

All-Optical Switching Effect in Novel Chiral Biazobenzene Polymer Films

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Introduction. Nonlinear optics has been recognized as a field of research with important potential applications in optoelectronic devices. For nonlinear optics, the material must be noncentrosymmetric on the molecular and macroscopic scales. Noncentrosymmetry on the molecular scale is easy to achieve, for example, by connecting an electron donor and acceptor by a one-dimensional conjugated bridge. On the other hand, macroscopic noncentrosymmetry is more difficult. Methods to achieve macroscopic noncentrosymmetry include electric poling, crystal growth, and self-assembly. An alternative approach is to use chiral materials, which are inherently noncentrosymmetric. The use of chirality in nonlinear optics has been theoretically investigated.^{1,2} These studies showed that chiral contributions can increase nonlinear optical response.

Fast all-optical switches are crucial components for high-bit-rate time-division-multiplexing optical communication systems or free-space optical-digital computing systems. So far, many types of all-optical switches have been studied; among them, the azobenzene-type optical switches have received great attention recently.³ The azobenzene molecules are well-known to show reversible photoisomerization between the trans and cis forms as well as the birefringent properties upon illumination by linearly polarized light.^{4,5} Ideal materials for optical switching should possess a large photo-induced birefringence and long-term stability. By introducing chirality into azobenzene polymer, it will improve the system's macroscopic noncentrosymmetry and nonlinearity, which in turn will increase the system's optical activity including birefringence. In addition, traditional all-optical switching usually requires high driving power (e.g., 1 MW/cm²), thus limiting its applications.⁶ To make practical optical switching devices, it is necessary to reduce the optical power requirements and achieve large modulation depth. To increase the magnitude and sensitivity of photoinduced birefringence, new azo polymers including chiral azo polymers are constantly being designed and synthesized.^{7–9} In this study, we synthesized a novel chiral biazobenzene polymer and studied its photoinduced birefringence and all-optical switching effect. The optical switching devices made herein can be operated with a relatively low driving power, a rising time and a falling time of about 0.4 ms, and a modulation depth more than 90%.

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Experimental Section. a. Synthesis. *p*-Aminoazobenzene, methacryloyl chloride, and *N,N*-dimethylformamide (DMF) were received from Aldrich Chemicals Co. D-(+)- α -Methylbenzylamine was received from Acros Organics. Tetrahydrofuran (THF) was dried over sodium/benzophenone and distilled just before use.

The biazobenzene chromophore was synthesized by diazotization reaction and coupling with D-(+)- α -methylbenzylamine; biazobenzene monomer was obtained through reaction of biazobenzene chromophore with methacryloyl chloride (Scheme 1).

Sodium nitrite (3.1 g) dissolved in water (50 mL) was added into a solution of *p*-aminoazobenzene (7.9 g) dissolved in a mixture of water (50 mL) and 36% aqueous hydrogen chloride (7.2 mL). Then the solution was kept at 0–5 °C for 2 h. D-(+)- α -Methylbenzylamine (4.85 g) dissolved in a mixture of water (125 mL) and 36% aqueous hydrogen chloride (7.5 mL) was added to the above solution over 30 min, and then the solution was stirred for 1 h at 0–5 °C and 4 h at 20 °C. The precipitate was obtained by filtration, washed with a large amount of water, dried, and recrystallized from ethanol to yield the biazobenzene chromophore. Biazobenzene chromophore (2.3 g) and methacryloyl chloride (1.1 g) were dissolved in 100 mL of dry THF. Triethylamine (1.4 g) was added dropwise to the solution. After stirring for 15 h at room temperature, the solution was filtered. Then THF in the filtrate was removed, and the reaction product was washed with 2 N sodium hydroxide, 0.1 N HCl, and distilled water successively. The dark red product (biazobenzene monomer) was dried under vacuum at 60 °C for 72 h. UV–vis in THF (chromophore): $\lambda_{\text{max}} = 410$ nm. ¹H NMR (monomer): δ (ppm), 8.1 (NH), 7.2–7.9 (aromatic H), 5.2–5.9 (C=CH₂), 2.9–3.0 (CH₂), 1.9 (CH₃). FT-IR (monomer): 3400 cm⁻¹ (ν_{NH}), 3075 cm⁻¹ ($\nu_{\text{C}=\text{CH}_2}$), 2950 and 2870 cm⁻¹ (ν_{CH} aliph), 1690 cm⁻¹ ($\nu_{\text{C}=\text{O}}$), 1640 cm⁻¹ ($\nu_{\text{C}=\text{C}}$, aliph), 1600 cm⁻¹ ($\nu_{\text{C}=\text{C}}$, arom), 1500 cm⁻¹ ($\nu_{\text{C}-\text{N}-\text{H}}$), 770 cm⁻¹ (ν_{CH} , arom).

The synthesized biazobenzene monomer (2 g for sample A and 1 g for sample B) was dissolved in dry DMF; 0.9 g of methyl methacrylate and 0.1 g of butyl methacrylate were added to the solution. The polymerization was carried out in the presence of azobisisobutyronitrile (AIBN, 2 wt %) as an initiator. The polymerization medium was outgassed twice before heating and stirring at 70 °C for 240 h under nitrogen. Then the polymerization mixture was poured into cold methanol. The isolated ternary copolymer was redissolved in THF and precipitated in cold methanol, filtered, and finally dried under vacuum at 60 °C for 72 h: $M_w = 3.1 \times 10^4$, polydispersity = 1.63 (sample A); $M_w = 4.2 \times 10^4$, polydispersity = 1.66 (sample B). Biazobenzene chromophore content obtained through elemental analysis: 63.0 wt % for sample A and 31.5 wt % for sample B. ¹H NMR: δ (ppm), 8.1 (NH), 7.2–7.9 (aromatic H), 4.2 (O=CCH₂), 3.6–3.8 (O–CH₃), 1.2–2.2 (CH₂), 0.9 (CH₃). FT-IR (KBr): 3200 cm⁻¹ (ν_{NH}), 2950 and 2870 cm⁻¹ (ν_{CH} aliph), 1730 cm⁻¹ ($\nu_{\text{C}=\text{O}}$), 1600 cm⁻¹ ($\nu_{\text{C}=\text{C}}$, arom), 1500 cm⁻¹ ($\nu_{\text{C}-\text{N}-\text{H}}$), 1270 and 1150 cm⁻¹ ($\nu_{\text{C}-\text{O}-\text{C}}$), 770 cm⁻¹ (ν_{CH} , arom). Optical rotation: $[\alpha]_{\text{D}}^{25} = +10.5^\circ$ (CHCl₃, *C* = 1 g/dL, sample B), $[\alpha]_{\text{D}}^{25} = +16.5^\circ$ (CHCl₃, *C* = 1 g/dL, sample A).

beam power increases. When the control beam is turned off, birefringence quickly decreases; this indicates that it is reversible photoinduced birefringence, which is ideal for good all-optical switching effect. There are two mechanisms in the polymer films which influence the photoinduced birefringence, which in turn determines the optical switching effect. One is the photoisomerization reorientation of biazobenzene moieties, and the other is the rotation of biazobenzene moieties due to thermal agitation. The competition between these two mechanisms can be used to explain the experimental results. Thermal agitation comes from the thermal effect of the control beam illumination owing to the absorption of the sample. As the control beam power increases, the temperature of the sample increases; biazobenzene chromophore moieties which are oriented due to photoisomerization are easier to return to their initial random state. Therefore, with higher control beam power, thermal disturbance which enhances the rotation of biazobenzene moieties and disorders the alignment of the sample becomes stronger, which in turn weakens the photoinduced birefringence.

In summary, chiral biazobenzene polymers have been synthesized. Large birefringence and all-optical switching effect have been realized in the polymer films at low optical driving power. The ability to induce large optical birefringence in the polymer films is expected to find applications in high-speed photonic devices, such as spatial light modulators, filters, polarizers, and beam splitters for optical communication and image processing.

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Supporting Information Available: FTIR spectra, NMR ^1H spectra, and UV-vis spectrum. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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