

Photochemical switching behavior of composites of polymer liquid crystal/cholesteric liquid crystal by photoisomerization of chiral azobenzene molecules

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Abstract

A chiral azobenzene compound was synthesized. Mixing a chiral azobenzene compound in a host nematic liquid crystal (LC) induced the cholesteric phase. The twisting power of the trans-form of the chiral azobenzene compound was larger than that of the cis-form produced by ultraviolet irradiation. A low molecular weight compensated nematic LC was prepared by mixing of the chiral azobenzene and a nonphotochromic chiral compound having mutual opposite helical sense in the host LC. Reversible optical switching between transparency and opaque was achieved by ultraviolet and visible light irradiation. The photochemically switched opaque state was not stable even in the dark. Stability of the opaque state was found to be improved by adding polymer LC to the low molecular weight compensated nematic LC.

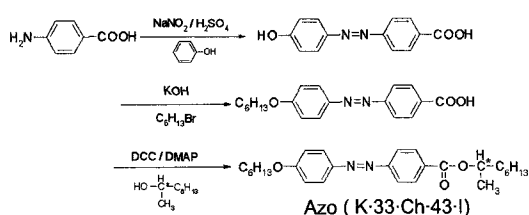
Key words: Photochemical switching, compensated nematic liquid crystal, cholesteric liquid crystal, chiral azobenzene.

1. Introduction

Cholesteric liquid crystals (Ch LC) having helical structure shows a selective reflection of light with wavelength proportional to the helical pitch. So, if the helical pitch can be modulated photochemically, the Ch LC materials will be promising for various optical devices such as photoaddressable display, photocontrollable light reflector, memory and so on. Many studies have been reported on the photochemical control of the helical structure of the cholesteric liquid crystals by means of photoisomerization of azobenzenes¹⁻⁴, menthone^{5,6}, spyropyrans⁷, flugides⁸, and others⁹. In this study, we explained the photochemical switching between transparency and opaque based on the photochemical phase transition between the compensated nematic and the Ch phases. The Ch phase scatters light strongly compared to the compensated nematic phase. The opaque state was not stable in the dark, because of cis-trans thermal back isomerization of the chiral azobenzene compound. The glassy state of polymers or glass forming materials or higher viscosity of polymers is known to hold an anisotropic molecular orientation of LC systems^{5,10}.

Therefore, composites of low molecular weight compensated nematic LC and polymer LC were prepared to improve the stability of photochemically switched opaque state and their photochemical switching behavior were investigated.

2. Result and discussion



Scheme1 Synthesis of Azo compound

The cholesteric structure was induced by adding a chiral azobenzene, Azo synthesized according to Scheme1, into a low molecular weight LC, E44 that was purchased from the Merck Co. In such a binary system consisting of a nonchiral host nematic LC and a chiral compound, the reciprocal of the helical pitch ($1/p$) increases linearly with concentration (c) of the chiral compound and the slope of the $1/p$ versus c is the twisting power of the chiral compound. The twisting power of Azo for E44 was $23 \times 10^2 \mu\text{m}^{-1} \cdot \text{Mol}^{-1} \cdot \text{g-E44}$ at

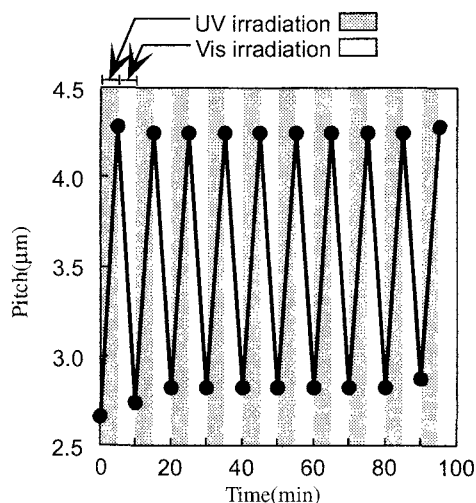


Fig.1 Reversible change in the helical pitch of the (E44/Azo)(95.5wt%) mixture by UV and Vis irradiation at 30°C.

40°C. The helical pitch induced with Azo was increased and decreased by ultraviolet (UV 366 nm) and visible (Vis 433 nm) light irradiation as shown in Fig.1. The trans-Azo isomerizes to cis-Azo by UV irradiation and the cis-Azo can return to the trans-Azo by Vis irradiation photochemically or thermally even in the dark. The twisting power of the trans-Azo is larger than that of the cis-Azo.

The helical structure induced by doping Azo in E44 was a left-handed helix¹¹. Thus, a compensated nematic phase can be obtained by adding R811 (Merck Co.) into the induced Ch LC consisting of Azo and E44 at a ratio of R811: Azo=43:57 wt%, as R811 gives

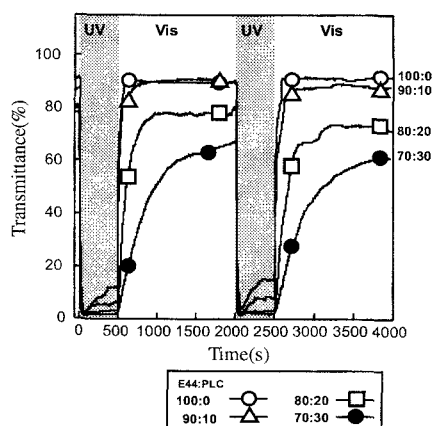
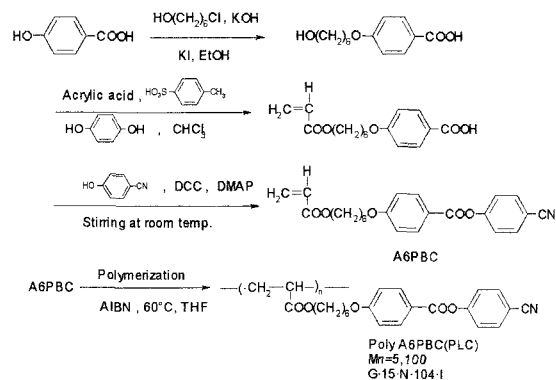


Fig.2 Changes in the transmittance of (E44/PLC)/(R811/Azo) mixtures in the 15μm-homogeneous glass cell by UV irradiation and Vis irradiation at 30°C. The ratio of (E44/PLC) to (R811/Azo) was 80:20wt%, where R811:Azo was 43:57 wt%, and E44:PLC was varied as 100:0, 90:10, 80:20, 70:30wt%.

right-handed helical structure¹¹. A low molecular weight compensated nematic LC consisting of E44, R811 and Azo was prepared in which the ratio of E44:(R811/Azo) was 80:20wt%. It was then filled in a 15 μm homogeneous glass cell. The compensated nematic LC mixture in the cell was found to show photochemical switching between transparency and opaque by UV and Vis irradiation as shown in the Fig.2. The intensity of the transmitted light from a diode laser (670 nm) was measured under UV and Vis irradiation. The LC sample was transparent before UV irradiation due to uniaxial molecular orientation. By UV irradiation it became opaque due to the transformation in to focal conic structure. The twisting power of the trans-Azo was higher than that of the cis-Azo produced by UV irradiation as shown in Fig.1. Consequently, the lower twisting power of the cis-Azo broke the compensated state and resulted in the appearance of the Ch phase, which scattered light strongly. However, the opaque state was not stable even in the dark because of the cis-trans thermal back isomerization.



Scheme 2 Synthesis of Poly A6PBC

The polymer liquid crystal, PLC was synthesized according to Scheme2. Composites of the low molecular weight compensated nematic LC and polymer LC, (E44/PLC)/(R811/Azo) were prepared. The ratio of (E44/PLC) to (R811/Azo) was maintained at 80:20 wt% for all composites and R811:Azo was 43:57 wt%. The ratio of E44 to PLC was varied as 90:10; 80:20; 70:30 wt%. Fig.2 shows photochemical switching behavior of the composites in 15 μm homogeneous cell by UV and Vis irradiation at 30°C.

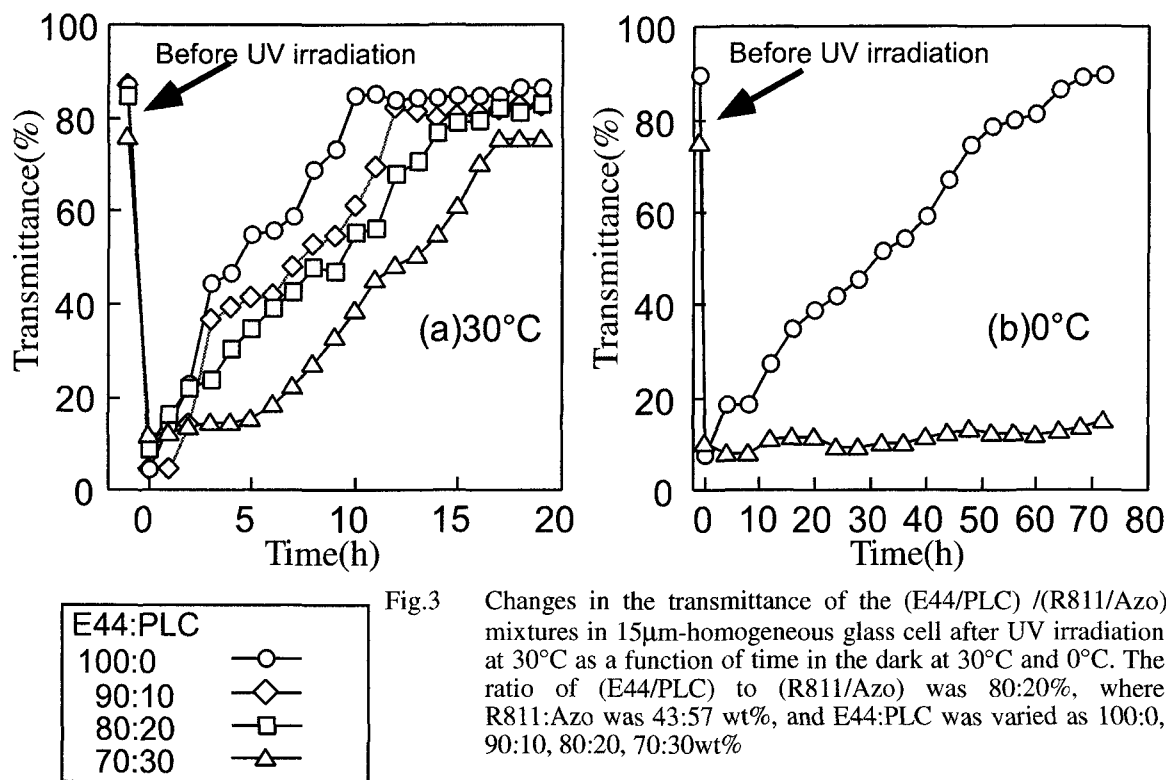


Fig.3 Changes in the transmittance of the (E44/PLC)/(R811/Azo) mixtures in 15µm-homogeneous glass cell after UV irradiation at 30°C as a function of time in the dark at 30°C and 0°C. The ratio of (E44/PLC) to (R811/Azo) was 80:20%, where R811:Azo was 43:57 wt%, and E44:PLC was varied as 100:0, 90:10, 80:20, 70:30wt%

The LC composites showed a lower transmittance than the based nematic LC due to the increase in viscosity of the composites. The composites without PLC exhibited almost similar decrease in the transmittance. Contrary to the decrease in the transmittance, recovery of transparency by Vis irradiation decreased with increasing the content of PLC. Tg of PLC was found to be 15°C determined by Differential Scanning Calorimetry (DSC) where as Tg of the composites could not be determined by DSC. The melting point of E44 is -6°C and it exists in the nematic phase up to 100°C¹². Therefore, it can be assumed that E44 acts as a plasticizer for PLC in the composites and Tg of the composites becomes consequently lower than 15°C. On the other hand, viscosity of the composites increases with the increase of the PLC content in the composites. The slow switching rate from opaque to transparent under Vis irradiation may be brought about by increasing the viscosity of the composites, rather than freezing effect in the molecular orientation below Tg.

Stability of the switched opaque state of the composites at 30°C and 0°C was shown in Fig.3.

Thermal recovery of transmittance of the composites was examined as a function of time in the dark after UV irradiation. At 30°C, time required for the E44/(R811/Azo) compensated nematic LC without PLC to return to transparent state in the dark was 10 h and that was more than 15 h in the case of the composite (E44/PLC=70:30wt%) as shown in Fig.3(a). So, the stability of the opaque state was improved by increasing the PLC content of the composites, but it was not enough. The results given in Fig.3(b) indicates a remarkable influence of temperature on the stability of the opaque state produced photochemically. Falling of temperature markedly prolonged the time required for the thermal recovery of the transparency. Very little change was observed in the case of the composite (E44/PLC=70:30 wt%) even after more than 70 h at 0°C. As Tg of the composites could not be determined, we could not discuss the stability in terms of the Tg of the composites.

3. Conclusion

It is likely that the increase in the viscosity of the composites contributes to improve the stability of the

switched opaque state. Since the T_g of PLC was lower than an ambient temperature. The composites required cooling to be stable opaque state in the dark. It is also expected that the use of polymer liquid crystal having higher T_g provides more stable memory property of the switched opaque state at a higher temperature.

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