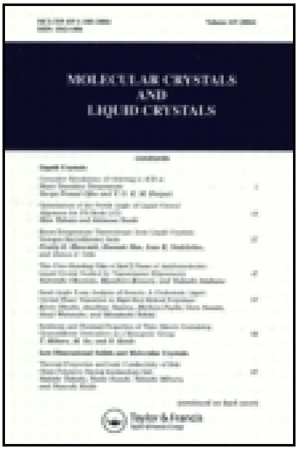

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Synthesis and Photoresponsive Behavior of a Liquid-Crystalline Polymer with a 4-Ring Azotolane Moiety with Huge Birefringence

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A novel liquid-crystalline polymer (LCP) containing an azobenzene group directly connected to a tolane moiety (azotolane moiety) was synthesized. The LCP showed a nematic phase in a broad temperature range (>200°C). Trans-cis *photoisomerization and* cis-trans *thermal isomerization occurred even though the LCP contains a long azotolane moiety. The homogeneously aligned film of the LCP exhibited an extremely large value of* Δn *(0.70 at 633 nm). Upon irradiation with a pumping beam in the LC phase, a large change in* Δn *was induced due to destruction of the homogeneous alignment of the azotolane moieties.*

Keywords: azotolane liquid-crystalline polymer; change in birefringence; high birefringence; photoisomerization

INTRODUCTION

Polymers containing azobenzene in the side chain are promising materials for optical applications because one can induce a change in birefringence (Δn) by photoisomerization [1,2]. A large change in Δn enables a control of incident light effectively, which is very useful and effective for optical materials. To develop a high-performance optical material using azobenzene polymers, it is necessary to induce a large change in Δn by pumping light. In azobenzene polymers, two processes of the change in Δn have been reported: reorientation of azobenzene moieties upon irradiation of isotropic films with polarized pumping light (disorder-order change) [3,4] and destruction of homogeneous

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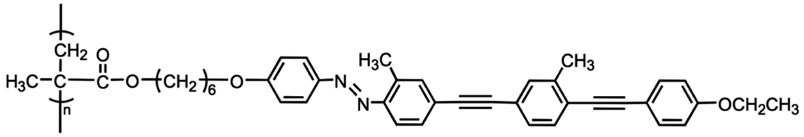


P4ATT

$M_n = 32{,}000$; $M_w/M_n = 1.8$

G 46 N >250

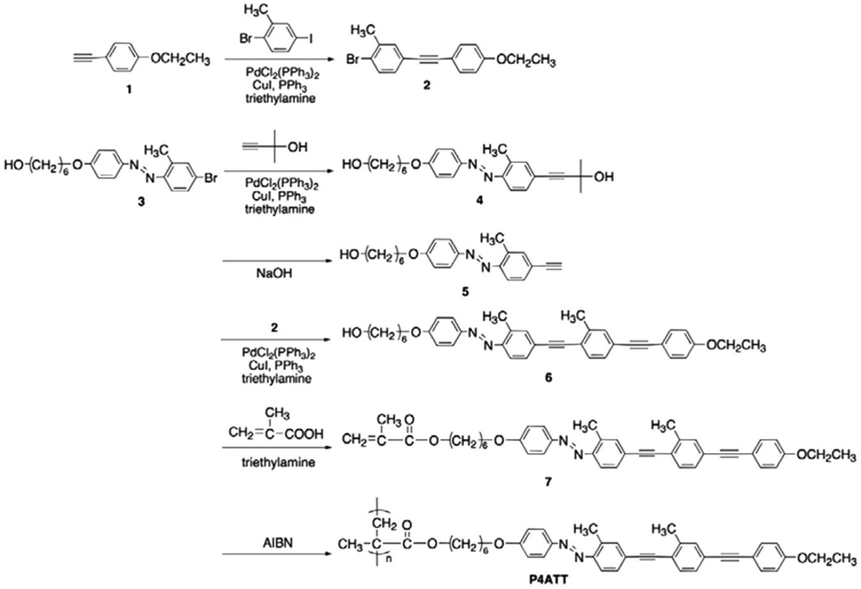
FIGURE 1 Chemical structure and properties of the LC used in this study. M_n, number-average molecular weight; M_w, weight-average molecular weight; N, nematic; G, glassy.

alignment of mesogenic azobenzenes by photochemical phase transition (order-disorder change) [5]. Actually, Atwater *et al.* have shown that a large value of Δn up to 0.56 at 660 nm is induced by the reorientation of an azobenzene moiety [6]. Moreover, Bieringer *et al.* focused on high-density optical data storage by using an amorphous azobenzene polymer [7]. On the other hand, we have performed so far systematic studies on the nematic-isotropic phase transition of azobenzene liquid-crystalline polymers (LCPs). An advantage of the azobenzene LCPs is the fact that a large change in Δn is induced quickly by photoisomerization of the azobenzene moieties. Based on this idea, we have proposed a new molecular architecture, LCPs containing an azotolane moiety in the side chain, to induce a large change in Δn upon irradiation of light [8]. In the molecular design, an azobenzene is photoresponsive group and a tolane is a highly birefringent moiety. In fact, Gauza *et al.* reported that long π-conjugated tolane derivatives show extremely high Δn (0.7–0.8) [9]. Azotolane LCP films exhibit high Δn in the homogeneously aligned state, and show a large change in Δn by destruction of the alignment by *trans*-*cis* photoisomerization of the azobenzene. Recently, we have developed an LCP containing a longer azotolane moiety (4-ring azotlane) which exhibits an extremely high value of Δn in the homogeneously aligned state [10]. In this study, we have synthesized a novel LCP with a 4-ring azotolane moiety (Fig. 1) and investigated its photoresponsive behavior. In analogy with previous studies [11,12], we expected that the alkyl side chain in the azotolane moiety improves stability of an LC phase.

EXPERIMENTAL

Materials

Unless otherwise noted, all commercial reagents were used as received. DMF and toluene used in polymerization were dried over



SCHEME 1 Synthetic procedure of P4ATT.

CaH_2 and freshly distilled prior to use. Compounds **1** and **3** were prepared according to the previously reported procedure [8(a), (b)]. Synthesis of **P4ATT** is outlined in Scheme 1.

2-Methyl-4-(4-ethoxyphenylethynyl)bromobenzene (2). Compound **1** (2.9 g, 20 mmol), 5-bromo-2-iodotoluene (7.4 g, 25 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 1.0 mmol), CuI (0.70 g, 0.37 mmol), PPh_3 (1.4 g, 5.3 mmol) were dissolved in triethylamine (30 mL) and THF (50 mL). The mixture was stirred at 60°C for 8 h under nitrogen atmosphere. The resulting solution was cooled to room temperature and extracted 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 (silica gel, ethyl acetate: hexane = 1:3 as eluent) to yield 4.5 g (72%) of yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 1.38 (t, $J = 6.9$ Hz, 3H), 2.38 (s, 3H), 3.97 (q, $J = 6.9$ Hz, 2H), 6.75 (d, $J = 9.0$ Hz, 2H), 6.98 (d, $J = 8.4$ Hz, 1H), 7.34 (d, $J = 9.0$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H).

4′-(3-Hydroxy-3-methyl-1-butynyl)-2′-methyl-4-(6-hydroxyhexyloxy)-azobenzene (4). Compound **3** (10 g, 26 mmol), 2-methyl-3-butyn-2-ol (3.9 g, 50 mmol), $PdCl_2(PPh_3)_2$ (0.60 g, 0.85 mmol), CuI (0.60 g, 3.3 mmol), PPh_3 (1.1 g, 4.3 mmol) were dissolved in triethylamine

(40 mL) and THF (60 mL). The mixture was stirred at 60°C for 8 h under nitrogen atmosphere. The resulting solution was cooled to room temperature and extracted 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 (silica gel, ethyl acetate: hexane = 1:1 as eluent) to yield 7.5 g (73%) of a brown solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.40–1.85 (m, 14H), 2.64 (s, 3H), 3.66 (t, $J = 6.6$ Hz, 2H), 4.03 (m, 2H), 6.98 (d, $J = 8.9$ Hz, 2H), 7.26–7.56 (m, 3H), 7.88 (d, $J = 8.7$ Hz, 2H).

4′-Ethynyl-2′-methyl-4-(6-hydroxyhexyloxy)azobenzene (5). A solution of compound **4** (7.0 g, 18 mmol) and NaOH (0.5 g) in toluene was stirred for 3 h at 100°C under nitrogen. The product was purified by column chromatography (silica gel, ethyl acetate:hexane = 1:1 as eluent) to yield 4.3 g (62%) of orange powder. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.47–1.85 (m, 8H), 2.65 (s, 3H), 3.84 (t, $J = 6.6$ Hz, 2H), 3.15 (s, 1H), 4.03–4.09 (m, 4H), 6.98 (d, $J = 9.0$ Hz, 2H), 7.34–7.66 (m, 3H), 7.89 (d, $J = 9.0$ Hz, 2H).

2′-Methyl-4′-[4-(4-ethoxyphenylethynyl)-2-methylphenylethynyl]-4-(6-hydroxyhexyloxy)azobenzene (6). Compound **5** (1.5 g, 4.5 mmol), **2** (1.6 g, 5.0 mmol), $PdCl_2(PPh_3)_2$ (0.18 g, 0.25 mmol), CuI (0.18 g, 0.92 mmol), PPh_3 (0.33 g, 1.3 mmol) were dissolved in triethylamine (20 mL) and THF (30 mL). The mixture was stirred at 60°C for 8 h under nitrogen atmosphere. The resulting solution was cooled to room temperature and extracted 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 (silica gel, ethyl acetate: hexane = 1:1 as eluent) to yield 1.0 g (39%) of an orange solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.38–1.85 (m, 11H), 2.49 (s, 3H), 2.69 (s, 3H), 3.72 (t, $J = 6.6$ Hz, 2H), 3.98–4.05 (m, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 7.31–7.64 (m, 8H), 7.89 (d, $J = 9.0$ Hz, 2H).

6-[4-[2-Methyl-4-[2-methyl-4-(4-ethoxyphenylethynyl)phenylethynyl]-phenylazo]phenoxy]hexyl methacrylate (7). A solution of methacryloyl chloride (0.60 g, 6.0 mmol) in THF (30 mL) was added dropwise at 0°C to a mixture of compound **6** (1.0 g, 1.8 mmol), triethylamine (0.60 g, 6.1 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 (silica gel, chloroform as eluent) and finally recrystallized from the mixture of chloroform and hexane (1:1) to yield 0.51 g (44%) of an orange solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.39–1.83 (m, 11H), 1.93 (s, 3H), 2.49 (s, 3H), 2.68 (s, 3H), 4.01–4.18 (m, 6H), 5.53 (s, 1H), 6.09 (s, 1H), 6.86 (d, $J = 9.0$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 7.31–7.62 (m, 8H), 7.88 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR: 14.71, 17.36, 18.27, 20.55, 25.69, 25.76, 28.52, 29.04, 63.80, 64.57, 67.83, 86.76, 90.81, 91.29, 95.37, 114.55, 114.67, 115.18, 115.50, 122.42, 123.62, 124.90, 125.17, 128.69, 128.80, 129.75, 131.53, 132.44, 132.89, 132.95, 134.22, 136.47, 137.65, 141.84, 147.38, 150.15, 159.25, 161.53, 167.43. MS (FAB): 639 (MH^+). Anal. Calcd for $C_{42}H_{42}N_2O_4$: C, 78.97; H, 6.63; N, 4.38. Found: C, 78.81; H, 6.44; N, 4.29.

Polymerization of monomer 7. Compound **7** (0.47 g, 0.73 mmol) and AIBN (1.0 mg, 7.3 μmol) were dissolved in dry DMF (5 mL) and placed in a polymerization tube. After several freeze-pump-thaw cycles, the tube was sealed under high vacuum. Then, the tube was kept at 60°C for 48 h. The resulting solution was cooled to room temperature and poured into 100 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 for 48 h to yield 0.24 g of compound **P4ATT** in 51% conversion.

Characterization of LCP

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Lambda-300 spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to internal standard $CDCl_3$ ($\delta = 7.24$ and 77.0), and listed as chemical shifts in ppm (δ). Mass spectra were obtained with a JMS-700 spectrometer with fast atom bombardment (FAB). 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 the LCP were determined with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a scanning rate of 10°C/min. At least three scans were performed for each sample to check the reproducibility. Wide angle X-ray diffraction (WAXD) were measured by X-ray diffractometry (MAC Science MXP, model 5301; Cu Kα 1 radiation from a 1.6 kW anode X-ray generator) at different temperatures with a horizontal sample holder. Absorption spectra were recorded with a UV-vis absorption spectrometer (JASCO, V-550).

Preparation of LCP Films

To obtain an oriented film, **P4ATT** was dissolved in toluene, 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. Thickness of the sample films was measured with a surface profiler (Veeco Instruments Inc., Dektak 3ST) and the surface roughness of the films was within ±5 nm.

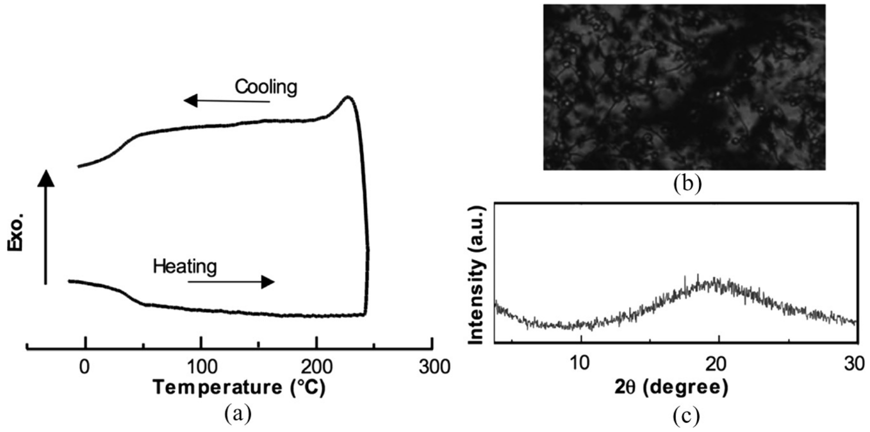
Measurement of the Value of Birefringence

The change in Δn was measured by means of an apparatus already reported [13]. The LCP film was placed in a thermostated block and irradiated at 366 nm with a 500 W high-pressure mercury lamp through glass filters (Asahi Technoglass, UV-D36A + UV-35 + IRA-25). The transmittance of the probe beam from diode lasers at 800 nm and 1550 nm or a He-Ne laser (633 nm) through two crossed polarizers, with the sample between them, was measured with a photodetector.

RESULTS AND DISCUSSION

Characterization of the Polymer

Figure 1 shows the chemical structure, the molecular weight, the molecular weight distribution and the phase transition temperature of the polymer prepared in this study. We measured DSC, polarizing optical microscopy and WAXD (Fig. 2) to characterize the LC properity of the polymer. In the DSC thermogram (Fig. 2(a)), a shift of the base line due to glass transition temperature (T_g) was observed. We observed a schlieren texture in the polymer above T_g (Fig. 2(b)). In the LC phase, the X-ray diffractgram shows a broad hallow about 20° corresponding to average intermolecular distances in azotolane moieties (Fig. 2(c)). From these results, it was found that the polymer showed a very stable nematic (N) phase in a broad temperature range, which is quite advantageous for photonic applications. Since tolane moieties having a long π-conjugation length behave as a long rod-like mesogen, the molecular structure shows a stable LC phase compared with conventional LCs [14]. Therefore, the azotolane moieties can form such a stable LC phase.



(a) (b) (c)

FIGURE 2 Characterization of LC properties of **P4ATT**: (a) DSC thermogram, (b) polarizing micrograph, (c) WAXD pattern.

Trans-cis Photoisomerization Behavior of the Azotolanes

We investigated the *trans-cis* photoisomerization behavior of the azobenzene moiety in the mesogen of **P4ATT** in toluene (Fig. 3). The LCP exhibited strong absorption at 378 nm, which is attributed to a π–π^* transition band of the azobenzene moiety. The absorption of the

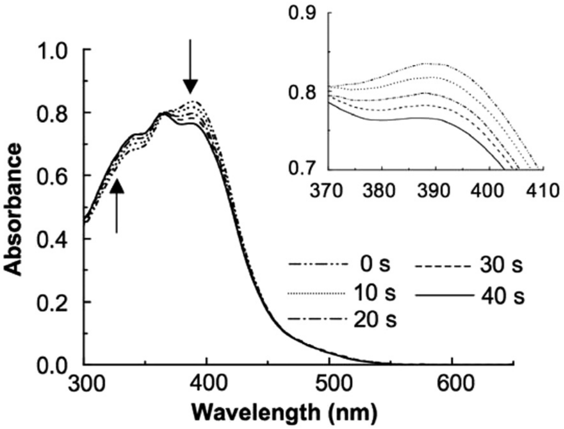


FIGURE 3 Change in absorption spectra of **P4ATT** in *o*-dichlorobenzene (2.4×10^{-5} M) upon irradiation at 366 nm (1.2 mW/cm^2). The inset shows a magnification of the decrease in the π–π^* absorption band of the azobenzene unit.

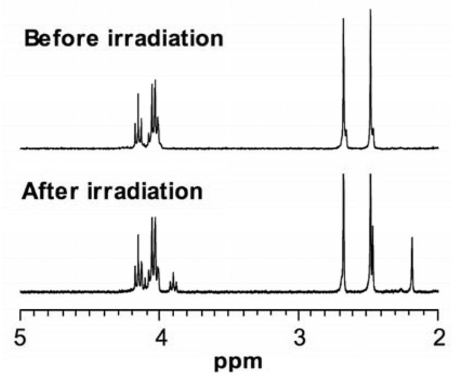


FIGURE 4 ^{1}H NMR spectra of compound **7** before and after photoirradiation at 366 nm.

π–π^* transition band decreased rapidly upon irradiation at 366 nm. When the LCP irradiated at 366 nm was kept in the dark, the absorption completely recovered to the initial state due to thermal *cis-trans* back-isomerization. Furthermore, as shown in Figure 4, their NMR spectra clearly indicated a difference in chemical shift of the methyl protons between *trans*- and *cis*-azobenzenes. The calculated ratio of *cis*-isomers in the photostationary state was estimated to be 26%. When photoirradiation was ceased, the NMR spectra reverted to the initial state. Furtheremore, it was found that the *trans-cis* photoisomerization and *cis-trans* thermal isomerization took place repeatedly without degradation.

The Birefringence Dispersion of the Uniaxially Oriented LCP Film

Probe beams at various wavelengths (633 nm, 800 nm and 1550 nm) were used to evaluate anisotropic properties of the LCP film. The LCP film was placed between a pair of crossed polarizers and the transmittance of these probe beams was carefully measured. One can estimate the value of Δn of the LCP film by Eq. (1) [13]:

$$T = \sin^2 \frac{\pi d \Delta n}{\lambda} \tag{1}$$

where d is the film thickness, Δn is the birefringence of the LCP film, T is the transmittance, and λ is the wavelength of the probe beam. Figure 5 shows the values of Δn at various wavelengths. The value of the order parameter of the LCP film determined by polarized UV

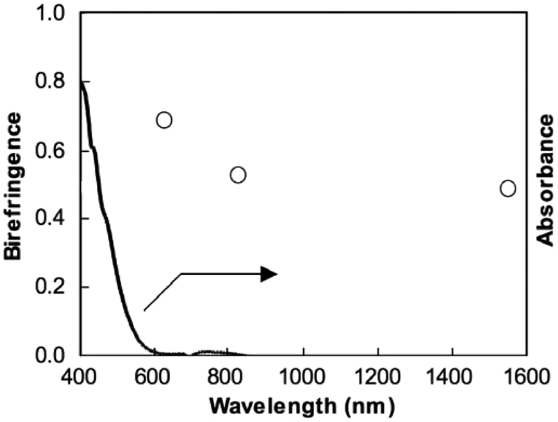


FIGURE 5 Effect of wavelength on the value of birefringence in the **P4ATT** film aligned homogeneously. The wavelengths of probe beams were 633 nm, 830 nm, and 1,550 nm. The absorption spectrum of the LCP film (400 nm–850 nm) is also shown.

absorption spectroscopy was 0.69. The **P4ATT** film showed extremely high values of Δn at any wavelength examined between 633 nm and 1,550 nm. Furthermore, the LCP exhibited ordinary wavelength dispersion of Δn; with a decrease in wavelength the value of Δn increased due to resonant enhancement [15].

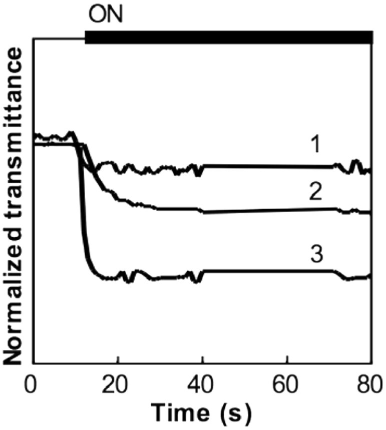


FIGURE 6 Photoinduced change in transmittance of the **P4ATT** film at 150°C. Light intensity of the pump beam: 1, 5 mW/cm^2; 2, 10 mW/cm^2; 3, 30 mW/cm^2.

Change in Alignment of the Azotolane Moiety

Figure 6 shows the change in transmittance at 633 nm upon irradiation of UV light (366 nm). We have measured the change in transmittance as a function of irradiation time with the pumping beam at 5.0 mW/cm^2, 10 mW/cm^2, 30 mW/cm^2 at 150°C. With an increase in the light intensity, a change in transmittance increased. The large change in transmittance was observed with an increase in the intensity of the pumping beam. This change in trancmittance indicates that the photoinduced change in alignment destroys the initial order of the azotolane moieties.

CONCLUSIONS

In this study, we have synthesized a novel azotolane LCP and investigated its photoresponsive behavior. The homogeneously aligned LCP film showed an extremely high value of Δn in the wide wavelength range. Furthermore, we have explored the photoinduced alignment change in azotolane moieties with a large change in Δn. The LCP, in which a very large change in Δn can be induced in the 633 nm–1550 nm wavelength range, is promising for photonic device applications such as optical memory and optical switching.

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