Photochemical Modulation of Bragg-Reflection Wavelengths in Cholesteric Liquid Crystals Containing a Chiral Azobenzene

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ABSTRACT

Photochemical modulation of Bragg-reflection wavelengths based on isomerization of an azobenzene (Azo) and subsequent change in reflectance was investigated in cholesteric liquid crystals (ChLCs) which reflect light in visible wavelength region. Irradiation at 366 nm, which causes an efficient transcis isomerization of Azo, led to change in reflected color of ChLCs toward shorter wavelengths with a concomitant lowering of phase transition. Reversible change in color was induced all-optically by alternate irradiation at effective wavelengths for reversible isomerization of Azo. A considerable variation in reflectance was also observed when the photoinduced change in color was measured by a probe light with the same handedness as the ChLCs. The spectral position of selective light reflection in the initial states played an important role to produce a normal-mode and a reverse-mode switching in photoinduced modulation of reflectance of the ChLCs with respect to the probe light.

가시광을 선택적으로 반사하는 광 응답성 코레스테릭 액정을 조제하고, 그 선택적 반사파장의 광화학적 변조를 시도함으로서 포토닉스(Photonices) 재료로서의 가능성을 검토했다. 고유의 선택 반사파장의 변조는 아조벤젠 유도체의 트란스(trans) · 시스(cis)간의 광이성화에 의해 상전이 온도와 칼라의 변화와 함께 가역적으로 제어되어질 수 있었다.

또한, 선택 반사파장의 변화에 수반되는 반사율의 변화는 코레스테릭 액정과 검출광의 광학적 성

질에 의해 크게 좌우되어 지고, 반사율의 가역적인 스위칭에 있었서는 검출광에 대한 코레스테릭 액
정의 초기 반사파장의 위치는 상반된 스위칭 모드(normal and reverse modes)를 산출하기에 매우
중요한 역할을 담당했다.

1. INTRODUCTION

Chemical switching materials, whose optical properties can be changed selectively and reversibly by light, have considerable potential for use in photonics.[1][5] Especially, liquid crystals (LCs) are one of the most convenient materials to modulate optical properties because they possess a large anisotropy in optical and dielectric properties, which are controllable by change in alignment of the molecules with external stimulus such as heat, electric and electromagnetic (light) fields.[6][13]

On the other hand, cholesteric LCs (ChLCs), in which rod-like-shaped molecules are arranged in layers, are unique color-producing materials among LCs of the several types.[14][16] It is well known that ChLCs are produced by some optically active organic compounds, or by mixing optically active compounds with ordinary nematic (N) LCs.[17][19] The helical structure of ChLCs shows constructive-interference effects that lead to spectrally selective light reflections by which color emerges if the pitch of the cholesteric helix coincides with the wavelength of visible light.[20,21] Such unique optical properties have been modulated thermally, electrically or photochemically in several optical applications.[22][30] Furthermore, the cholesteric systems would be attractive for the optical switching materials with high-performance ability because the optical effect is distinguishable visibly and does not require the use of polarizers, which is very effective in preventing the loss of optical efficiency.

We have already reported several attempts to provide LCs with photoresponsive properties and have performed photonic control of light by means of photoisomerization of azobenzenes.[31][34] The azobenzene derivatives are very effective to control LCs by light because the geometrical change by photoisomerization could yield a concomitant change in chemical and physical properties not only in the azobenzene itself but in the macroenvironments around it. Such photonic control has been mainly applied in N phase by means of transmission-, reflection- and light-scattering modes.[2,4,35][38]

In this study, we prepared chiral NLC systems (i.e. cholesteric LC systems) which can reflect selectively visible light, and investigated all-optical switching behaviors between selective wavelengths with special reference to the change in reflectance by means of the

systems containing an azobenzene derivative as a photochromic guest molecule.

2. EXPERIMENT

2.1. Materials

A commercially available mixture of several NLCs which were substituted cyanobiphenyls, E48 (Merck Japan Ltd.) was used as a host LC without further purification. This host shows an N phase between -19 and 89 °C. Chemical structures of a chiral dopant and an azobenzene used in this study are shown in Figure 1. A chiral agent, 1-4(4-hexyloxybenzoyloxy)-benzoic acid-2-octyl ester (Merck Japan Ltd.) which induces a left-handed helical structure, was dissolved in the host NLC to produce a cholesteric phase. The azobenzene derivative (Azo) was synthesized and was used as a photoresponsive molecule.39
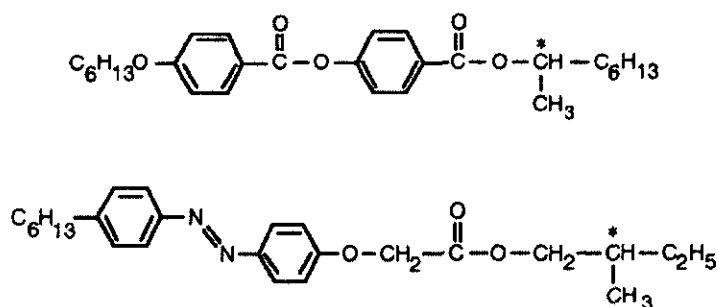

Figure 1. Chemical structure of chiral dopant(S811) and

photochromic molecule(Azo) used in this study

2.2. Sample Preparation

Two cholesteric samples (ChLC-1 & ChLC-2) were prepared from these homogeneous mixtures, which the concentration ratio of the chiral dopant to the host NLC was varied to produce selective light reflection at different wavelengths in visible region. The ratios in ChLC-1 and ChLC-2 were 28 and 25 wt%, respectively, and Azo was fixed at 6 wt% in

both samples. Each mixture was introduced into glass cells with a gap of 5 ㎛ by capillary action. Planar-oriented cholesteric samples were obtained in the substrates having uniaxially rubbed polyimide layers on their inner surfaces.

2.3. Optical Evaluation

Spectral characteristics in the light reflection of ChLCs were evaluated by using a UV/Vis spectrophotometer (JASCO V-550). Photoinduced behavior in reflectance was estimated by using an experimental setup shown in Figure 2. Lights at 366 and >420 nm, which were isolated with proper glass filters from a 500 W high-pressure mercury lamp, were used as pumping lights to induce isomerization of Azo. Optical behavior on of the samples was followed by measuring intensity of a probe light (HeNe laser, 633 nm) reflected on the samples with a photodiode. The probe light was polarized circularly by a wave retarder (ĕ/4) to detect efficiently the selective reflection property of the samples. The phase transition temperature from a cholesteric to an isotropic phase (TChI) was defined as the temperature at which anisotropic texture of ChLCs disappeared entirely in a polarizing microscope (Olympus BH-2) with a pair of crossed polarizers.
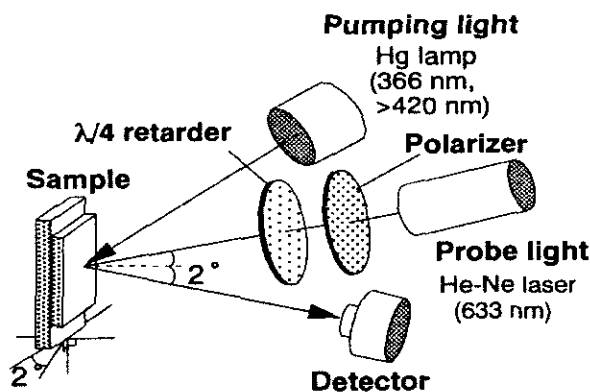

Figure 2. Schematic representation of an experimental setup.

3. RESULTS AND DISSCUSSION

3.1. Thermal Behavior of Reflected Wavelength

Thermal sensitivity of the selective light reflection in ChLC-2 shown in Figure 3. ChLC-2 appeared red at room temperature, which indicates a maximum of selective reflection (ëmax) at a long wavelength (710 nm). When temperature increased to 45 ºC, ëmax shifted to shorter wavelength region until it reached 580 nm (curve C), where the sample appeared yellowish green. A further increase in temperature led to decrease in intensity of the reflection light rather than the change in color. This indicates that phase transition from a cholesteric to an isotropic phase began to proceed thermally. Finally, the colored reflection light vanished completely at TChI, 54 ºC, and ChLC-2 became a transparent state of non-color. Therefore, the thermal behavior in the chiral N induced by S811 would be characterized by dual processes: shift of the selective light reflection to shorter wavelength which implies compression of pitch in the cholesteric helix and the following process for extinction of the reflected color by phase transition, which leads to disappearance of the helical pitch. Similar thermal behavior could also be observed in ChLC-1.
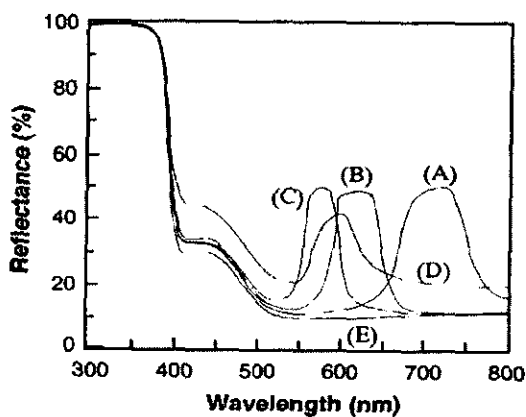

Figure 3. Thermally induced change in selective reflection
in ChLC-2: (A), r.t; (B), 32 ºC; (C), 45 ºC; (D), 50 ºC;
(E), 54 ºC.

3.2. Isomerization of Azobenzene

Figure 4 shows absorption spectra of Azo in a solution. Azo shows a high intensity * band around 350 nm where absorption of the trans-form is centered and a low intensity n∂* band in the visible region (curve A).

Upon irradiation at 366 nm, the absorbance at around 350 nm was decreasd with increase in the low intensity band due to transcis photoisomerization. Eventually, the isomerization reached the photostationary state at which a cis-form has a broader absorption spectrum with a much weaker absorbance (vide curve B). When the photoirradiated solution was kept in the dark or re-irradiated with visible light, the photostationary state was recovered to the initial state due to back-isomerization from the cis-to trans-Azo. These indicate that the back-isomerization of Azo took place either thermally or photochemically.
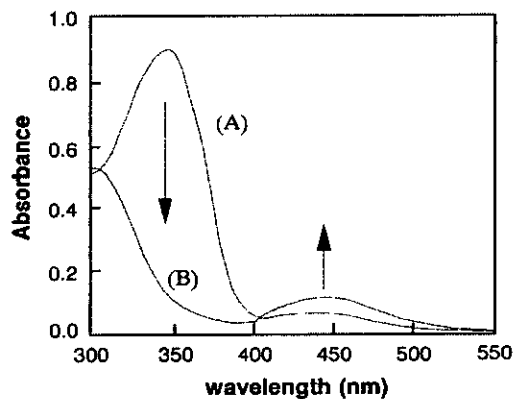

Figure 4. UV absorption spectra of Azo in chloroform
solution (3.4 X 10^{-5} M): (A), before irradiation;
(B), photostationary state upon irradiation at 366 nm.

3.3. Photo-triggered change in selectively reflected light

Figure 5 shows change in wavelength of ChLCs on photoirradiation at a fixed temperature (25 °C). The initial states of ChLC-1 and ChLC-2 before irradiation exhibited the Bragg reflection at around 620 nm and 710 nm, respectively. However, new reflection bands were reproduced continuously at shorter wavelength regions during irradiation at 366 nm which causes the transcis isomerization of Azo. Finally, the bands appeared that reflect selectively light at wavelength regions with spectral properties of green (ChLC-1)

and yellowish green (ChLC-2), respectively. The bands may be regarded as fully photoinduced states because no shift to the blue region and no decrease in the reflective intensity were observed on further photoirradiation any more. Quick recovery could be induced by irradiation at >420 nm, which brings about cistrans back-isomerization of Azo. These results show that an efficient modulation between selective reflection wavelengths could be achieved all-optically by alternate irradiation at two different wavelengths for the reversible isomerization of Azo
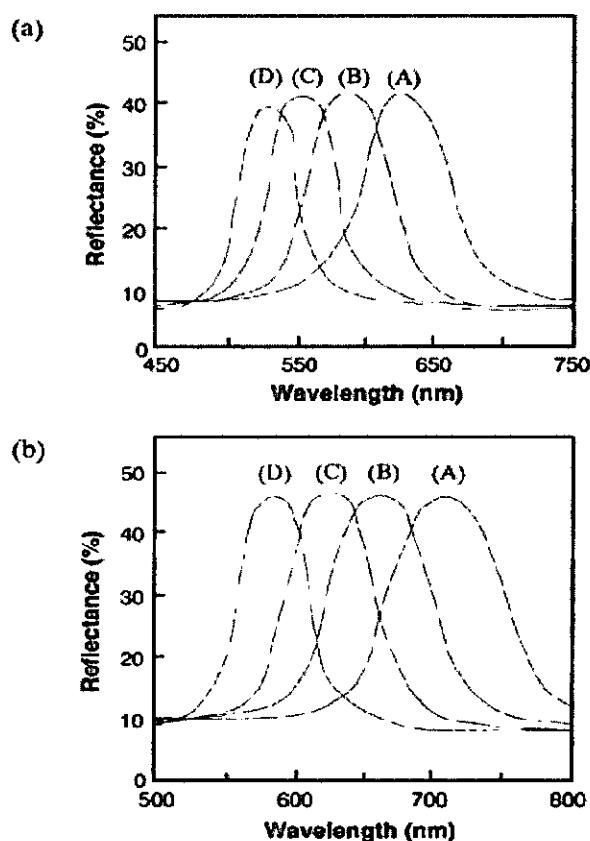

Figure 5. Change in wavelength of selective reflection in ChLC-1 (a) and
ChLC-2 (b) on photoirradiation at 366 nm: (A), 0 mJ/cm^2; (B),
5 mJ/cm^2; (C), 15 mJ/cm^2; (D), 50 mJ/cm^2.

The photoinduced modulation of the reflected colors indicate that the reversible isomerization between the two isomers took place efficiently in the cholesteric arround and the subsequent event appeared effect revealed as the change in pitch of ChLCs. Generally,

ChLCs are an ordered assembly in which NLCs are arranged in their layers providing an anisotropic environment. Hence the trans-form is favorable for stabilization of cholesteric phase similar to N phase due to its rod-like shape although it is not LC.[41] On the other hand, the bent cis-from tends to destabilize the phase structure, resulting in lowering of phase transition temperature as in the case of the depression of the melting point because it acts as an "impurity" in the system.[42] Thus, the change in color induced by irradiation at 366 nm is closely related to lowering of TChI caused by accumulation of the cis-azobenzene which implies an increase in "impurity".

3.4. All-Optical Switching in Reflectance of ChLCs

The selective reflection wavelengths were evaluated as a change in reflectance at a fixed wavelength. Figure 6 shows the change in reflectance of ChLC-1 by light at room temperature. The reflectance was followed as a function of time under various handedness of the incident probe light: a left-handed circularly polarized wave (a), a right-handed circularly polarized wave (b), and a linearly polarized wave (c). When the left-handed circularly polarized light was used as the probe light, the inherent reflectance of ChLC-1 was very high, whereas the other two waves were transmitted almost fully (b) or around half (c). Upon irradiation at 366 nm, a significant reduction in reflectance occurred rapidly in the case of the left-handed wave until the reflectance reached its lowest level. Furthermore, the changed state was immediately recovered to the initial state by photoirradiation at >420 nm. The alternative irradiation resulted in an optical effect modulated repeatedly wiht high contrast in reflectance. On the other hand, no change in reflectance was observed for the right-handed probe light on photoirradiaion.

Incident linearly polarized light can be regarded generally as the sum of the two countercircular components, which are left- and right-handed circularly polarized waves containing a half of the incident energy, respectively. One of them will be reflected and the other transmitted: a selective reflection occurs by a component whose handedness matches that of the helix of the cholesteric LC, whereas opposite-handed light is transmitted. From this optical feature of the ChLCs, the observed distinct switching behavior of the incident probe lights indicates that the Bragg-reflected light in ChLC-1 resulted from a left-handed helical structure. As shown in Figure 5 (a), before photoirradiation the probe light at 633 nm was very close to the λ max of the selective reflection.

In the switching process recorded by the left-handed wave, the initial high-reflectance

is interpreted as the incident probe light was almost reflected due to the same helical sense as ChLC-1. The reduction is attributable to a decrease in reflection sensitivity at the probe wavelength because the reflection band shifted to a shorter wavelength range on photoirradiation.

When the shifting occurred fully, ChLC-1 showed a minimum state in reflectance since the probe light could not be reflected at the newly produced wavelength band any more. Recovery to the initial reflectance on irradiation at >420 nm can be interpreted in terms of the counterprocess. On the other hand, in the case of the right-handed wave the reflectance was constantly at low values irrespective of the initial state or the photoinduced states, because the probe wave had a reverse sense to the helical structure of ChLC-1, which reflects only the same component as the helical sense.
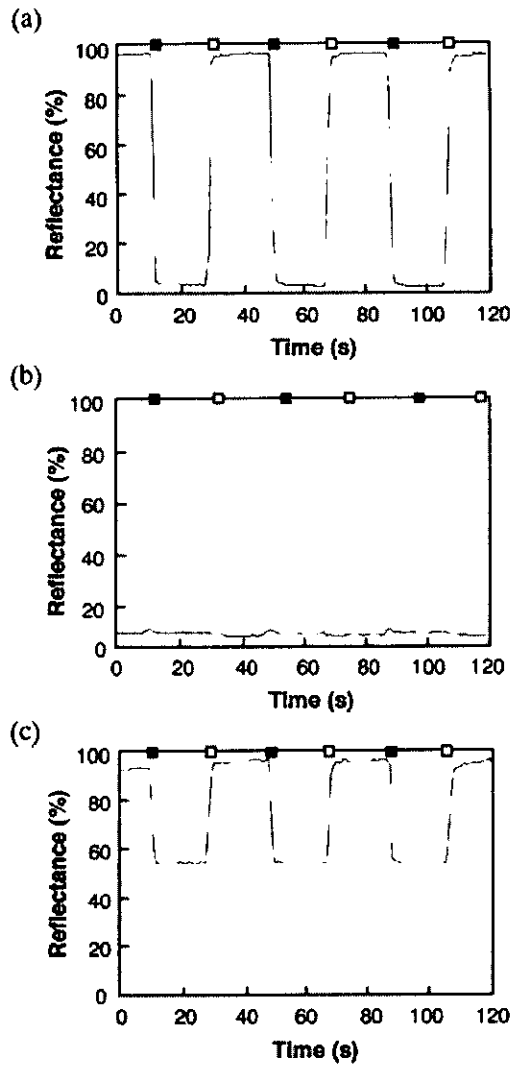
Figure 6. Change in reflectance of ChLC-1 at 633 nm under various handedness induced by alternate irradiation at 366 nm (■, 15 mW/cm^2) and > 420 nm (□). Reflectance was followed with left-handed circularly polarized wave (a), right-handed circularly polarized wave (b), and linearly polarized wave (c) as probe light at room temperature.

3.5. Photoinduced Reversal Mode in Optical Switching

Another switching behavior was evaluated in ChLC-2 reflecting light selectively at longer wavelength range than ChLC-1 in the initial state. Figure 7 shows the change in reflectance induced by photoirradiation at room temperature. During the alternate irradiation with the two pumping light beams to modulate the reflected color, the resultant effect was estimated as the reflectance of the left-handed circularly polarized wave as a probe light.

Although the modulation principle in reflectance is identical with that for ChLC-1, intriguingly a compelling result was observed: the optical behavior exhibited a reverse switching mode, providing a positive variation in reflectance. Furthermore, unlikely ChLC-1, ChLC-2 showed a transient switching behavior on photoirradiation either at 366 or >420 nm.

Before irradiation, low reflectance was observed since ChLC-2 reflected very weakly at the wavelength of the probe light. Photoirradiation at 366 nm induced a shift of the reflection band to the wavelength range close to that of the probe light. Consequently, the reflectance increased with an increase in the reflected intensity at 633 nm on further irradiation at 366 nm. ëmax continuously shifted toward the green wavelength region and the reflectance decreased again because the reflection band strayed from the wavelength of the probe light. A similar switching behavior was also observed in the recovery process on irradiation at >420 nm which undergoes shift of ëmax toward longer wavelength region.

In the recovery process, the reflection band before photoirradiation was located around at 580 nm (Fig. 5(b)) where the reflectance of the probe light is low, and on irradiation at >420 nm the reflection band shifted to longer wavelength region. When the reflection band shifted to the wavelength region where the probe light is selectively reflected, the reflectance became high. Further irradiation caused a further shift of the reflection band and the probe light was no longer reflected, which resulted in an decrease in reflectance. These results demonstrate that the optical modulation of reflectance in ChLC-2 was more efficient than that in ChLC-1. Consequently, to conduct the optical modulation of the reflectance effectively, it would be important to take the spectral positions of the inherent selective reflection and the probe wavelength into account.
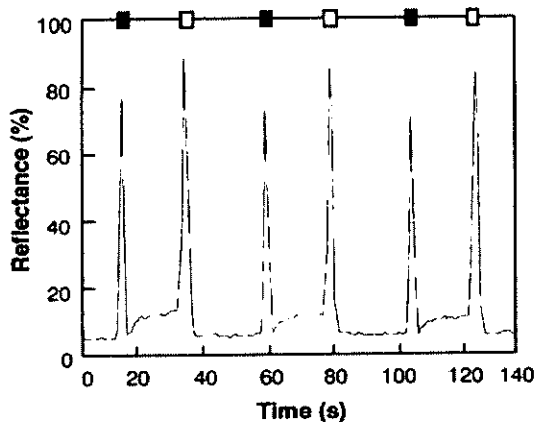
Figure 7. Change in reflectance of ChLC-2 to left-handed
circularly polarized probe light (633 nm) induced by
alternate irradiation at 366 nm (■, 15 mW/cm^2)
and > 420 nm (□).

4. CONCLUSION

It has been shown that all-optical switching in reflectance based on the photoinduced change in Bragg-reflection wavelengths can be performed by means of cholesteric systems containing Azo as a photoresponsive guest molecule. The reversible isomerization of Azo occurred in the cholesteric microenvironments, and the subsequent events followed not only as the depression of TChI but also as the shift of the selective reflection wavelength exhibiting a specifically distinct brilliant color. A considerable optical modulation in reflectance could be efficiently achieved when the photoinduced shift of ëmax was detected continuously by using a circularly polarized wave of the same handedness as the helical sense of ChLCs. It was found that the spectral positions of the initial and the photoinduced Bragg-reflection wavelengths play a crucial role to induce the two different modes of optical switching: the normal mode (ChLC-1) and the reverse mode (ChLC-2) in switching of reflectance. It is expected that these systems may be potential materials for photoswitchable reflectors, bend-pass filters and shutters.

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