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# Azotolane Liquid-Crystalline Polymers: Huge Change in Birefringence by Photoinduced Alignment Change

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A change in birefringence ($\Delta n$) resulting from external stimuli enables the control of incident light. Therefore, azopolymer systems, in which a change in $\Delta n$ can be induced by photoisomerization, have attracted increasing attention for optical applications.[1,2] In azobenzene polymers, two processes of the change in $\Delta n$ have been explored: (1) reorientation of azobenzene moieties upon irradiation of isotropic films with polarized pumping light (disorder−order change)[3] and (2) destruction of a homogeneous alignment of mesogenic azobenzenes by a photochemical phase transition (order−disorder change). Thus far, we have performed systematic studies on the nematic−isotropic phase transition of azobenzene liquid-crystalline polymers (LCPs) because the order−disorder change shows an efficient change in $\Delta n$.[4] On the basis of this idea, we have proposed a new molecular architecture, LCPs containing an azotolane moiety in the side chain, to induce a large change in $\Delta n$ upon irradiation of light.[5] Azotolane LCP films exhibit high $\Delta n$ in the homogeneously aligned state, and show a large change in $\Delta n$ by destruction of the alignment by trans−cis photoisomerization. Furthermore, we developed an LCP containing a longer azotolane moiety.[6] Although the LCP exhibited an extremely high value of $\Delta n$, a large change in $\Delta n$ could not be induced effectively.

Herein, to improve the photosensitivity, we prepared novel polymers containing a long azotolane moiety (**2**−**4**) and investigated photoresponsive behavior. Compounds **1**−**3** show differences in the position of the azobenzene moiety in the mesogenic core, and the azotolane group in compound **4** has two azobenzene units.

By investigation of LC properties, it was found that all polymers show a nematic phase in a broad temperature range (Figure 1). A nemetic phase is quite advantageous for photonic applications because the sensitivity to external stimuli is higher than that of other LC phases. Next, we investigated the trans−cis photoisomerization behavior of the azobenzene unit in the mesogen of the LCPs in *o*-dichlorobenzene. In all polymers, the absorption of the $\pi-\pi^*$ transition band decreased upon irradiation at 366 nm. When the LCPs irradiated at 366 nm were kept in the dark, the absorption recovered to the initial state due to thermal cis−trans back-isomerization. These results show that the trans−cis photoisomerization and cis−trans thermal isomerization occur repeatedly even in the LCPs containing the long azotolane moiety. In addition, we calculated the values of the ratio of cis-isomers in the photostationary state from NMR spectra (Table 1). Among the compounds, **4** showed the largest value of the cis-isomer ratio (31%). This result could be attributed to the presence of two azobenzene units. Furthermore, in compound **4**, 8.2% of the two azotolane moieties were found to have cis,cis conformation at the two azobenzene moieties in the photostationary state (Supporting Information).

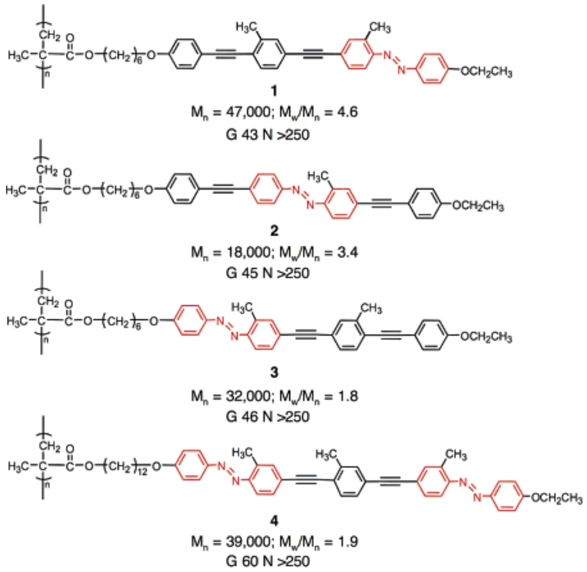

***Figure 1.*** Chemical structures and properties of polymers. $M_n$, number-average molecular weight; $M_w$, weight-average molecular weight. G, glassy; N, nematic.

***Table 1.*** Characterization of Polymers

| polymer | $\lambda_{max}$ (nm) ($\epsilon$)[a] | cis-isomer ration (%)[b] | $d$[c] (nm) | $S$[d] | $\Delta n$[e] $\lambda$[f] 633 nm | $\lambda$ 830 nm | $\lambda$ 1550 nm |
|---|---|---|---|---|---|---|---|
| **1** | 386(3.2 × $10^4$) | 26 | 350 | 0.71 | 0.71 | 0.55 | 0.49 |
| **2** | 409(3.3 × $10^4$) | 25 | 300 | 0.65 | 0.73 | 0.63 | 0.52 |
| **3** | 389(3.2 × $10^4$) | 26 | 290 | 0.69 | 0.68 | 0.52 | 0.48 |
| **4** | 396(4.7 × $10^4$) | 31 | 330 | 0.71 | 0.76 | 0.68 | 0.55 |

[a] Measured in *o*-dichlorobenzene. [b] Evaluated by $^1$H NMR of each monomer. [c] Film thickness. [d] Order parameter determined by polarized UV spectrometry. [e] Birefringence. [f] Wavelength of the probe light.

To obtain homogeneously aligned films and evaluate optical properties, LCPs were dissolved in *o*-dichlorobenzene, and then a small portion of the resultant solution was cast on a rubbed polyimide-coated glass substrate by a barcoater method. Homogeneously aligned films were obtained after annealing at 200 °C for 2 h. From polarized absorption spectra, we evaluated the values of order parameter ($S$) in the films. As shown in Table 1, the values of $S$ of the films exhibited $>$0.65. These values are much higher than those of three-ring azotolane LCPs reported previously.[5] It is known that a long mesogenic core exhibits a high value of $S$ even in a glassy nematic state.[7] The highly ordered mesogenic system is preferable to improve the value of $\Delta n$ because $\Delta n$ is proportional to $S$. Furthermore, linearly conjugated molecular structures, such as three-ring-tolane,[8a] thiophenyl-tolane,[8b] and isothiocyanato-tolane,[8c] exhibit high values of $\Delta n$ (0.4−0.8). Actually, thanks to the high value of $S$ and the long $\pi$-conjugated mesogen core, the LCPs showed extremely high values of $\Delta n$ at any wavelength examined between 633 and 1550 nm (Table 1). The LCPs film

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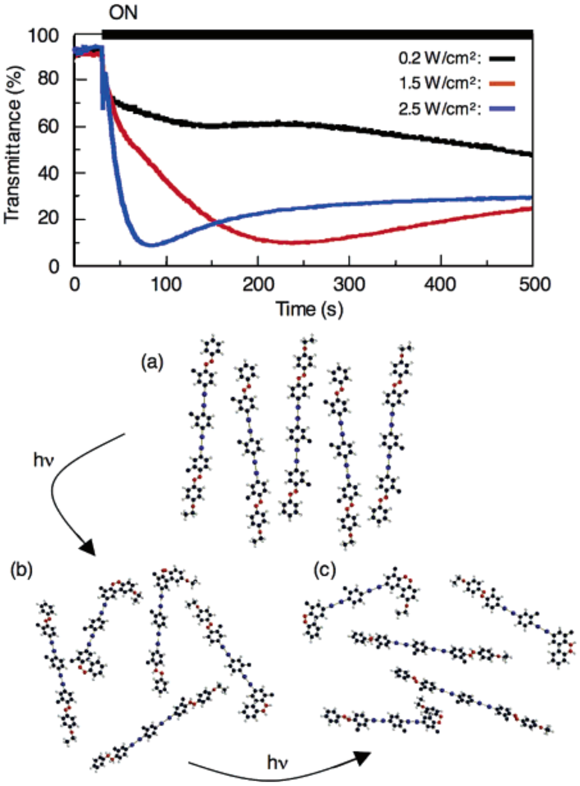

***Figure 2.*** Effect of light intensity on the change in transmittance at 20 °C. Probe beam: 633 nm. (a−c) Plausible mechanism of the change in alignment of the azotolane moieties in film **4** upon irradiation of the pump beam: (a) homogeneously aligned state before irradiation, (b) destruction of the alignment in the azotolane moieties by irradiation of the beam, (c) reorientation of the azotolane moieties by isomerization cycles. Film thickness: 330 nm.

indicated ordinary wavelength dispersion of $\Delta n$; with a decrease in wavelength the value of $\Delta n$ increased due to resonant enhancement.

We further investigated a photoinduced change in transmittance of the LCPs at room temperature and in the LC phase. The value of $\Delta n$ was estimated by the standard method.[9] All LCPs showed the change in transmittance accompanied by the photoinduced alignment change (Supporting Information). Among the LCPs, the compound **4** containing two azobenzene units showed the largest change in transmittance. This result is reasonable because, as shown in Table 1, **4** exhibits the largest degree of photoisomerization among the compounds examined. Moreover, in the LC phase, **4** gave a greater change in transmittance compared to the glassy state. We assume that the LC phase enhances the change in the alignment of the azotolane with two azobenzene units.

As shown in Figure 2, compound **4** was chosen to investigate the effect of light intensity on the change in transmittance and to evaluate the change in $\Delta n$ because **4** has the highest photosensitivity. When the intensity of the pump beam was 0.2 W/cm$^2$ in the glassy state, the transmittance decreased slowly.

On the other hand, at the intensity of $\geq$1.5 W/cm$^2$, one can see that the transmittance of the probe beam decayed to $\sim$10%. This result implies that the homogeneous alignment in the azotolane moieties (Figure 2a) is almost destroyed upon irradiation of light (Figure 2b). In other words, the high value of $\Delta n$ in the homogeneously aligned state can be effectively converted to the change in $\Delta n$ by the photoinduced change in the alignment of the azotolane moieties. Actually, the calculated values of the change in $\Delta n$ were $\geq$0.65 at the intensity of $\geq$1.5 W/cm$^2$ even in the glassy state. Further irradiation of the pump beam increased the transmittance gradually. The increase is ascribed to the generation of a new alignment upon irradiation of s-polarized light (parallel to the rubbing direction); namely, the azotolane moieties become aligned perpendicular to the electronic vector of the actinic beam due to the reorientation process as mentioned above (Figure 2c). From these results, we have revealed that the azotolane moiety with a higher content of the azo unit enhances the change in $\Delta n$ remarkably.

In summary, we have developed highly birefringent LCPs containing a long azotolane moiety and have investigated the effects of the structural factors on the photoinduced alignment change. Specifically, the azotolane LCP with two azobenzene units showed the most efficient change in $\Delta n$ ($\geq$0.65). The molecular architecture is useful for extensive optical applications in high performance photonic devices (such as high-density optical recording, as well as holographic and multibit recording) and photoswitching materials.

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**Supporting Information Available:** Additional data and synthetic preparations. This material is available free of charge via the Internet at http://pubs.acs.org.

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