A Light Induced Change in Cholesteric Pitch by Photoracemization of a Chiral Pyrenyl Sulfoxide

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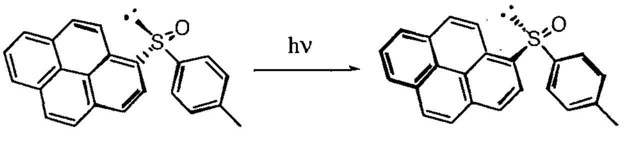
A cholesteric phase of 4'-pentyl-4-biphenyl carbonitrile (5CB) doped with (R)-(+)-1-pyrenyl-4-tolyl sulfoxide (**1**) was observed. Changes in a cholesteric pitch, p, in the liquid crystalline phase was induced by photoracemization and agreed with a theoretical line. A helical twisting power, β_M, of **1** in 5CB was obtained to be -1.1 μm^{-1} M^{-1}. Anisotropy factor, g, of **1** in acetonitrile was determined to be 2.1 × 10^{-3} at 375 nm and 2.9 × 10^{-3} at 302 nm.

Recently, in order to apply to a light switch or an optical memory device, a light control of a liquid crystal with the photochromic molecules has been studied.[1-4] Although a light switch or an optical memory with photochromic molecules alone in polymer matrices has been studied for long years, there is a problem of the destructive read-out due to a read-out process using a change in absorption of photochromic molecules.[5,6] However, in the case of the light control of the liquid crystal, since a change can be detected by the change in a polarization of light at a longer wavelength than that of absorption, a problem of the destructive read-out can be resolved.

The light control of a liquid crystal using photochromic molecules can be divided in those using azo-benzene derivatives,[1,2] or those changing a helical structure or a chirality of the molecules.[3,4] In order to induce a change in an order structure of the liquid crystal, it is necessary to induce a change in a dipole, a chirality, or a helix sense of molecules by a photochemical reaction. Recently, Feringa *et. al.*[3] reported the light control of a liquid crystal with irradiation of circularly polarized light to a helical molecule in a liquid crystalline sample which changes its chirality by photoinversion reaction. However, a change in a liquid crystalline phase by photoinversion reaction of chiral molecules has not been studied quantitatively. In this study, we use sulfoxide as a simpler chiral molecule and present a change in cholesteric pitch by photoinversion reaction quantitatively as a function of light intensity, quantum yields, *etc.*

We have paid attention to photoinversion reaction of a chiral sulfoxide. We prepared (R)-(+)-1-pyrenyl 4-tolyl sulfoxide (**1**), obtained quantum yields of its photoinversion in solution and in polymer matrices, and confirmed that the reaction proceeds in polymer matrices in the same efficiency at room temperature as that in solution.[7] From the fluorescence measurements and MO calculations of several sulfoxides that have several sizes of aromatic rings, excited states of diaryl sulfoxides were discussed. It was found that photoinversion occurs during a change in electronic states from the n–σ* states to the ground state.[8]



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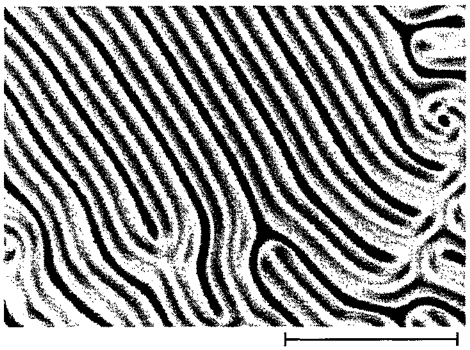

Figure 1. Cholesteric fingerprint texture of 5CB doped with 1 wt% of **1**.

Generally, a change in an optical rotation of a solution or a polymer sample is very small. However, in the case of a liquid crystal, detection of a change in a chirality is much enhanced because of the occurrence of a change in the order structure of the whole liquid crystalline phase by the cooperativity. Here we report the first observation of a change in a cholesteric pitch of the liquid crystal induced by photoracemization of a sulfoxide.

As a sample, a nematic liquid crystal 4'-pentyl-4-biphenyl carbonitrile (5CB) doped with **1** was used (concentrations are 0.3, 0.5, 0.7, 1.0 and 1.5 wt%). The synthesis of **1** was reported before.[7] In order to observe the change in a cholesteric pitch during photoracemization, a cell was prepared with quartz plates coupled with dimethyloctadecyl-3-trimethoxylsilylpropyl-ammonium chloride (Shin-etsu silicon) on surfaces and polyethylene film spacer (thickness 12 μm). A finger-print texture was observed with a polarized light microscopy, (Figure 1) and the cholesteric pitch, p, was measured at 27 °C. A helix sense was obtained by the Grandjean-Cano method,[9] with a lens (circular rubbing) and a quartz plate (parallel rubbing) after coating with polyimide.

When the nematic liquid crystal is doped with a low concentration of chiral dopant, a cholesteric pitch p is inversely proportional to the concentration, C, and expressed as follows,[10]

$$p = 1 / (\beta_M C\gamma) \qquad (1)$$

where β_M is the helical twisting power of chiral dopant and γ is an enantiomer excess.

A helical twisting power, β_M, for **1** in 5CB was determined to be -1.1 μm^{-1} M^{-1}. This value is much smaller than that of molecules which have a rigid and helical structure such as binaphthalene derivatives.[10]

A cell filled with 5CB doped with **1** was irradiated at 365 nm with a 250 W high pressure mercury lamp with an interference filter (KL-36) and a cut filter (UV-25). A change in a cholesteric pitch during irradiation was measured until a homogeneity of the fingerprint texture was lost. Finally, a cholesteric phase changed to a nematic phase almost completely after enough irradiation.

The enantiomer excess, γ, is expressed as follows,

$$\gamma = \{C_R(t) - C_S(t)\} / C_0 \qquad (2)$$

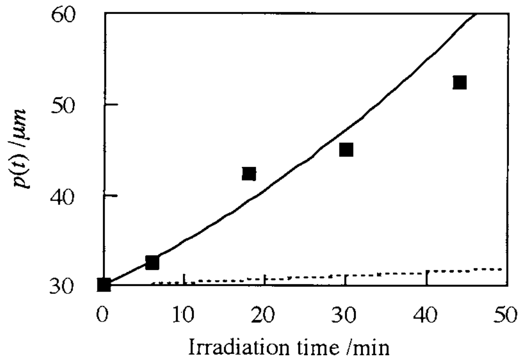

Figure 2. Changes in cholesteric pitch, *p*(*t*), of 5CB doped with 1 wt% of **1** during photoracemization of **1**. A solid curve and a dotted curve are a predicted curve calculated for changes due to photoinversion and photolysis (solid curve) and that due to photolysis only (dotted curve), respectively. Light intensity measured at 440 nm with an interference filter (KL-44) and a cut filter (L-39) is 120 μW.

where $C_R(t)$ and $C_S(t)$ are the concentration of sulfoxide of R configuration and S configuration, respectively. C_0 is the initial concentration. $C_R(t)$ - $C_S(t)$ is obtained by integrating reaction rates as described before.[8] Eq 3 is derived from eq 1, eq 2 and $C_R(t)$ - $C_S(t)$,

$$p(t) = p_0 exp\{I_0(1 - 10^{-OD})(2\Phi_{inv} + \Phi_{dec}) \times 10^3 t/(C_0 l)\} \quad (3)$$

where I_0 is the number of irradiated photons per unit time and unit cross section, l is the thickness of the system, Φ_{inv} and Φ_{dec} are the quantum yield of photoinversion and photolysis, respectively, OD is the optical density, and t is the time.

The value of cholesteric pitch, $p(t)$, at time, t, can be predicted from eq 3, by using the values of I_0, C_0, OD obtained from UV measurement, Φ_{inv} = 0.024 and Φ_{dec} = 0.0044 in acetonitrile,[7] and l = 12 μm from the thickness of the spacer. Light intensity, I_0, at an irradiated wavelength was calculated from transmittance of filter, wavelength distribution of mercury lamp intensity, sensitivity of the optical powermeter, and measured light intensity at 440 nm, as described previously.[7]

Changes in $p(t)$ during light irradiation and a predicted curve from eq 3 are shown in Figure 2. In the case of Figure 2, $p(t)$ changed from 30 μm to 52.5 μm during light irradiation. The experimental changes in $p(t)$ are in good accord with the predicted curve. In order to know if an initial concentration of **1** influences the range of a change in $p(t)$, several samples with initial concentrations varying from 0.3 wt% to 1.5 wt% were prepared as shown in Table 1. Although fingerprint texture was not observed in sample **1a**, the other samples showed texture and were irradiated. The longest pitch lengths, p_1, measured at time, t_1, before the disappearance of homogeneity of texture are listed in Table 1.

In Table 1, although there might be a tendency that p_1 becomes small for the samples with relatively high initial concentrations, it is roughly estimated that the homogeneity of the fingerprint texture is collapsed in the range of pitch between 50 μm and 65 μm. This result was compared to that of another chiral molecule which however does not undergo photoracemization, (S)-(-)-1,1'-bi-2-naphthol (**2**), in 5CB. The β_M was measured to be +2.8 μm^{-1}M^{-1}, and the largest observed pitch was 42.5 μm for 0.25 wt% sample. For the sample with 0.2 wt% of **2**, a pitch was not observed, while its calculated hypothetical pitch is 53.1 μm. In these 5CB samples the largest pitch which we could observe in a homogeneous fingerprint texture did not change drastically by changing the kind of chiral dopants.

Table 1. Initial concentration of **1** in 5CB, initial pitch lengths, p_0, the longest pitch lengths observed in a homogeneous fingerprint texture, p_1, at irradiation time t_1

Sample	Initial concentration /wt%	p_0 /μm	p_1 /μm	t_1 /min
1a	0.3			
1b	0.5	57.5	65.0	3
1c	0.7	50	62.5	8
1d	1.0	30	52.5	44
1e	1.5	25	42.5	40

In order to estimate the possibility of control of a liquid crystal by circularly polarized light, we determined the anisotropy factors of pyrenyl tolyl sulfoxide, g, from its UV spectra and CD spectra in acetonitrile (maximum values are 2.1 × 10^{-3} at 375 nm and 2.9 × 10^{-3} at 302 nm). These small values of g factors are characteristics of absorption of the π–π* transition,[11] and are in the same order of magnitudes as those for the helical molecule of Feringa *et. al.*.[3] Since the value of $C_R(t)$ - $C_S(t)$ in the photostationary-state is equal to $C_0 g$ / 2 for the irradiation of circularly polarized light,[11] the pitch for the sample doped with 20 wt% of **1** was estimated to be 1.4 × 10^3 μm, if it were observed. In order to obtain the pitch length of 50 μm after irradiation of circularly polarized light, the molecules which have β_M larger than 31 μm^{-1}M^{-1} and the same value of g as **1** are needed. We propose to fix rotational conformation of aromatic rings or to introduce long alkyl chains at both ends of a chiral dopant for a design of a molecule having larger β_M.

In this letter, we first reported a change in cholesteric pitch induced by photoracemization. Experimental results with a chiral pyrenyl sulfoxide agreed well with a calculated line predicted from the values of I_0, Φ_{inv}, and Φ_{dec}. In case of application to photo-optical switching of liquid crystals by circularly polarized light, molecules which show larger β_M and less photolysis should be preferably used.

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