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Communications to the Editor

Fast Photochemical Switching of a Liquid-Crystalline Polymer Network Containing Azobenzene Molecules

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Many studies have been reported on liquid-crystalline polymers (LCPs) with photosensitive molecules in the field of optical devices.[1−10] Photochromic compounds such as azobenzene and spiropyran change their molecular shapes upon irradiation. The change in the molecular shapes of the guest molecules in the LCPs can cause a depression of LC-isotropic phase-transition temperatures of the LCPs and consequently induce an isothermal phase transition at the irradiated sites. Time-resolved measurements have revealed that the photochemical phase transition was induced in 50−200 ms when a small amount of azobenzene compound was dispersed in low-molecular-weight nematic LCs and LCPs.[8,9] In addition, it was recently found that the monomeric and polymeric LCs having azobenzene moiety in each mesogen caused the photochemical phase transition in 200 μs upon pulse irradiation.[7,10] The fast response will enable us to use the LC systems not only for display devices but also for various optical devices such as optical switching and optical computing.

However, we consider that we do not need to induce complete phase transition of LC systems photochemically for application to the optical devices. If we can detect enough signal based on the photochemical changes in the physical properties of the LC systems such as transparency and birefringence, we will be able to use the LC systems for the optical devices.

On the other hand, it has been reported that LCP networks showing excellent transparency and high birefringence can be prepared by polymerization of LC monomers in a unidirectional orientation.[11−18] In addition, LCP networks with slight cross-linking were found not only to hold the macroscopic molecular orientation but also to show a reversible phase transition between LC and isotropic phases.[19] Therefore, it is expected that the high performance of the optical properties of the LCP networks promises to detect subtly a slight change in the optical properties such as transparency and birefringence induced by photoisomerization of the azobenzene compound, even if the photochemical phase transition is not induced completely. In this study, we describe the preparation of macroscopically anisotropic LCP network containing azobenzene molecules by polymerization of a mixture of LC monomers and an azobenzene compound in the unidirectional orientation, and time-resolved measurements of the photochemical change in the birefringence of the LCP networks.

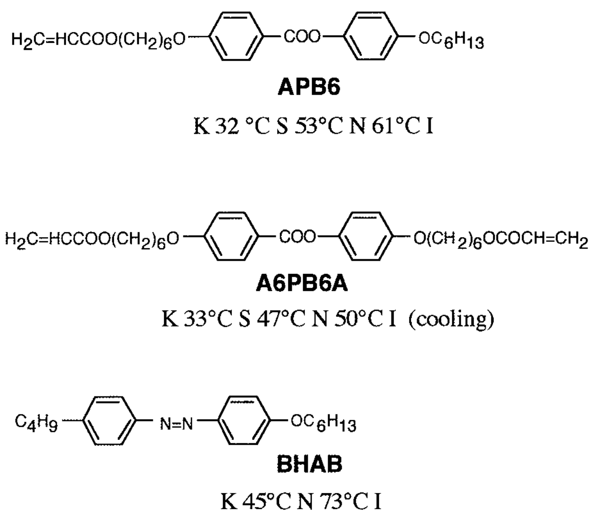

Figure 1. Structures and phase-transition temperatures of compounds used in this study. K, cystal; S, smectic; N, nematic; I, istropic.

The chemical structures of compounds used in this study are shown in Figure 1. Monoacrylate and the azobenzene compound, **APB6** and **BHAB**, exhibit enantiotropic liquid crystallinity. Diacrylate, **A6PB6A**, is a monotropic liquid crystal. The syntheses of **APB6** and **BHAB** are described in the literatures.[19,20] **A6PB6A** was synthesized in a similar manner described previously.[21,22] The structure of **A6PB6A** was confirmed by IR, NMR spectra, and an elemental analysis. A polymerizable mixture was prepared by adding 3 mol % of benzoyl peroxide to the (**APB6**/**A6PB6A**/**BMAB**) mixture (90:5:5 in mol %) as a radical initiator. This mixture shows the nematic phase in a temperature range between 49 and 59 °C. The mixture was injected into the Cano-wedge cell or a homogeneous glass cell with a 5-μm-cell gap at the isotropic phase. The Cano-wedge cell is a wedge-shaped cell with a homogeneous planar alignment. The polymerization of the mixture was carried out by heating at 57 °C for 1 h.

Figure 2A shows changes in the birefringence of the poly(**APB6**/**A6PB6A**/**BHAB**) network as a function of temperature. The birefringence (Δn) was determined by measuring the number of interference lines of the poly(**APB6**/**A6PB6A**/**BHAB**) network in the Cano-wedge cell between two crossed polarizers with a probe light from a laser diode (Suruga Seiki Co.; 670 nm; 5mW). Before polymerization, the (**APB6**/**A6PB6A**/**BHAB**) mixture existed in the nematic phase at 57 °C,

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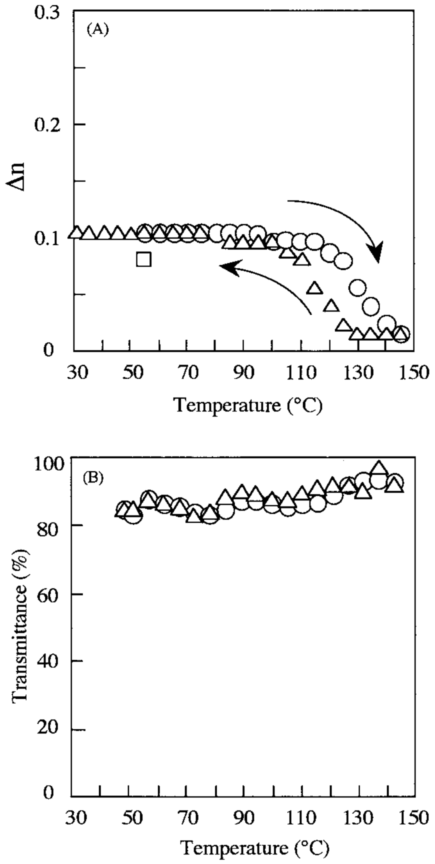

Figure 2. Changes in birefringence (Δ*n*) (A) and transmittance (B) of the poly(APB6/A6PB6A/BHAB) network as a function of temperature. (□), before polymerization; (○), heating; (△), cooling.

at which temperature the molecules were in the homogeneous alignment in both the homogeneous glass cell and the Cano-wedge cell. The polymerization caused no significant change in Δ*n* as shown in Figure 2A. The Δ*n* of the poly(**APB6**/**A6PB6A**/**BHAB**) network was around 0.1 and kept constant up to 120 °C. Above 120 °C, Δ*n* decreased rapidly due to the phase transition to the isotropic phase. By subsequent cooling, Δ*n* was increased and restored to the initial level of Δ*n*. Figure 2B shows changes in the transmittance of the poly(**APB6**/**A6PB6A**/**BHAB**) network in the homogeneous glass cell as a function of temperature. No change in the transmittance was induced by polymerization, and it was kept at about 90% by heating to 120 °C and cooling. The results clearly demonstrate that the poly(**APB6**/**A6PB6A**/**BHAB**) network not only holds the macroscopically uniaxial molecular orientation but also shows the reversible phase transition. Contrary to the poly(**APB6**/**A6PB6A**/**BHAB**) network, the polymerization of **APB6** without **A6PB6A** in the homogeneous glass cell resulted in a significant decrease in the transmittance. In addition, Δ*n* of the poly(**APB6**) without cross-linking disappeared by heating above 130 °C and was not restored by subsequent cooling. Polarized optical microscopy revealed that the significant decrease in the transmittance arose from the transformation from the uniaxial monodomain structure to a multidomain structure during polymerization. The results imply that the slight cross-linking of LCPs has contributed to the macroscopically uniaxial molecular orientation of the LCP networks, originating in both excellent transparency and thermotropically reversible phase transition.

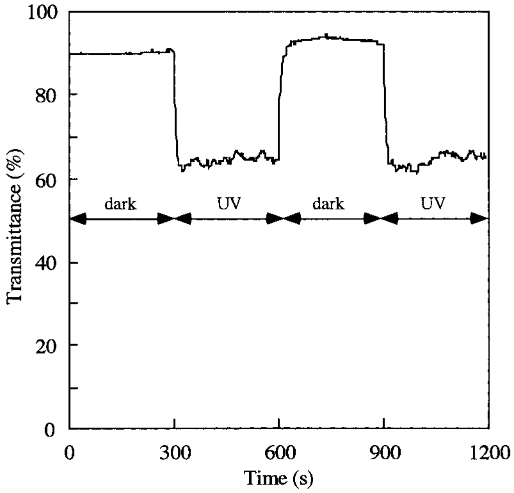

Figure 3. Change in the transmittance of the poly(APB6/A6PB6A/BHAB) network between two crossed polarizers by UV irradiation at T_{red} = 0.98.

To investigate the effect of the photoisomerization of **BHAB** on the optical properties of the polymer network, a change in the birefringence of the poly(**APB6**/**A6PB6A**/**BHAB**) network was examined upon irradiation. The poly(**APB6**/**A6PB6A**/**BHAB**) network polymerized in the homogeneous glass cell with a 5-μm gap was placed between two crossed polarizers and thermostated at 125 °C ($T_{red} = T/T_{NI} = 0.98$). The polarizing direction of the two polarizers was set at an angle of 45° with respect to the orientation axis of the cell. The change in the transmitted intensity of a probe light from the laser diode was monitored with a laser power meter (Neo Ark, PM-221) while the sample was irradiating with UV light. The UV irradiation was carried out by a 75-W Hg high-pressure lamp with a cut filter (Sigma, UTVAF-35U) to cause trans–cis photoisomerization of **BHAB** in the polymer network. Figure 3 shows the change in the transmittance of the poly(**APB6**/**A6PB6A**/**BHAB**) network by UV irradiation.[23] Before UV irradiation, the transmittance was around 90%, because of the macroscopically uniaxial molecular orientation of the poly(**APB6**/**A6PB6A**/**BHAB**) network. The transmittance was decreased rapidly to 60% by UV irradiation and was kept there while the polymer network was irradiating. The transmittance was restored to the initial level by turning off the UV irradiation. The value of Δ*n* was estimated by measuring the transmitted light intensities of the polymer network between two crossed polarizers and between two parallel polarizers before and under UV irradiation. The estimated values of Δ*n* were 0.034 and 0.027 before and under UV irradiation, respectively. The result implies that the change in the transmittance is enough to detect, although the photochemical phase transition of the polymer network cannot be induced completely. The rapid restoration of the birefringence in the dark may be related to fast cis–trans thermal isomerization of **BHAB** and highly ordered molecular orientation of the poly(**APB6**/**A6PB6A**/**BHAB**) network.

To explore the optical switching behavior of the polymer network, time-resolved measurements of the photochemical change in the birefringence were carried out by means of pulse irradiation. The poly(**APB6**/**A6PB6A**/**BHAB**) network was thermostated and set between two crossed polarizers. The polymer network

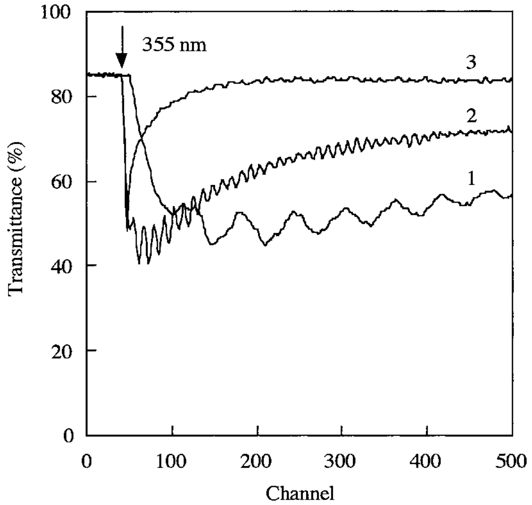

Figure 4. Time-resolved measurements of change in the transmittance of the poly(APB6/A6PB6A/BHAB) network between two crossed polarizers on pulse irradiation (355 nm, 15 ns fwhm, 10 mJ/cm^2). (1) 10 ns/channel; (2) 50 ns/channel; (3) 1 μs/channel.

was irradiated with a single pulse of a Nd:YAG laser (Continuum NY 60; the third harmonic, 355 nm; 10 mJ/cm^2; 15 ns, fwhm). The transmittance of the probe light from the laser diode through two crossed polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded on a Philips PM3350A storage scope. Figure 4 shows the time-resolved measurements of the photochemical change in the transmittance of the polymer network. Upon pulse irradiation, the transmittance was decreased and reached the minimum value. Subsequently, the transmittance increased and returned to the initial value. To discuss the optical switching behavior, the response time and decay time were defined as the time required to decrease to the minimum value and as the time required to raise to 90% of the initial value, respectively. The response time was in a time range of a few microtens of seconds. The decay time was longer than the response time and was in the time range of a few microhundreds of seconds.

In summary, we prepared the liquid-crystalline polymer network containing the azobenzene compound, poly(**APB6**/**A6PB6A**/**BHAB**), and explored the photochemical switching behavior. UV irradiation resulted in the decrease in the transmittance from 90% to 60% with respect to the change in the birefringence induced by photoisomerization of **BHAB**. In addition, the pulse irradiation experiments revealed that the response and decay time of the polymer network were in the time ranges of a few microtens and a few microhundreds of seconds, respectively. Further studies on the photochemical switching behavior is now in progress.

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(23) Reference light intensity (I_0) for the transmittance measurements was defined as the transmitted light intensity through two parallel polarizers.

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