Photochemical Control of the Macrostructure of Cholesteric Liquid Crystals by Means of Photoisomerization of Chiral Azobenzene Molecules

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Chiral azobenzene compounds were prepared. A cholesteric phase was induced by mixing each azobenzene compound in a host nematic liquid crystal. A twisting power of the chiral azobenzene compounds was dependent on the distance between an azobenzene moiety and chiral moiety. The twisting power of the chiral azobenzene compounds was decreased by ultraviolet irradiation to cause trans to cis photoisomerization of the azobenzene compounds. The effects of the trans−cis photoisomerization on the phase structures of cholesteric liquid crystals, those that were prepared by mixing chiral azobenzene molecules and non-photochromic chiral molecules, will be discussed.

Introduction

Many studies have been reported on polymers and liquid crystalline (LC) polymers containing azobenzene molecules in the field of optical devices such as optical memory, optical display, and optical switching.[1−9] Azobenzene compounds are well-known for showing photochromism between trans isomers with a rodlike shape and cis isomers with a bent shape. The trans isomers dissolve in a host liquid crystal (LC) without extreme disorganization effect on the molecular orientation of the host LC, while the cis isomers disorganize that of the host LC.[10] This is explained as the similarity of the molecular shapes between the isomers and the host LC molecules. Thus, the optical information can be detected as changes in the optical properties such as birefringence before and after photoisomerization of the azobenzene molecules in the LC systems.

On the other hand, the cholesteric LCs are typically characterized by a helical structure, resulting in a selective reflection of light with wavelength proportional to the pitch length. Therefore, if we will be able to modulate the helical pitch photochemically, the cholesteric LC materials will be promising for various optical devices such as photoaddressable display, photocontrollable light reflector, memory, and so on. In addition, it is well-known that the helical structure can be induced by adding nonmesogenic chiral molecules in nonchiral LCs. Thus, there are some studies for the photochemical control of cholesteric pitch by photoisomerization of chiral photochromic compounds in low molecular weight LC and polymer LC systems.[11−15] It was also described that the trans−cis photoisomerization of a guest azobenzene compound without a chiral moiety caused a change in the cholesteric pitch of a host cholesteric LC.[16,17] We also reported the photochemical switching of a compensated nematic LC, which was prepared by adding a chiral azobenzene compound and a nonphotochromic chiral compound with an opposite twisting ability in a host low molecular weight LC.[18] In this preliminary work, a photochemically reversible switching between the compensated nematic and the cholesteric phases was achieved by means of the reversible trans−cis photoisomerization of the chiral azobenzene compound.

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(1) Cole, H. J.; Simon, R. *Polymer* **1985**, *26*, 1801.

(2) Eich, M.; Wendroff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 59.

(3) Ikeda, T.; Horiuchi, D. B. Karanjit, D. B.; Kurihara, Tazuke, S. *Macromolecules* **1990**, *23*, 36.

(4) (a) Ikeda, T.; Tsutsumi, O. *Science* **1995,** *268*, 1873. (b) Shisido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N. *J. Am. Chem. Soc.* **1997**, *101*, 22806.

(5) (a) Akiyama, H.; Momose, M.; Ichimura, K.; Yamamura, S. *Macromolecules* **1995**, *28*, 288. (b) Han, M.; Morino, S.; Ichimura, K. *Macromolecules* **2000**, *33*, 6360.

(6) (a) Natansohn, A.; Rochon, P.; Pezolet, Audet, P.; Brown, D.; To, S. *Macromolecules* **1994**, *27*, 2580. (b) Labarthet, F. L.; Freiberg, S.; Pellerin, C.; Pezolet, M.; Natansohn, A.; Rochon, P. *Macromolecules* **2000**, *33*, 6815.

(7) (a) Corvazier, L.; Zhao, Y. *Macromolecules* **1999**, *32*, 3195. (b) Zhao, Y.; Chenard, Y. *Macromolecules* **2000**, *33*, 5891.

(8) Stumpe, J.; Fischer, T.; Rutloh, M.; Rosenhauer, R.; Meier, J. G. *Proc. SPIE* **1999**, *3800*, 150.

(9) Kurihara, S.; Sakamoto, A.; Nonaka, T. *Macromolecules* **1998**, *31*, 4648.

(10) Onogi, Y.; Hayashi, T.; Mizushima, Y.; Yamamoto, M. *Nippon Kagaku Kaishi* **1990**, *8*, 815.

(11) Janichi, S. Z.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 8524.

(12) (a) Feringa, B. L.; Huck, NP. M.; van Doren, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 9929. (b) Feringa, B. L.; Huck, NP. M.; Schoevaars, A. M. *Adv. Mater.* **1996**, *8*, 681.

(13) (a) Yokoyama, Y.; Sagisaka, T. *Chem. Lett.* **1997**, 687. (b) Sagisaka, T.; Yokoyama, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 191.

(14) (a) Brehmer, M.; Lub, J.; van de Witte, P. *Adv. Mater.* **1998**, *10*, 1438. (b) van de Witte, P.; Brehmer, M.; Lub, J. *J. Mater. Chem.* **1999**, *9*, 2087.

(15) (a) Bobrovsky, A. Y.; Boiko, N. I.; Shivaev, V. P. *Liq. Cryst.* **1998**, *25*, 679. (b) Bobrovsky, A. Y.; Boiko, N. I.; Shivaev, V. P.; Springer, J. *Adv. Mater.* **2000**, *12*, 1180.

(16) Sackmann, E. *J. Am. Chem. Soc.* **1971**, *93*, 7088.

(17) Lee, H.-K.; Doi, K.; Harada, H.; Tsutsumi, O.; Kanazawa, A.; Shiona, T.; Ikeda, T. *J. Phys. Chem.* **2000**, *104*, 7023.

(18) Kurihara, S.; Nomiyama, S.; Nonaka, T. *Chem. Mater.* **2000**, *12*, 9.

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This paper describes further investigation of the effects of the photoisomerization of the chiral azobenzene compounds as well as cooperation effect of the chiral azobenzene and nonphotochromic chiral compounds on the helical structure of the induced cholesteric LCs.

Experimental Section

Materials. Azobenzene compounds (**Azo-1**, **Azo-2**, and **Azo-3)** were synthesized by the diazo-coupling reaction and following esterification with chiral alcohols in the presence of *p*-toluenesulfonic acid in benzene. Purification was carried out by column chromatography (silica gel, $CHCl_3$ as an eluent) and recrystallization from ethanol. A low molecular weight host LC **(E44)** and chiral dopants **(R811** and **S811)** were purchased from Merck Co. Ltd. **R811** and **S811** are enantiomers. Cyanine dye, **NK-529,** was purchased from Nippon Kankoh Shikiso Kenkyusho Co., Ltd. Other chemicals are commercially available and used without further purification.

Data for **Azo-l**: ^{1}H NMR ($CDCl_3$): δ (ppm) 0.7−1.8 (m, 27H, methylene), 4.0 (t, 2H, $ArOCH_2$−), 5.0 (m, 1H, COOCH−), 7.0−8.2 (m, 8H, aromatic). IR (KBr) (cm^{-1}): 1720 ($\nu_{C=O}$). Anal. Calcd. for $C_{27}H_{38}N_2O_3$: C, 73.9; H, 8.73; N, 6.39. Found: C, 73.8; H, 8.63; N, 6.63. Data for **Azo-2:** ^{1}H NMR ($CDCl_3$): δ (ppm) 0.8−2.0 (m, 20H, methylene), 4.0 (t, 2H, $ArOCH_2$−), 4.2 (m, 2H, $COOCH_2$−), 7.0−8.2 (m, 8H, aromatic). IR (KBr) (cm^{-1}): 1720 ($\nu_{C=O}$). Anal. Calcd. for $C_{24}H_{32}N_2O_3$: C, 72.7; H, 8.13; N, 7.06. Found: C, 72.7; H, 8.13; N, 7.04. Data for **Azo-3**: ^{1}H NMR ($CDCl_3$): δ (ppm) 0.8−1.8 (m, 20H, methylene), 2.7 (t, 2H, $PhCH_2$−), 4.0 (m, 2H, $COOCH_2$−), 4.7 (s, 2H, OCH_2-COO), 7.0−8.0 (m, 8H, aromatic). IR (KBr) (cm^{-1}): 1750 ($\nu_{C=O}$). Anal. Calcd. for $C_{25}H_{34}N_2O_3$: C, 73.1; H, 8.34; N, 6.82. Found: C, 72.7; H, 8.13; N, 6.75.

Characterization. Samples were prepared by adding each azobenzene compound and/or a nonphotochromic chiral compound in **E44**. Thermal phase transition behavior of the samples was examined by means of differential scanning calorimetry (DSC, Seiko I&G SSC-5020) and polarizing optical microscopic observation (POM, Olympus BHSP polarizing optical microscope; Mettler FP80 and FP82 hot stage and controller). Helical pitch was determined by the Cano's method.[19]

Photoresponsive Properties. Samples were injected into a homogeneous glass cell, a homeotropic glass cell with a 5-μm cell gap (EHC Co., Ltd.), or two glass plates without special treatment. After photoirradiation, a change in the helical structure was explored by means of POM observation and by monitoring of transmitted light intensity through the samples with a diode laser (Suruga Seiki Co.; 670 nm; 5 mW). The photoirradiation was carried out by a 500-W high-pressure Hg lamp (Ushio) equipped with a glass filter, UTVAF-35 (Sigma Koki Co.), for ultraviolet (UV) irradiation (366 nm) or SCF-42L (Sigma Koki Co.) for visible irradiation (436 nm).

Circular dichroic spectra of cholesteric LCs with or without **NK-529** were measured on a spectropolarimeter (J-725, JASCO).

Results and Discussion

Properties of Chiral Azobenzenes. Figure 1 shows the azobenzene compounds synthesized and their thermotropic properties. **Azo-1** exhibits a cholesteric phase between 33 and 43 °C only by cooling, and no LC phase was observed for others. A cholesteric phase could be induced by mixing each chiral azobenzene compound in **E44.** The phase diagram of binary mixtures of **Azo-1** and **E44** up to 20 wt % of **Azo-1** is shown in Figure 2. All mixtures show only the cholesteric phase from room temperature, and the phase transition temperature from the cholesteric phase to an isotropic phase decreases slightly with an increase in the amount of **Azo-1**. Other azobenzenes, **Azo-2** and **Azo-3,** gave similar phase transition behavior to that for the binary mixtures consisting of **Azo-1** and **E44.**

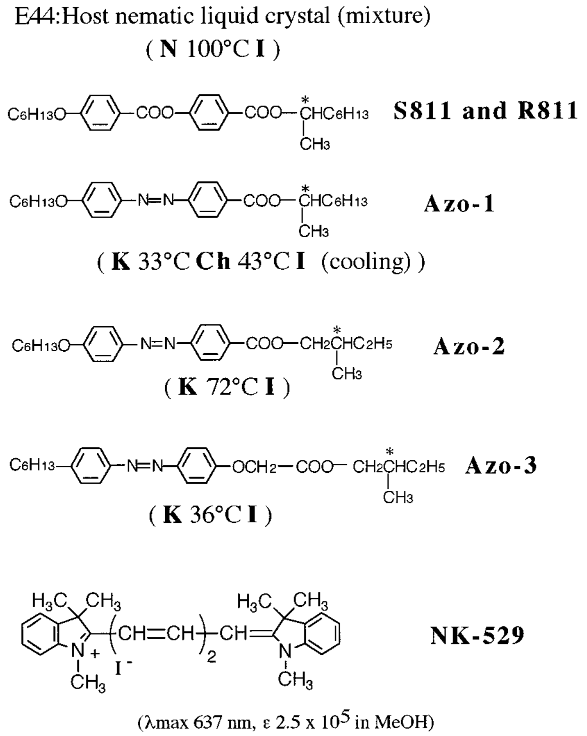

Figure 1. Structures and phase transition temperatures of compounds used in this study.

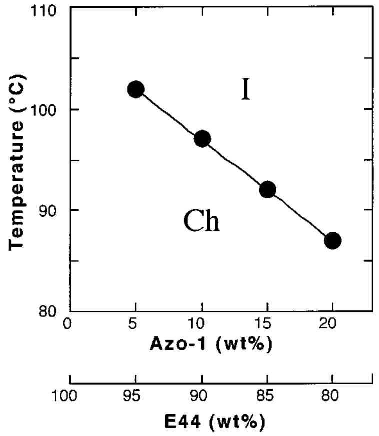

Figure 2. Thermotropic properties of mixtures of **E44** and **Azo-1**.

In such a binary system consisting of a nonchiral host nematic LC and a chiral compound, the reciprocal of the helical pitch (1/*p*) is known to increase linearly with the concentration (*c*) of the chiral compound at lower *c*.[19,20] The twisting power of a chiral compound can be defined as the slope of the 1/*p* versus *c*. Figure 3 shows changes in the 1/*p* of the induced cholesteric LCs as a function of the amounts of the chiral azobenzene (*c*) in **E44** at 40 °C. The helical pitch was determined by Cano's method.[19] The 1/*p* increases almost linearly with the increase of *c*. The twisting power of the chiral azoben-

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(19) Escher, C. B.; Fliegner, D.; Heppke, G.; Molsen, H. *Ber. Bunsen-Ges. Phys. Chem.* **1991,** *95,* 1233.

(20) Finkelmann, H.; Stegmeyer, H. Z. *Naturforsch* **1973,** *28a,* 799.

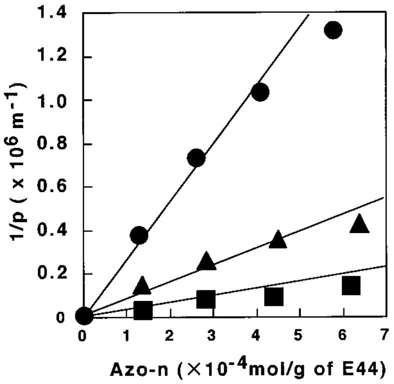

Figure 3. Changes in reciprocal pitch (1/*p*) of the induced cholesteric phases as a function of the concentration of chiral compounds in a gram of **E44** at 30 °C. ●, **Azo-1**; ▲, **Azo-2**; ■, **Azo-3**.

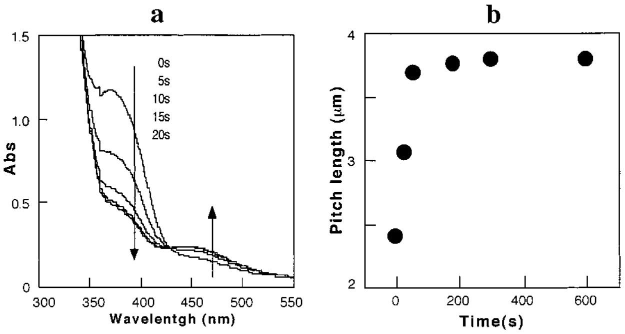

Figure 4. Changes in absorption spectra (a) of the mixture consisting of **E44** and **Azo-1** (95/5 in wt %) in the dark (solid line) and after UV irradiation for 3 min (dotted line) and in the helical pitch (b). UV irradiation was carried out by a 500-W Hg lamp equipped with a cut filter (intensity, 0.5 W/cm^2).

zenes was in the order of **Azo-1** > **Azo-2** > **Azo-3**: 23 × 10^2 for **Azo-1** , 6.6 × 10^2 for **Azo-2**, and 2.6 × 10^2 (μm^{-1}·mol^{-1}·g-**E44**) for **Azo-3** at 40 °C, respectively. It has been reported that the more similar in structure a chiral dopant becomes to that of the host LC molecules, the larger the twisting power becomes.[21,22] Only **Azo-1** showed cholesteric phase upon cooling. The highest twisting power for **Azo-1** among the three chiral azobenzenes may be related to factors such as similarity in the molecular shape and its liquid crystallinity. Thus, **Azo-1** was used as the photochromic chiral dopant in this study because the cholesteric phase can be induced by doping small amounts of **Azo-1** compared to others, and **Azo-1** has a similar structure to that of the nonphotochromic chiral dopant used in this study, **R811** and **S811**.

Effect of Photoisomerization on the Twisting Ability. UV irradiation caused both a decrease in absorbance around 370 nm and an increase in absorbance around 450 nm, indicating trans–cis photoisomerization of **Azo-1** (Figure 4a). Reverse cis–trans isomerization was also brought about by thermal means or by visible light irradiation. The helical pitch was decreased by UV irradiation, as can be seen in Figure 4b. The result indicates that the twisting power of the trans isomers of **Azo-1** is larger than that of cis isomers. The trans isomer has a rod shape, whereas the cis one has a bent shape. **E44** is a mixture of several rod-shaped compounds. The photochemical change in the twisting power of **Azo-1** may be related to the similarity in the molecular shape between cis-**Azo-1**, trans-**Azo-1**, and host LC molecules.

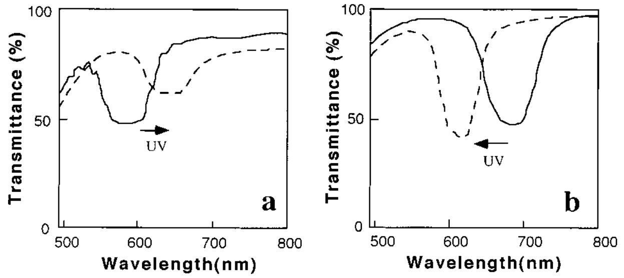

Figure 5. Transmittance spectra of the mixtures consisting of **E44**, **Azo-1**, and chiral dopants before (solid lines) and after (dotted lines) UV irradiation at T_{red} of 0.95. (a) **E44/Azo-1/S811** = 67:17:16 in wt % at 530 °C; (b) **E44/Azo-1/R811** = 67:5:28 in wt % at 42 °C.

R811 and **S811** are reported to give right- and left-handed helices, respectively.[19] Therefore, the helical sense induced with **Azo-1** can be identified by measuring change in the helical pitch of the induced cholesteric LC containing **R811** or **S811** before and after doping of **Azo-1.** In this way, **Azo-1** was found to induce a left-handed helix.

There are two combinations for **R811**, **S811**, and **Azo-1**: One is a combination of **S811** and **Azo-1** and the other contains **R811** instead of **S811.** The first combination is simple because both **S811** and **Azo-1** give the left-handed helices (case 1). On the other hand, the second combination provides more three LC phases depending on the relative intensity of twisting powers due to **R811** and **Azo-1** because they induce helices with an opposite helical sense. First is $\mathrm{TTP}_{\mathrm{R811}} > \mathrm{TTP}_{\mathrm{Azo-1}}$ (a right-handed helix, case 2), the second case is $\mathrm{TTP}_{\mathrm{R811}} = \mathrm{TTP}_{\mathrm{Azo-1}}$ (a compensated nematic phase, case 3), and the third case is $\mathrm{TTP}_{\mathrm{R811}} < \mathrm{TTP}_{\mathrm{Azo-1}}$ (a left-handed helix, case 4), where $\mathrm{TTP}_{\mathrm{R811}}$ and $\mathrm{TTP}_{\mathrm{Azo-1}}$ represent each total twisting power corresponding to **R811** or **Azo-1.**

Photochemical Control of Selective Reflection (Cases 1 and 2). Figure 5a shows transmittance spectra of cholesteric LC, which is composed of **E44**, **S811**, and **Azo-1** (67:16:17 in wt %) before and after UV irradiation (case 1). The selective reflection was shifted to a longer wavelength by UV irradiation. On the other hand, the effect of UV irradiation on the transmittance for case 2 is shown in Figure 5b, where the cholesteric LC is consisting of **E44**, **R811**, and **Azo-1** (67:28:5 wt %). Contrary to the result for case 1, the shift of the selective reflection to a shorter wavelength was brought about by UV irradiation. The results demonstrate that the helical pitch can be controlled in both directions to longer and shorter wavelengths by the combination of the chiral photochromic and nonphotochromic molecules and the same photochromic reaction in the systems.

Photochemical Phase Transition between Nematic and Twisted Nematic Phases (Case 3). As described above, the compensated nematic phase can be obtained adjusting $\mathrm{TTP}_{\mathrm{R811}}$ and $\mathrm{TTP}_{\mathrm{Azo-1}}$ to be equal. The mixture containing **E44, R811**, and **Azo-1** (80:8.6:

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[21] Udayakumar, B. S.; Schuster, G. B. *J. Org. Chem.* **1993,** *58,* 4165.

[22] Gottarelli, G.; Samori, B.; Fuganti, C.; Graselli, C. *J. Am. Chem. Soc.* **1981**, *103,* 471.

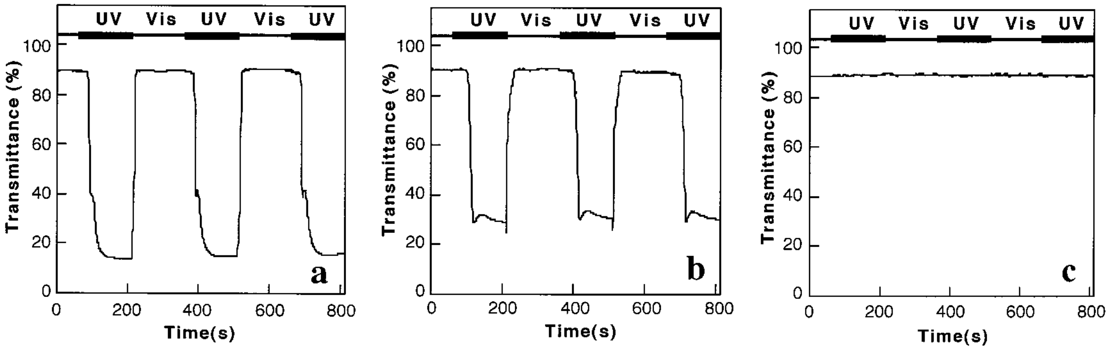

Figure 6. Changes in transmittance of **E44/R811/Azo-1** mixtures in a homeotropic glass cell by UV and visible light irradiation at 30 °C. (a) **E44/R811/Azo-1** = 80:8.6:11.4 in wt %; (b) **E44/R811/Azo-1** = 85:6.5:8.5 in wt %; (c) **E44/R811/Azo-1** = 90:4.3:5.7 in wt %.

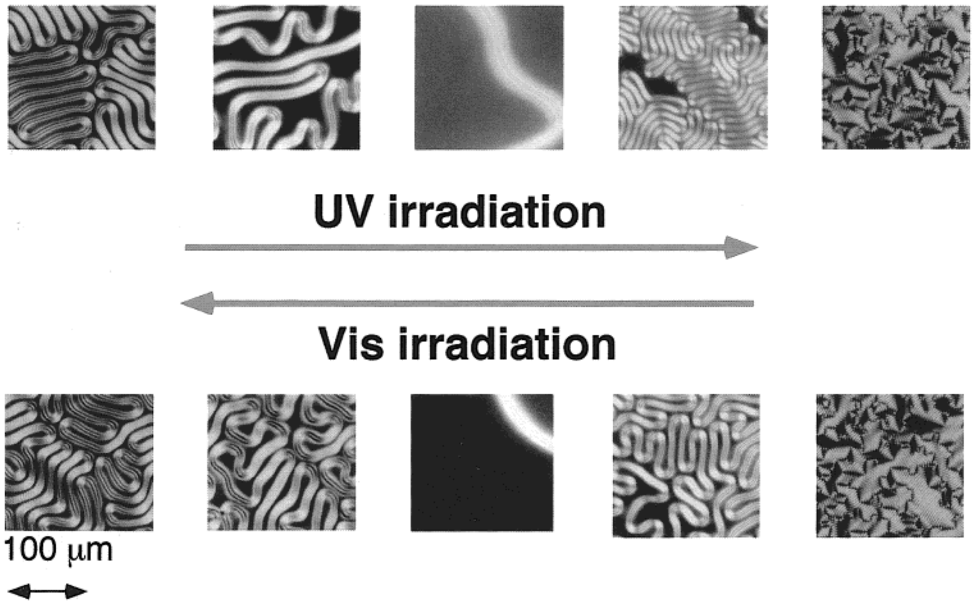

Figure 7. Polarized optical micrographs of the **E44/R811/Azo-1** (80:8.4 11.6 wt %) mixture upon ultraviolet and visible light irradiation. The LC mixture was in a 5-μm glass cell without any alignment treatment. The micrographs were taken at 30 °C upon irradiation.

11.4 wt %) was assigned as the compensated nematic phase from the Shlieren texture in the temperature range below 73 °C. The Shlieren texture was transformed into fingerprint texture by UV irradiation at 30 °C. The photochemical decrease in the twisting power of **Azo-1** broke the compensated state; consequently, the helical structure appeared. The Shlieren texture appeared again by visible light irradiation. Namely, the reversible photochemical phase transition between the compensated nematic phase and the cholesteric phase can be achieved by the reversible photoisomerization of **Azo-1**. In addition, the photochemically induced cholesteric phase scattered light strongly compared to the compensated nematic phase.

It is worthwhile here to explore the light scattering behavior of the compensated nematic LC containing **Azo-1** and **R811**. Figure 6 shows changes in the transmittance of the **E44/R811/Azo-1** cholesteric LCs in a 5-μm homeotropic glass cell by UV and visible light irradiation at 30 °C. The transmittance was measured by using a probe light from a diode laser (670 nm) without a polarizer, and the reference was a transmitted light intensity without the sample. Before UV irradiation, the transmittance was kept at about 90%. The transmittance was decreased by UV irradiation and restored by subsequent visible light irradiation. It is presumed that the molecules in the compensated nematic phase align macroscopically normal to the surface of the homeotropic cell. The twisting ability induced photochemically forces the homeotropic molecular alignment to transform into a focal conic structure, resulting in the light scattering. Therefore, the reversible change between transparent and light scattering states can be induced by UV and visible light irradiation. The light scattering intensity was found to depend on the amount of chiral compounds in the cholesteric LCs. Three compensated nematic LCs given in Figure 6 contain different total amounts of chiral compounds, while the ratio of **R811** to **Azo-1** was maintained constant. Little change in the transmittance was observed for the **E44/R811/Azo-1** cholesteric LC (90:4.3:5.7 wt %). The lower the total amount of chiral compounds, the less twisting power produced photochemically. On the other hand, the light scattering of the **E44/R811/Azo-1** cholesteric LC (75:10.8:14.2 wt %) was smaller than that of the **E44/R811/Azo-1** cholesteric LC (80:8.6:11.4 wt %). In addition, the light scattering intensity was decreased at temperatures near the isotropization temperature. Pho-

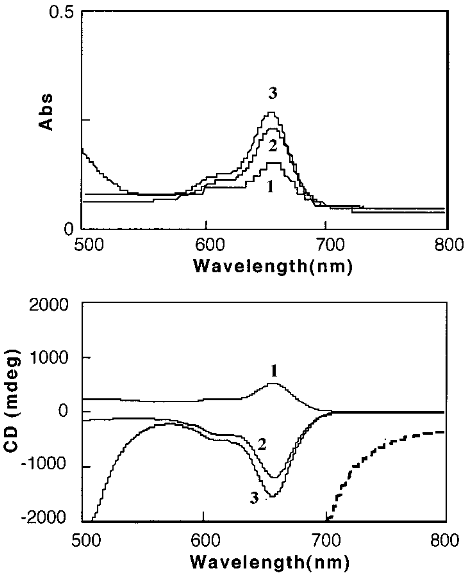

Figure 8. Absorption spectra and induced circular dichroic spectra of **NK-529** (curves 1−3) in cholesteric liquid crystals and circular dichroism of the **E44/R811** (67:28 wt %) mixture (dotted line) in a 5-μm homogeneous glass cell at 30 °C. **1**, **NK-529** (0.1 wt %) in the **E44/R811** (95:5 wt %) mixture; **2**, **NK-529** (0.1 wt %) in the **E44/S811** (95:5 wt %) mixture; **3**, **NK-529** (0.1 wt %) in the **E44/Azo-1** (95:5 wt %) mixture.

tochemical phase transition to the isotropic phase may be attributed to the decrease in the light scattering by elevating irradiation temperature or increasing the amount of chiral compounds.

Photochemical Reversible Helical Inversion of Induced Cholesteric LCs (Case 4). An excess doping **Azo-1** into the compensated nematic LCs breaks the compensated state and consequently produces a left-handed helix. Figure 7 shows an effect of UV and visible light irradiation on the texture of the **E44/R811/Azo-1** mixture (80:8.4:11.6 wt %). A fingerprint texture before UV irradiation indicates that the mixture exists in the helical structure. The helical pitch was estimated to be a few tens of micrometers based on the fingerprint texture. The helical pitch increased and became infinite by UV irradiation, indicating transformation into a nematic phase. Then, the fingerprint texture appeared again by further UV irradiation. The reversal in the texture was caused by successive visible light irradiation.

To explore the photochemical change in the helical structure, circular dichroism (CD) was measured. It is known that achiral molecules do not show CD. However, one can observe CD for molecular assemblies that are composed of chiral and achiral molecules. This is called induced circular dichroism (ICD). Figure 8 shows absorption spectra and ICD of cyanine dye **NK-529** in the cholesteric LCs. The CD of the **E44/R811** cholesteric LC (67:28 wt %) is also given in Figure 8 (dotted line). The **E44/R811** cholesteric LC shows the selective reflection around 550 nm. The negative CD of the **E44/R811** cholesteric LC may arise from the selective reflection, and helical sense is assigned to the right from the negative CD sign.

Contrary to the CD of the **E44/R811** cholesteric LC, the ICD of **NK-529** in the **E44/R811** cholesteric LC (95:5 wt %) was positive. Saeva and Wysocki have reported a similar result for the ICD spectrum of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline **(MBBA)** in host cholesteric LCs consisting of cholesteryl chloride and cholesteryl nonanoate.[23] They described that the ICD sign of **MBBA** was opposite that of the CD corresponding to the selective reflection of the host cholesteric LCs and presumed that **MBBA** molecules preferred to stack in an opposing helical structure to that of the host cholesteric LCs. We cannot explain satisfactorily the difference in the sign between the ICD of **NK-529** and CD of the selective reflection. But it is likely that **NK-529** aligns in a left-handed helix in the **E44/R811** cholesteric LC, and the positive ICD of **NK-529** refers to the right helix of the host cholesteric LCs. On the other hand, the ICD of **NK-529** in the **E44/S811** and the **E44/Azo-1** cholesteric LCs exhibited a negative sign, indicating the right-handed helices for the host **E44/S811** and the **E44/Azo-1** cholesteric LCs.

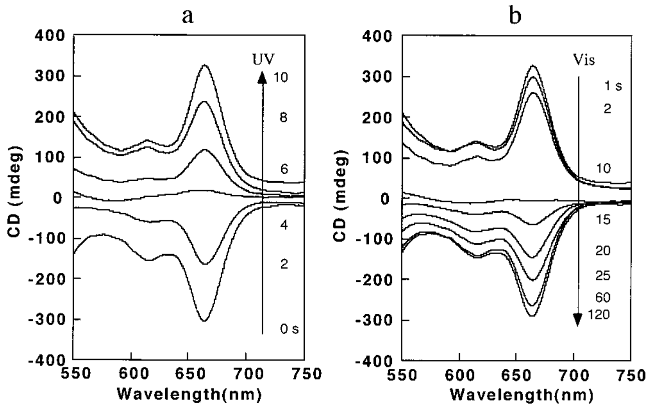

Figure 9. Change in induced circular dichroic spectra of **NK-529** (0.1 wt %) in the **E44/R811/Azo-1** (85:6:9 wt %) cholesteric LC in the homogeneous glass cell by UV (a) and visible light (b) irradiation.

Changes in the ICD spectra of **NK-529** in the **E44/R811/Azo-1** cholesteric LC (85:6:9 wt %) in a 5-μm homogeneous glass cell by UV and visible light irradiation are shown in Figure 9. This cholesteric LC was also found to show the reversible helical inversion via the nematic phase photochemically confirmed by POM observation. **NK-529** was doped in the **E44/R811/Azo-1** cholesteric LC at 0.1 wt %, and the spectra were measured at 30 °C. Before irradiation, the cholesteric LC was found to be in the left-handed helix from the negative ICD sign of **NK-529**. Further UV irradiation changed the ICD from negative to positive, indicating transformation from the left-handed helix into the right-handed one. Successive visible light irradiation caused the reverse helix.

Conclusion

The twisting power of trans-chiral azobenzene molecules is larger than that of cis-chiral azobenzene molecules. The combination of the chiral azobenzene and nonphotochromic chiral compounds provides fundamental aspects for photochemical control of the helical structure such as the photochemical control of the helical pitch in any direction to longer or shorter, photochemical phase transition between the compen-

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[23] Seava, F. D.; Wysocki, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 5928.

sated nematic and the cholesteric phases, and photochemical inversion of the helical structure. In particular, the reversible change in the transparency was achieved by the photochemical phase transition between the compensated nematic and the cholesteric phases. This result demonstrates that the liquid crystalline materials would be useful for applications such as all optically tunable display without the use of polarizers and automatically tunable coatings for sun protection.

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