.* **2003**, *94*, 2162.
- [17] H. Sumimura, T. Fukuda, J. Y. Kim, D. Barada, M. Itoh, T. Yatagai, *Jpn. J. Appl. Phys., Part 1* **2006**, *45*, 451.
- [18] R. M. Tejedor, M. Millaruelo, L. Oriol, J. L. Serrano, R. Alcalá, F. J. Rodríguez, B. Villacampa, *J. Mater. Chem.* **2006**, *16*, 1674.
- [19] M. J. Kim, E. M. Seo, D. Vak, D. Y. Kim, *Chem. Mater.* **2003**, *15*, 4021.
- [20] H. Rau, in *Photoreactive Organic Thin Films* (Eds: Z. Sekkat, W. Knoll), Academic, Amsterdam **2002**, Ch. 1.
- [21] *Circular Dichroism: Principles and Applications* (Eds: N. Berova, K. Nakanishi, R. W. Woody), Wiley-VCH, New York **2000**, Ch. 1, 12.
- [22] *Analytical Applications of Circular Dichroism* (Eds: N. Purdie, H. G. Brittain), Elsevier Science, Oxford **1994**, Chs. 5, 6.
- [23] X. Wang, J. Kumar, S. K. Tripathy, L. Li, J.-I. Chen, S. Marturankul, *Macromolecules* **1997**, *30*, 219.