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Synthesis and Properties of Highly Birefringent Azo-Tolane Liquid-Crystalline Polymers: Effect of the Position of the Tolane Moiety in the Side Chain

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We have synthesized two types of azobenzene liquid-crystalline polymers with a tolane moiety exhibiting high birefringence: one is the copolymer having an azobenzene moiety and a 3-ring tolane group in the side chain (PA-3T) and the other is the polymer containing a long mesogen core, in which the azobenzene group is directly connected to the tolane moiety (P3AT). The values of 0.35 and 0.39 in birefringence were obtained in PA-3T and P3AT, respectively. When the film was irradiated with a writing beam at 488 nm, the change in birefringence was efficiently induced with P3AT compared with PA-3T.

Keywords: azobenzene; change in birefringence; liquid-crystalline polymer; tolane

INTRODUCTION

Azo-dye-containing organic and polymeric compounds are promising materials for optical applications. They have been extensively studied because of their applicability for nonlinear optics [1], optical memory [2,3], photoswitching devices [4], and holography [5–7]. Among diversified azobenzene-containing polymers, liquid-crystalline polymers (LCPs) with the azobenzene in the side chain have

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attracted much attention because a photoinduced change in birefringence Δn is large when compared with amorphous counterparts [8–11]. The azobenzene moiety in a *trans* form, which is rodlike, stabilizes the phase structure of liquid crystals (LCs). On the other hand, bent *cis* isomers disorganize the phase structure of the LCs. Consequently, *trans-cis* photoisomerization of the azobenzene chromophores leads to a change in large Δn by disorganizing the alignment of LCs. It has also been known that polarized light can induce reorientation of azobenzene groups through photochemically induced *trans-cis-trans* isomerization cycles. Previously, we have revealed that a large change in Δn was induced by photoisomerization [12–14] of the azobenzene and the resultant alignment change [15,16].

Tolane moieties are known as a highly birefringent mesogen because of large anisotropy of polarizability [18]. Therefore, to obtain a larger change in Δn in LCPs, we previously prepared a copolymer having a 2-ring tolane and an azobenzene in the side chain, and found that the polymer exhibits higher birefringence than that of conventional LCPs [17]. In this study, we have synthesized two types of azobenzene LCPs with a tolane moiety to induce larger Δn : one is the copolymer having an azobenzene moiety and a 3-ring tolane group in the side chain (**PA-3T**), and the other is the polymer containing a long mesogen core in which the azobenzene group is directly connected to the tolane moiety (**P3AT**). In addition, we investigated the photoinduced birefringence of the films upon exposure to linearly polarized light.

EXPERIMENTAL

Characterization

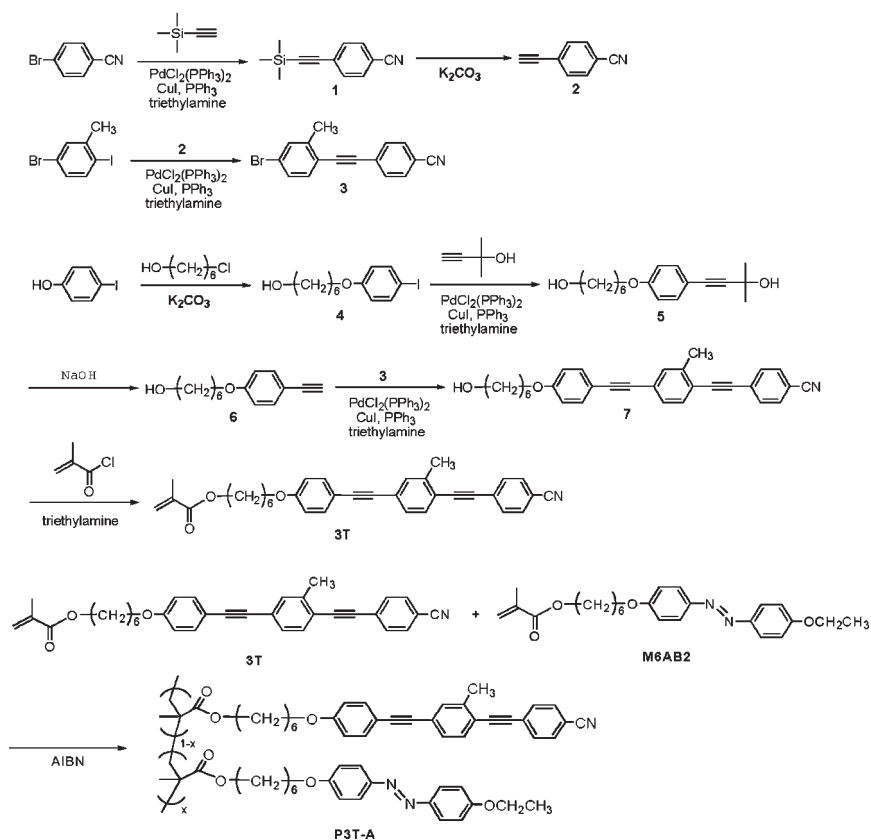
NMR spectra were recorded in CDCl_3 with Lambda-300. Molecular weight of the polymer was determined by gel permeation chromatography (GPC; JASCO DG-980-50; column, Shodex GPC K802 + K803 + K804 + K805; eluent, chloroform) calibrated with standard polystyrenes. LC behavior and phase transition behavior were examined on an Olympus Model BH-2 polarizing microscope equipped with Mettler hot-stage models FP-90 and FP-82. Thermotropic properties of LCPs were determined with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of $10^\circ\text{C}/\text{min}$. At least three scans were performed for each sample to check reproducibility. Absorption spectra were recorded with a UV-vis absorption spectrometer (JASCO, V-550).

Materials

The monomer, 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl methacrylate (**M6AB2**), was prepared and purified as previously reported [19,20]. The synthesis of monomer, 6-[4-[3-methyl-4-(4-cyanophenylethynyl)-phenylethynyl]phenoxy]hexyl methacrylate (**3T**), is outlined in Scheme 1. Six compounds from **1** to **6** shown in Scheme 1 were prepared using a procedure similar to the literature [18]. The synthesis and thermal property of **P3AT** was previously reported [21].

1-[(6-hydroxyhexyloxyphenyl)ethynyl]-3-methyl-4-[(4-cyanophenyl)ethynyl]benzene(**7**)

1-Bromo-3-methyl-4-[(4-cyanophenyl)ethynyl]benzene (**3**) (2.6 g, 4.5 mmol), 1-(6-hydroxyhexyloxy)-4-ethynylbenzene (**6M**) (1.8 g, 4.1 mmol),



SCHEME 1 Synthetic route of the polymer used in this study.

$\text{PdCl}_2(\text{PPh}_3)_2$ (0.28 g, 0.4 mmol), CuI (0.28 g, 0.5 mmol), PPh_3 (0.56 g, 3.0 mmol) were dissolved in triethylamine (10 ml) and THF (10 ml). The mixture was stirred under nitrogen at 60°C for 8 h, and then cooled to room temperature, followed by extraction with ethyl acetate. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed by evaporation. The product was purified by column chromatography on silica gel (eluent: ethyl acetate:hexane = 1:1) to yield 2.2 g (5.3 mmol, 59%) of yellow powder.

6-[4-[3-methyl-4-(4-cyanophenylethynyl) phenylethynyl] phenoxy]hexyl methacrylate 3T

A solution of methacryloyl chloride (0.5 g, 4.8 mmol) in THF (10 ml) was added dropwise at 0°C to a mixture of **7** (2.0 g, 4.8 mmol), triethylamine (0.5 g, 4.8 mmol), and a trace amount of hydroquinone, and the reaction mixture was stirred at room temperature for 24 h. The solution was poured into saturated aqueous sodium hydrogen carbonate, and the product was extracted with ethyl acetate. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed by evaporation. The crude solid was purified by column chromatography on silica gel (eluent: chloroform) and finally recrystallized from methanol to yield 1.5 g (3.0 mmol, 63%) of white powder. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 1.46–1.54 (m, 8H), 1.58–1.82 (m, 4H), 1.93 (s, 3H), 2.48 (s, 3H), 3.96 (t, $J = 6.3$ Hz, 2H), 4.14 (t, $J = 6.6$ Hz, 2H), 5.53 (s, 3H), 6.80 (s, 3H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.29–7.46 (m, 5H), 7.61 (q, $J = 8.7$ Hz, 4H). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 18.28, 20.52, 25.71, 25.77, 28.53, 29.05, 64.60, 67.84, 87.78, 91.60, 92.59, 92.99, 111.46, 114.55, 114.82, 118.51, 121.46, 124.39, 125.23, 128.25, 128.72, 131.93, 131.98, 132.07, 132.40, 133.09, 136.47, 140.44, 159.34, 167.52. Anal. Calcd for $\text{C}_{34}\text{H}_{31}\text{NO}_3$: C, 81.40; H, 6.23; N, 2.79. Found: C, 81.23; H, 6.35; N, 2.91.

Copolymerization

The procedure for copolymerization of **P3T-A** is shown in Scheme 1. **3T** (0.9 g, 2.5 mmol), **M6AB2** (0.1 g, 0.28 mmol) and AIBN (0.05 g, 2.8 μmol) were dissolved in dry DMF (5 ml) in a sealed tube and kept at 60°C for 48 h. The resulting solution was cooled to room temperature and poured into 400 ml of methanol with vigorously stirring to precipitate the polymer. The polymer obtained was purified by repeated reprecipitation from DMF into a large excess of methanol and dried under vacuum to yield 0.80 g of **P3T-A** in 80% conversion.

Preparation of Films

P3AT was dissolved in chloroform, and then a small portion of the resultant solution was cast on a polyimide-coated glass substrate, which had been rubbed to align mesogens. Homogeneously aligned films were obtained after annealing at 200°C for 30 min. Thickness of the sample films was measured as 400 nm with a surface profiler (Veeco Instruments Inc., Dektak 3ST). This film was used for the investigation of the photoinduced alignment change.

Optical Setup and Experimental Conditions

Photoinduced alignment change of LCPs was investigated by the following procedure. The polymer film was irradiated with linearly polarized light at 488 nm from an Ar⁺ laser in a glassy state. The direction of the polarization of light was parallel to the aligned direction of mesogens, i.e., *s*-polarization. Intensity of the probe light at 633 nm from a He-Ne laser (NEC, GLC5370, 1 mW) transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode.

RESULTS AND DISCUSSION

Characterization of Polymers

Figure 1 shows the ¹H NMR spectrum for the copolymer **P3T-A**. From the peak assignments, the composition of the copolymer can easily be calculated.

The phase transition behavior of **P3T-A** was investigated by means of DSC and polarizing optical microscopy. From the third heating curves of DSC, glass transition and an endothermic peak were observed at 48°C and 210°C, respectively. Since the LC phase showed typical Shlieren texture (Fig. 2), we concluded that **P3T-A** exhibited a nematic phase between 48°C and 250°C, which is a much wider temperature range than that of conventional LCPs without 3-ring tolane moiety or an azo-tolane moiety. The structures and thermodynamic properties of the LCPs used in this study are shown in Figure 3.

Photoisomerization of LCPs

We attempted the *trans-cis* photoisomerization of the azobenzene moiety in the side chain of **P3AT** and **P3T-A** upon irradiation at 366 nm, which roughly corresponds to the absorption band of normal *trans* azobenzene moieties (Fig. 4). As shown in Figure 4(a), **P3AT**

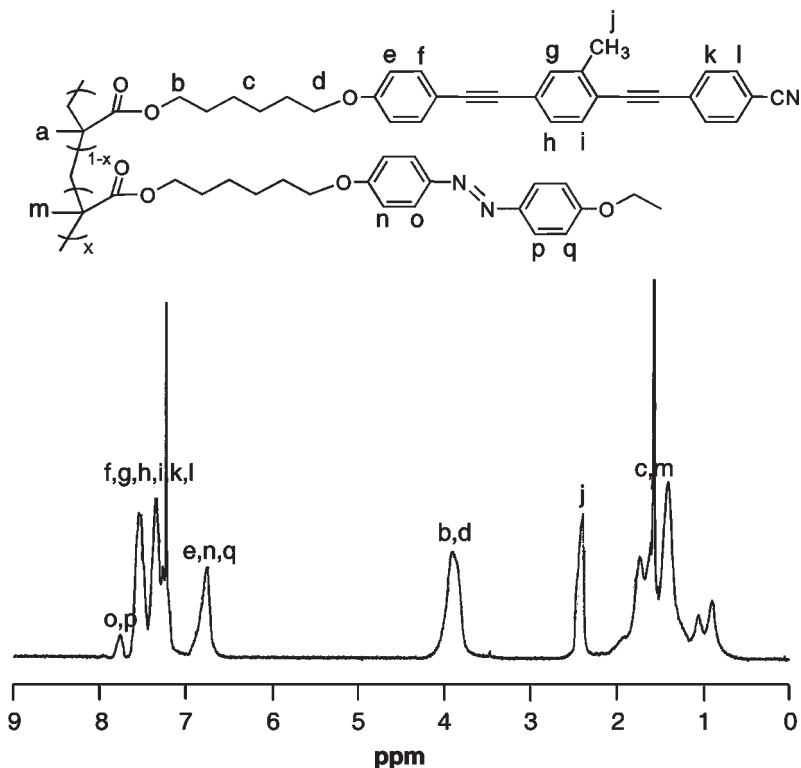


FIGURE 1 ^1H NMR spectrum for the copolymer **P3T-A**.

exhibited strong absorption around 400 nm, which may be attributed to the π - π^* transition band of the *trans*-azobenzene moiety (λ_{max} at 379 nm in DMF). This absorption rapidly decreased upon irradiation at 366 nm. The isosbestic points were observed at 337 nm and 463 nm. These spectral changes clearly indicate that the azobenzene moieties underwent the *trans-cis* isomerization. Furthermore, we evaluated the ratio of *cis*-azobenzene moieties at the photostationary state by the following equation:

$$S = (A_0 - A_t)/A_0 \times 100$$

where A_0 and A_t are absorbance at λ_{max} before and after irradiation, respectively. It was found that about 60% of *cis*-azobenzene moieties were produced at the photostationary state.

In **P3T-A**, on the other hand, no change in the spectra was recognized under irradiation (Fig. 4(b)). This is probably because the

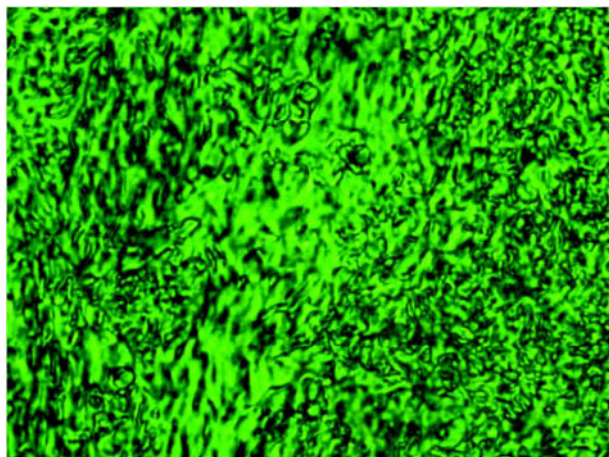
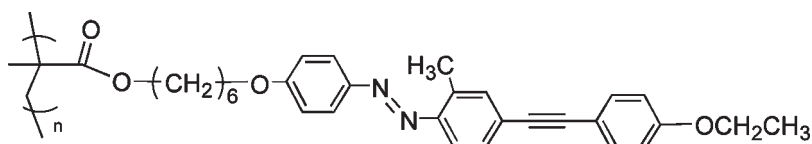
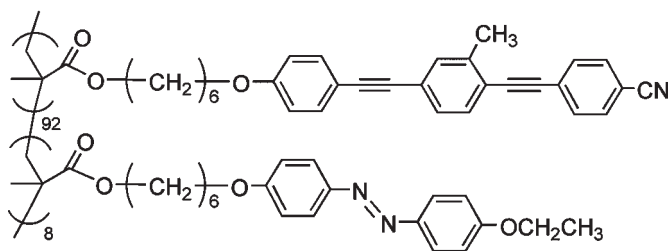


FIGURE 2 Polarizing optical micrograph of the texture of **P3T-A** at 200°C.



P3AT

$M_n = 21,000$; $M_w/M_n = 3.9$
G 47 N 220 I



P3T-A

$M_n = 24,000$; $M_w/M_n = 1.8$
G 48 N 250 I

FIGURE 3 Chemical structure and properties of **P3AT** and **P3T-A** used in this study. M_n , number-average molecular weight; M_w , weight-average molecular weight; G, glass; N, nematic; I, isotropic phase.

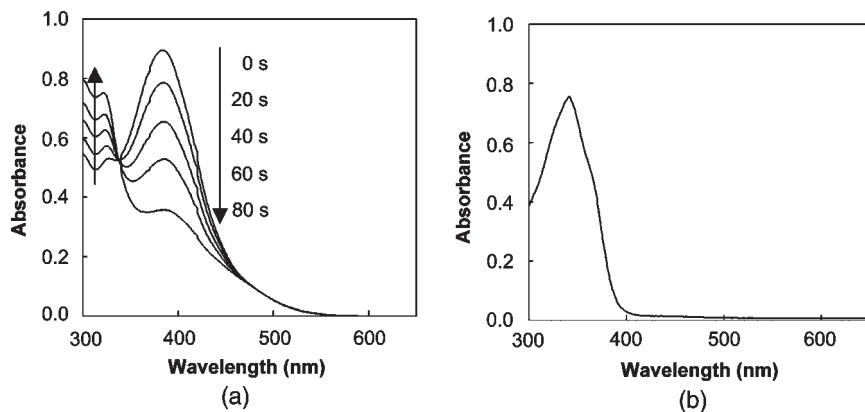


FIGURE 4 Change in the absorption spectrum of **P3AT** (a) and **P3T-A** (b) in DMF at 25°C. Times of UV (366 nm) irradiation are indicated in the figure.

absorption of 3-ring tolane moieties (strong absorption around 340 nm) is completely overlapped with the π - π^* transition band of the *trans*-azobenzene moiety.

Change in Alignment of the LCP

As shown in Figure 5, we have estimated the order parameter (S) of the monodomain film by the following equation:

$$S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$$

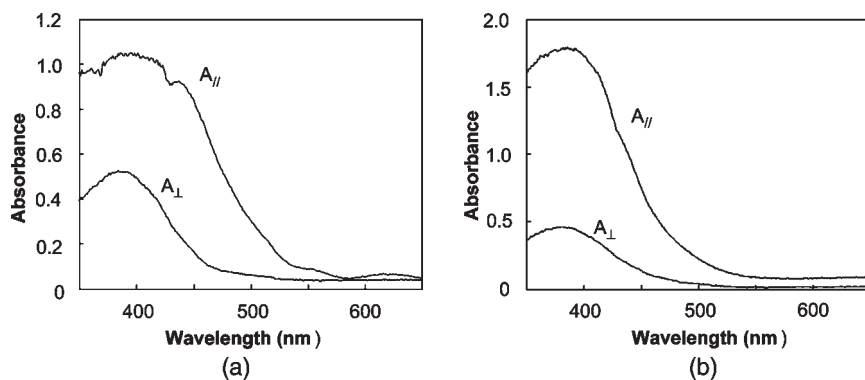


FIGURE 5 Polarized absorption spectra of monodomain films of **P3AT** (a) and **P3T-A** (b).

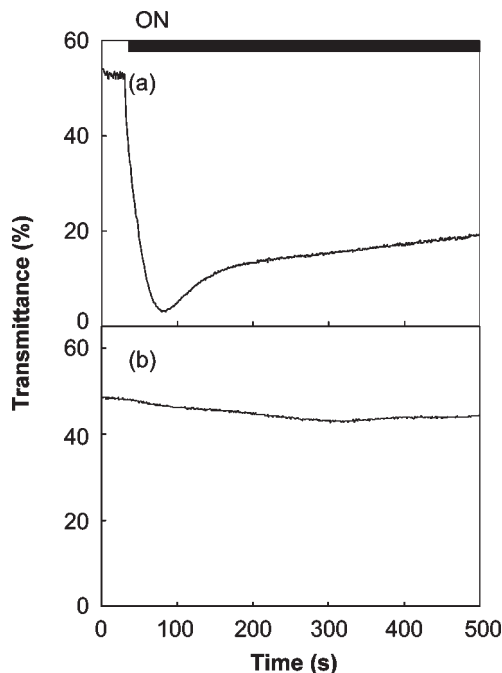


FIGURE 6 Change in transmittance as a function of irradiation time of **P3AT** (a) and **P3T-A** (b). Photoirradiation at 488 nm (250 mW/cm^2) was performed at 80°C .

where A_{\parallel} and A_{\perp} are absorbance parallel and perpendicular to the polarization direction of the irradiation light. The value of S in **P3AT** and **P3T-A** was 0.41 and 0.50, respectively. These monodomain films transmitted the probe light through a pair of crossed polarizers, with the sample film between them, because of the birefringence of the LCPs. From the transmittance (T) of the probe light, we have estimated the values of birefringence (Δn) by using the following equation: [22,23]

$$T = \sin^2(\pi d \Delta n / \lambda)$$

where d is the film thickness and λ is the wavelength of the probe light (633 nm). In the initial state, the calculated values of the LCP films were 0.39 (**P3AT**), and 0.35 (**P3T-A**), respectively. Next, from the change in transmittance, we investigated the photoinduced alignment change in **P3AT** and **P3T-A** (Fig. 6) The transmittance of the probe light decayed upon irradiation of s-polarized light in **P3AT**. This result

indicates that photoinduced alignment change causes the destruction of the initial order of homogeneously aligned azo-tolane moieties, and induces a large change in Δn (≈ 0.35). On the other hand, in **P3T-A**, the reduction of the transmittance was very low. As mentioned above, this result could be assigned to the overlapping of the absorption of tolane moieties with that of the π - π^* transition bands of the *trans*-azobenzene moieties.

CONCLUSION

In this study, we have synthesized two types LCPs containing a tolane moiety and explored the effect of the position of the tolane moiety in the side chain. Both polymers showed a nematic phase in a broad temperature range. The homopolymer containing an azo-tolane moiety showed *trans-cis* photoisomerization reversibly. On the other hand, in the copolymer having an azobenzene moiety and a 3-ring tolane moiety, photoisomerization didn't induced photoisomerization because the absorption of 3-ring tolane moieties was overlapped with the π - π^* transition bands of the *trans*-azobenzene moieties. Despite both LCPs exhibit the large value of Δn (> 0.35), the change in Δn of the homopolymer is much efficiently induced (≈ 0.35) compared with that of the copolymer.

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