

Synthesis of an Azobenzene-containing Main-chain Crystalline Polymer and Photodeformation Behaviors of Its Supramolecular Hydrogen-bonded Fibers

Zheng-Zheng Wang and Hui-Qi Zhang*

State Key Laboratory of Medicinal Chemical Biology, Key Laboratory of Functional Polymer Materials (Ministry of Education), Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), and College of Chemistry, Nankai University, Tianjin 300071, China

 Electronic Supplementary Information

Abstract The synthesis of a new azobenzene (azo)-containing main-chain crystalline polymer with reactive secondary amino groups in its backbone and photodeformation behaviors of its supramolecular hydrogen-bonded fibers are described. This main-chain azo polymer (namely Azo-MP6) was prepared *via* first the synthesis of a diacrylate-type azo monomer and its subsequent Michael addition copolymerization with *trans*-1,4-cyclohexanediamine under a mild reaction condition. Azo-MP6 was found to have a linear main-chain chemical structure instead of a branched one, as verified by comparing its ¹H-NMR spectrum with that of the azo polymer prepared *via* the polymer analogous reaction of Azo-MP6 with acetic anhydride. The thermal stability, phase transition behavior, and photoresponsivity of Azo-MP6 were characterized with TGA, DSC, POM, XRD, and UV-Vis spectroscopy. The experimental results revealed that it had good thermal stability, low glass transition temperature, broad crystalline phase temperature range, and highly reversible photoresponsivity. Physically crosslinked supramolecular hydrogen-bonded fibers with good mechanical properties and a high alignment order of azo mesogens were readily fabricated from Azo-MP6 by using the simple melt spinning method, and they could show “reversible” photoinduced bending under the same UV light irradiation and good anti-fatigue properties.

Keywords Main-chain azobenzene polymer; Crystalline polymer; Michael addition polymerization; Physically crosslinked network; Photodeformation

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INTRODUCTION

Photodeformable azobenzene (azo)-containing polymers (in brief, azo polymers) have drawn great attention in recent years because of their great potential in photo-driven artificial muscles, photomechanical actuators, and microfluidic devices.^[1–7] The photodeformation of such azo polymers stems from the collective microscopic movement of photoresponsive azo moieties (*i.e.*, the rapid and reversible photoisomerization of *trans*- and *cis*-azo isomers) under the illumination of UV and visible light, which can bring about significantly different structural conformations and volumes of azo units and the simultaneous structural reconfiguration of the surrounding polymer chains, thus leading to rapid, precise, and remote conversion of light energy into mechanical power and photo-driven macroscopic motion.

To date, a great number of photodeformable azo polymers have been developed,^[1–7] and the presence of appropriate

crosslinking degrees in these azo polymer systems has proven to be indispensable for spreading the microscopic forces produced by the photoisomerization of azo groups to the whole system so as to exert reversible macroscopic photomechanical effects.^[4] According to the location of azo groups in the polymer chains, photodeformable azo polymers can be mainly divided into side-chain type and main-chain type.^[2,5] It has been well established that in comparison with side-chain azo polymers, main-chain azo polymers normally have better thermal and mechanical properties, and particularly, they possess much stronger chain anisotropy and higher coupling ability between the azo mesogens and polymer chains, which can impart them with largely improved photomechanical properties.^[2] Despite significant progress made in the field of photodeformable azo polymers, the development of photodeformable main-chain azo polymers remains a challenging task, mainly because of the rather complicated synthesis of main-chain azo polymers with crosslinkable groups.^[8] Recently, we have reported the successful preparation of a series of azo-containing main-chain liquid crystalline polymers (LCPs) with secondary amino^[8] or amide^[9] groups in their backbones (*via* Michael addition polymeriza-

* Corresponding author, E-mail: zhanghuiqi@nankai.edu.cn

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tion and Michael addition-amidation cooperative polymerization, respectively) and the fabrication of their physically cross-linked photodeformable fibers through the simple melt spinning method. The hydrogen bonds formed among the secondary amino or amide groups of these main-chain azo LCPs play a decisive role in the photomobility of their uniaxially oriented fibers. Such supramolecular hydrogen-bonded main-chain azo polymer fibers could exhibit much higher mechanical strength and more rapid photoinduced bending than many physically and chemically crosslinked photomobile side-chain LCP systems. In spite of the above encouraging results, rather limited knowledge on the structure-property relationship for such photodeformable main-chain azo polymers has been achieved up to now. Therefore, developing new physically crosslinked photodeformable main-chain azo polymers is of significant importance for gaining more insight into this type of photomechanical system and for further fabricating more advanced photodeformable azo polymers.

Herein, we report for the first time the synthesis of a main-chain crystalline azo polymer with secondary amino groups in its backbone and photodeformation behaviors of its physically crosslinked supramolecular hydrogen-bonded fibers. This azo polymer (namely Azo-MP6) was readily prepared *via* first the synthesis of a diacrylate-type azo monomer (*i.e.*, Azo-dA6) and its subsequent Michael addition copolymerization with *trans*-1,4-cyclohexanediamine under a mild reaction condition (Scheme 1a). Its chemical structure, thermal and phase transition behaviors, and photoresponsivity were characterized by using $^1\text{H-NMR}$, TGA, DSC, POM, XRD, and UV-Vis spectroscopy. In addition, the successful fabrication of its supramolecular hydrogen-bonded fibers (by using the simple melt spinning method) with a high alignment order of azo mesogens, good mechanical properties, and “reversible” photode-

formation behaviors was also demonstrated.

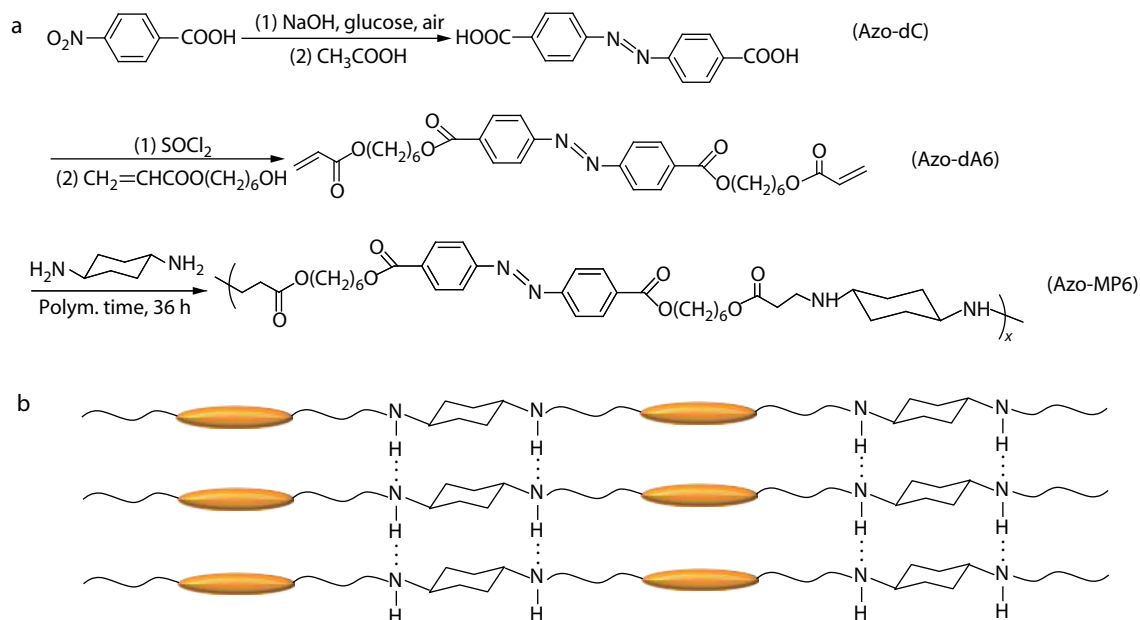
EXPERIMENTAL

Materials

Tetrahydrofuran (THF, Concord Technology (Tianjin) Co., Ltd. China, 99%) was refluxed over sodium and then distilled. Dichloromethane (Tianjin Jiangtian Chemical Technology Co., Ltd. 99%), methanol (Tianjin Jiangtian Chemical Technology Co., Ltd. 99%), ethyl acetate (Tianjin Jiangtian Chemical Technology Co., Ltd. 99%), and chloroform (Tianjin Chemical Reagents Wholesale Co., analytical reagent (AR)) were refluxed over calcium hydride and then distilled. Triethylamine (TEA, Tianjin Jiangtian Chemical Technology Co., Ltd. 99%) was dried with anhydrous sodium sulfate and then distilled. Thionyl chloride (Tianjin Jiangtian Chemical Technology Co., Ltd. 99.5%) was purified by distillation just prior to use. Azobenzene-4,4'-dicarboxylic acid (Azo-dC, Scheme 1a)^[10] and 6-hydroxyhexyl acrylate (Scheme 1a)^[11] were synthesized according to literature methods. All the other chemicals were commercially available and used without further purification.

Synthesis of the Diacrylate-type Azo Monomer Azo-dA6

A mixture of Azo-dC (500.1 mg, 1.85 mmol) and thionyl chloride (5 mL) was refluxed until a clear red solution was obtained. After another 5 h of refluxing, excessive thionyl chloride was removed from the above reaction mixture by distillation under vacuum. The resulting solid was washed with dried dichloromethane thrice and then dissolved in dried THF (20 mL). To the above solution was added 6-hydroxyhexyl acrylate (955.1 mg, 5.55 mmol) and TEA (1.85 mL, 13.3 mmol) successively. After magnetically stirred at room temperature for 20 h, the reaction mixture was filtered and the solvent of the filtrate was removed by using a rotary evaporator. The resulting solid was purified by



Scheme 1 (a) Synthetic route and chemical structures of the diacrylate-type azo monomer (Azo-dA6) and its main-chain azo polymer (Azo-MP6) prepared *via* Michael addition polymerization; (b) Schematic illustration of the physically crosslinked supramolecular hydrogen-bonded networks formed in the uniaxially oriented fiber of Azo-MP6.

silica gel column chromatography with a mixture of dichloromethane, petroleum ether (boiling point range: 60–90 °C), and ethyl acetate (20:10:1, V:V:V) as the eluent to afford an orange-yellow product (yield: 60%); melting point: 84–85 °C (determined by a polarizing optical microscope (POM) at a heating rate of 10 °C·min⁻¹); UV-Vis (DMF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 330 (36920), around 440 (not available due to the overlap of the absorption bands). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 8.24–8.18 (d, 4H, Ar–H), 8.03–7.96 (d, 4H, Ar–H), 6.43–6.36 (d, 2H, CH=C–COO–), 6.16–6.07 (dd, 2H, C=CH–COO–), 5.84–5.78 (d, 2H, CH=C–COO–), 4.41–4.33 (t, 4H, Ar–COOCH₂–), 4.22–4.15 (t, 4H, C=C–COOCH₂–), 1.88–1.44 (m, 16H, –(CH₂)₄–).

Synthesis of the Main-chain Azo Polymer Azo-MP6

To a solution of Azo-dA6 (100.1 mg, 0.173 mmol) in chloroform (3 mL) was added dropwise a solution of *trans*-1,4-cyclohexanediamine (19.7 mg, 0.173 mmol) in methanol (1 mL). After magnetically stirred at 40 °C for 36 h, the reaction mixture was cooled to room temperature and then precipitated into diethyl ether. The precipitate was filtered and the obtained solid was washed with diethyl ether until no monomer was detected with thin layer chromatography. Finally, the product was dried at 40 °C under a vacuum to a constant weight to afford the orange-yellow main-chain azo polymer (yield: 45 %).

Polymer Analogous Reaction of Azo-MP6 with Acetic Anhydride

To a solution of Azo-MP6 (29.9 mg, containing 0.043 mmol of repeat unit) in dried chloroform (2 mL) was added acetic anhydride (200 μL , 2 mmol). After the reaction mixture was magnetically stirred at 25 °C for 5 h, the resulting solution was poured into diethyl ether (20 mL). The precipitate was collected through centrifugation, thoroughly washed with diethyl ether, and then dried at 40 °C under a vacuum to a constant weight, which gave the orange-yellow acetic anhydride-modified Azo-MP6 (or briefly Azo-MP6-Am) (yield: 95%).

Fabrication of Azo-MP6 Fibers

The simple melt spinning method was used to produce uniaxially oriented Azo-MP6 fibers according to the following procedure: 2 mg of Azo-MP6 was heated to 120 °C on a clean glass slide placed on a hot stage (IKA, C-MAG HP7), which was kept at that temperature until it became fully melted. The azo polymer fibers were then drawn by dipping the tip of a metallic tweezer into the melt sample and pulling it quickly.

Characterization

¹H-NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer.

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 instrument in a nitrogen atmosphere at a heating rate of 10 °C·min⁻¹.

Differential scanning calorimetry (DSC, Netzsch 200 F3) was used to study the phase transitions of the azo polymer at a heating/cooling rate of 10 °C·min⁻¹ under nitrogen. The temperature and heat flow scale were calibrated with standard materials including indium (70–190 °C), tin (150–270 °C), zinc (350–450 °C), bismuth (190–310 °C), and mercury (–100–0 °C) in different temperature ranges. The glass transition temperatures (T_g) of the azo polymer were determined as the step change midpoints of the heat capacities, while the phase

transition temperatures were measured from the maximum/minimum of the endothermic/exothermic peaks.

An Olympus BX51 POM (with crossed polarizer and analyzer) was used to characterize the melting point of the azo monomer, the crystalline texture of the azo polymer, and the alignment state of the polymer fiber, which was equipped with a Linksys 32 THMSE600 hot stage and a digital camera (Micropublisher 5.0 RTV).

X-ray diffraction (XRD) spectrum of the azo polymer was recorded on a Rigaku Miniflex-600 X-ray diffractometer at room temperature. The measured 2θ ranged from 2° to 30° and the scanning rate was 2 (°)·min⁻¹. Sample preparation for the above measurement involved first heating the azo polymer above its melting point (+10 °C·min⁻¹), cooling to 50 °C (–10 °C·min⁻¹), holding at 50 °C for 3 h, and then putting it into liquid nitrogen to preserve its phase structure.

A UV-Vis scanning spectrophotometer (TU1900, Beijing Purkinje General Instrument Co., Ltd.) was used to obtain the UV-Vis spectra of the studied azo monomer and polymer solutions at 25 °C. Photochemical isomerization of the polymer solution was investigated by irradiating it first with a 365 nm UV lamp (12 W) until the photostationary state was reached and then with a 450 nm visible light lamp (18 W, wavelength range 400–550 nm, $\lambda_{\text{max}} = 450 \text{ nm}$).

Mechanical properties of one representative Azo-MP6 fiber were studied at ambient temperature by using an automatic single fiber tensile strength tester (YM-06A, Laizhou, China).

Photodeformation behaviors of the azo polymer fibers were studied as follows. The polymer fibers were pasted onto an aluminum block, whose temperature could be adjusted by using a hot stage under the control of a thermocouple (IKA CMAG HP7). The polymer fibers were exposed to 365 nm UV light emitted from a high-pressure mercury lamp (USHIO SP-7) (the distance between the UV light source and the fiber was 4.5 cm). A CCD camera (KBier-1202) was used to record the photoresponsivity of polymer fibers.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Main-chain Azo Polymer Azo-MP6

Michael addition polymerization has proven highly versatile for the design and synthesis of various functional polymers either *via* the homopolymerization of a monomer bearing both an acrylate group and an amino group or *via* the copolymerization of a diacrylate-type monomer with a diamine.^[12] In a previous work, we have successfully prepared a series of azo-containing main-chain LCPs with secondary amino groups in their backbones *via* the homopolymerization of an azo monomer with both a terminal acrylate group and a terminal amino group.^[8] Herein, the new main-chain azo polymer Azo-MP6 was prepared *via* the Michael addition copolymerization of a diacrylate-type azo monomer Azo-dA6 with a diamine (*i.e.*, *trans*-1,4-cyclohexanediamine) (Scheme 1a). The synthesis of the diacrylate-type azo monomer Azo-dA6 involved first the preparation of azobenzene-4,4'-dicarboxyl chloride through the reaction of azobenzene-4,4'-dicarboxylic acid (Azo-dC) with thionyl chloride and the subsequent esterification with 6-hydroxyhexyl acrylate. The Michael addition copolymerization of Azo-dA6 with *trans*-1,4-cyclohexanediamine was carried out at a stoichiometric ratio

in a mixture of chloroform and methanol (3:1, V:V) at 40 °C for 36 h. An orange-yellow polymer was readily obtained by pouring the reaction mixture into diethyl ether and thoroughly washing the resulting precipitate with diethyl ether to remove the unreacted monomers. The purity of the diacrylate-type azo monomer Azo-dA6 and the main-chain azo polymer Azo-MP6 was confirmed by both $^1\text{H-NMR}$ (Figs. 1a and 1b) and silica gel column chromatography.

To verify the successful preparation of a linear main-chain azo polymer with only secondary amino groups in its backbone instead of a branched azo polymer with tertiary amino groups in its backbone (owing to the further reaction of secondary amino groups in the azo polymer backbone with the terminal acrylate group of the azo monomer or that of the resulting oligomer), the polymer analogous reaction of Azo-MP6 with acetic anhydride was performed to provide the acetic anhydride-modified Azo-MP6 (or briefly Azo-MP6-Am, Fig. 1c). A detailed comparison of the proton signals from $-\text{CH}_2-$ and $-\text{CH}-$ groups (*i.e.*, protons a and j in the chemical structures of Azo-MP6 and Azo-MP6-Am, Figs. 1b and 1c)

connected with the nitrogen atom in Azo-MP6 and Azo-MP6-Am clearly demonstrated the presence of only a second amino group in the repeat unit of Azo-MP6 instead of a tertiary one, mainly because the above polymer analogous reaction of Azo-MP6 brought about significant and complete shift of these proton signals (Fig. 1c).

The number-average molecular weight ($M_{n,\text{NMR}}$) of Azo-MP6 was derived from its $^1\text{H-NMR}$ spectrum, which was calculated as $7780 \text{ g}\cdot\text{mol}^{-1}$ by comparing the signal integral for one proton in the terminal acrylate group (see the complete structure of Azo-MP6 in Fig. S1 in the electronic supplementary information, ESI) and that for four protons in the aromatic ring in its $^1\text{H-NMR}$ spectrum (Fig. S1 in ESI and Table 1).

The thermal stability and phase transition behaviors of Azo-MP6 were then studied by using TGA, DSC, POM, and XRD. Azo-MP6 was found to have a decomposition temperature of 241 °C (Fig. S2 in ESI, Table 1), demonstrating its good thermal stability. DSC thermograms of Azo-MP6 revealed the existence of one rather small glass transition step ($T_g = 23$ and 42 °C from the DSC first cooling scan and from the second

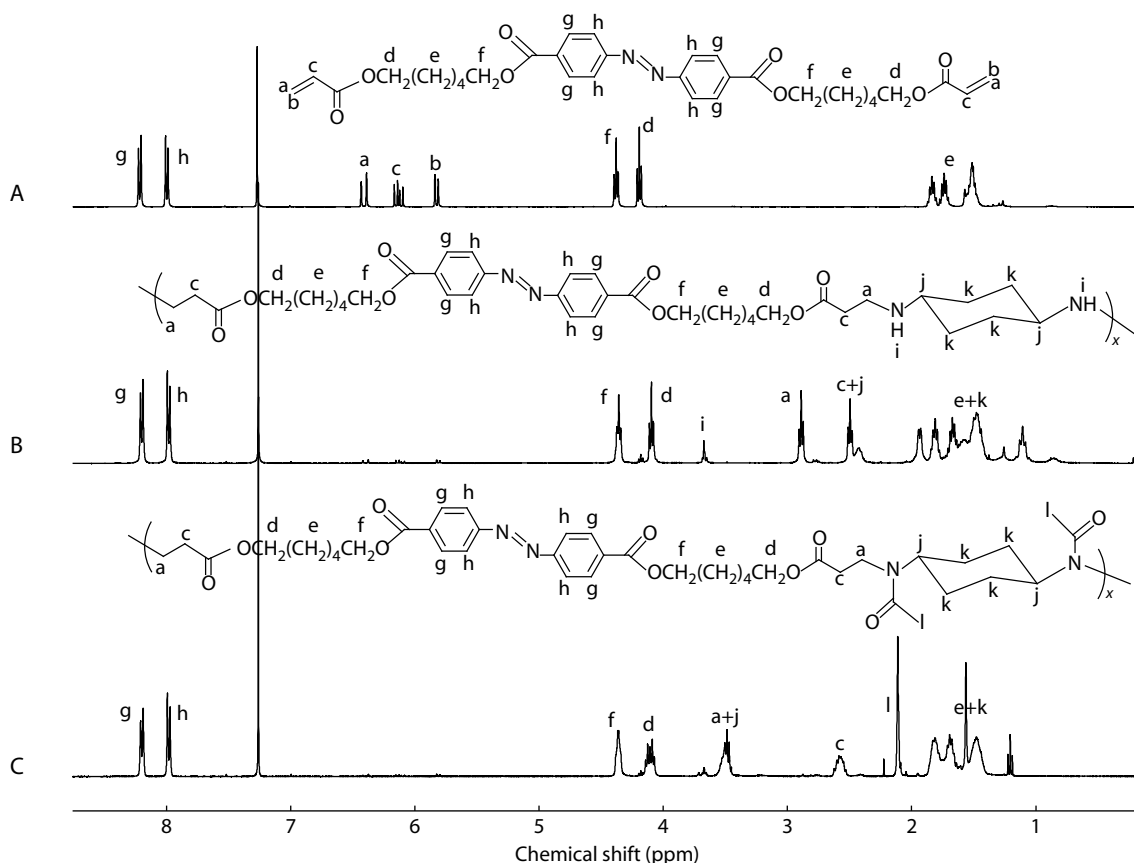


Fig. 1 $^1\text{H-NMR}$ spectra of Azo-dA6 (A), Azo-MP6 (B), and Azo-MP6-Am (C) in CDCl_3 .

Table 1 Synthesis and characterization data of the main-chain crystalline azo polymer.

Sample	Yield (%)	$M_{n,\text{NMR}}^a$ ($\text{g}\cdot\text{mol}^{-1}$)	Thermal transition ^{b} (°C)	ΔH^e ($\text{J}\cdot\text{g}^{-1}$)	$T_{\text{decomp.}}^f$ (°C)
Azo-MP6	45	7780	G 42 Cr 96.4 I ^{c} 170.9 Cr 23 G ^{d}	25 -18	241

^{a} Number-average molecular weight determined by $^1\text{H-NMR}$; ^{b} G = glassy; Cr = crystalline; I = isotropic; ^{c} DSC second heating scan under nitrogen ($+10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$); ^{d} DSC first cooling scan under nitrogen ($-10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$); ^{e} Transition enthalpy between crystalline and isotropic phases; ^{f} The temperature at 5% weight loss of the sample under nitrogen measured by TGA heating experiment ($+10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$).

heating scan, respectively) and one big phase transition peak ($T = 70.9$ and 96.4 °C from the DSC first cooling scan and from the second heating scan, respectively) (Fig. 2). A rather high supercooling degree of the phase transition peaks (i.e., from 96.4 °C (the second heating scan) to 70.9 °C (the first cooling scan)) was observed, suggesting that there might exist a crystalline phase instead of a liquid crystalline phase for Azo-MP6.^[13] This hypothesis was verified by the XRD characterization result of Azo-MP6, which showed several sharp crystal-

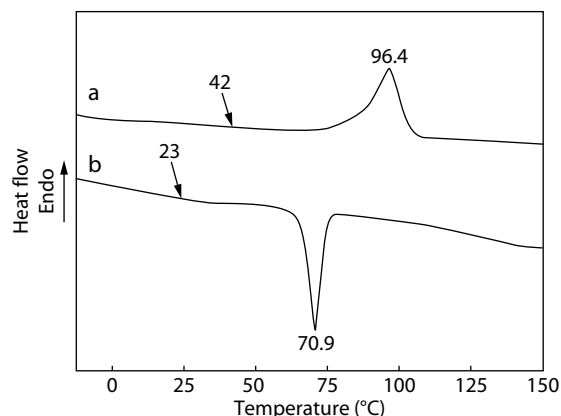


Fig. 2 DSC curves of Azo-MP6 from the second heating scan (a) and from the first cooling scan (b) (± 10 °C·min⁻¹).

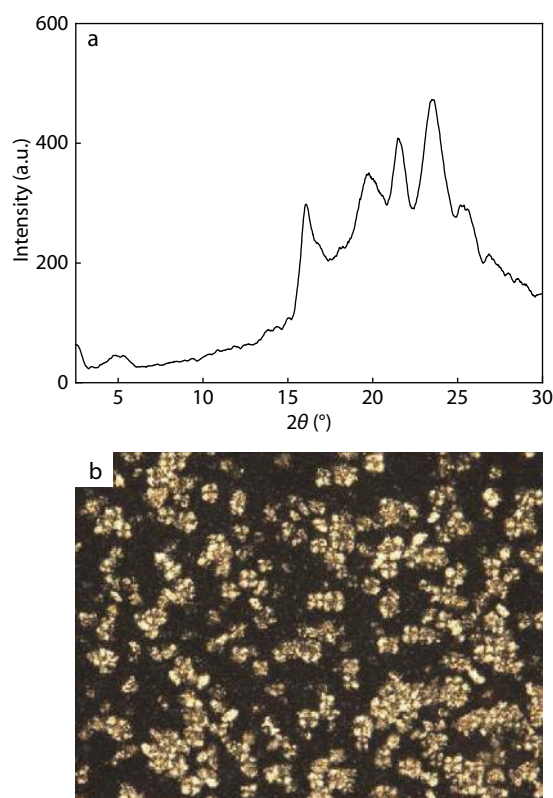


Fig. 3 (a) Wide angle XRD pattern of the main-chain azo polymer Azo-MP6 (which was cooled from the isotropic state to 50 °C and then annealed at 50 °C for 3 h before the XRD measurement); (b) POM image of Azo-MP6 upon cooling from the isotropic state to 50 °C and annealed at 50 °C for 1 h.

line peaks around $2\theta = 20^\circ$ (Fig. 3a). POM observation further confirmed that Azo-MP6 had an enantiotropic crystalline phase with some textures of spherulites (Fig. 3b). Therefore, the phase transition peaks of Azo-MP6 in its first cooling DSC thermogram and second heating DSC thermogram represented the transition between the isotropic phase and crystalline phase and that between the crystalline phase and isotropic phase, respectively. The presence of the crystalline phase for Azo-MP6 should be attributed to its very symmetrical chemical structure (derived from the symmetrical azo monomer Azo-dA6 and *trans*-1,4- cyclohexanediamine).

Figs. 4(a) and 4(b) present the UV-Vis spectral changes depending on time for a diluted Azo-MP6 solution in DMF upon its exposure to UV and visible light. The Azo-MP6 solution exhibited one strong $\pi\text{-}\pi^*$ transition band around 330 nm (from the *trans*-azo isomer) and one rather weak $n\text{-}\pi^*$ transition band around 440 nm (from the *cis*-azo isomer).^[14] Illumination of the azo polymer solution with 365 nm UV light led to a decrease in the absorption band around 330 nm and a simultaneous increase in the absorption band around 440 nm prior to the establishment of the photostationary state, mainly owing to *trans* to *cis* photoisomerization of the azo units (Fig. 4a). Exposure of the above Azo-MP6 solution in a photostationary state to visible light resulted in the occur-

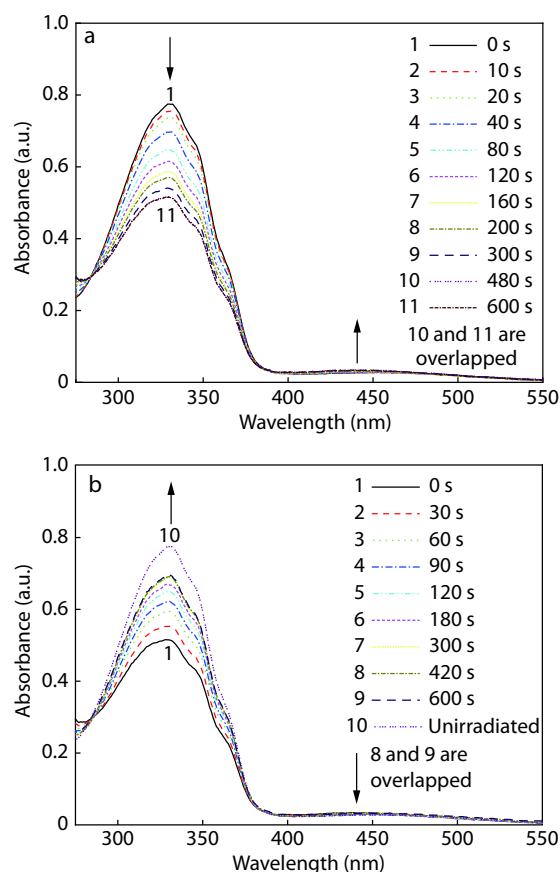


Fig. 4 UV-Vis spectral changes along with time for the diluted Azo-MP6 solution in DMF ($c = 20$ $\mu\text{mol}\cdot\text{L}^{-1}$ repeat unit of Azo-MP6) at 25 °C upon irradiation with 365 nm UV light (a) and irradiation of the Azo-MP6 solution in the photostationary state with visible light (b).

rence of *cis* to *trans* photoisomerization of azo units, but only 89% of the *trans*-isomer was recovered when a new photo-stationary state was reached (Fig. 4b). A similar phenomenon was also observed previously by us^[8,9] and others.^[15,16] Nevertheless, highly reversible *trans/cis* photoisomerization was achieved for the Azo-MP6 solution upon its exposure to the alternative UV and visible light irradiation (Fig. S3 in ESI).

Fabrication of Uniaxially Oriented Fibers of Azo-MP6 and Their Mechanical and Photodeformation Properties

Uniaxially oriented fibers of Azo-MP6 with easily tunable diameters were readily obtained by using the simple melt spinning method following the previously reported method.^[8,9,17–19] Fig. 5 presents the POM texture images of one representative Azo-MP6 fiber. Periodic change in the dark and bright images under the POM (with crossed polarizer and analyzer) was clearly observed upon rotating the fiber sample with respect to the analyzer, demonstrating the high alignment order of azo mesogens along the fiber axis.^[8,9,17–19] This, together with the existence of hydrogen bonding interaction among the secondary amino groups (instead of between —N—H and C=O groups) in azo polymer chains (as confirmed in our previous work^[8]), suggests the formation of the physically crosslinked supramolecular hydrogen-bonded network structure in the uniaxially oriented Azo-MP6 fiber (Scheme 1b).

The stress-strain curve of one representative Azo-MP6 fiber was recorded by using an automatic single fiber tensile

strength tester at ambient temperature to evaluate its mechanical properties (Fig. 6). The Azo-MP6 fiber was found to have a tensile strength (δ_b) and an elastic modulus (G) of 12.2 and 440 MPa, respectively, which are higher than those of the previously reported physically crosslinked photodeformable side-chain LCP fibers (e.g., the δ_b and G values of a physically crosslinked (by hydrogen bonding) side-chain LCP fiber were about 6.1 and 285 MPa, respectively, and the δ_b and G values of its modified fiber with carboxyl-functionalized single-walled carbon nanotube (CNT) were 9.5 and 355 MPa, respectively^[20]) and close to those of the chemically crosslinked photodeformable side-chain LCP films (e.g., the δ_b and G values of a typical chemically crosslinked LCP film were 16 and 400 MPa, respectively^[21]). In this context, it is worth mentioning that the Azo-MP6 fiber showed lower δ_b and G in comparison with those of our previously reported photodeformable supramolecular hydrogen-bonded fiber made from a main-chain azo LCP with secondary amino groups in its backbone (its δ_b and G values were 44 MPa and 5.8 GPa, respectively^[8]), which might be attributed to their different chemical structures and aggregation states (i.e., crystalline state versus liquid crystalline state). For instance, the rapid formation of crystalline structure in the azo polymer fiber during its fabrication (following the quick decrease in temperature from 120 °C to the ambient temperature) might lead to some defects in the oriented fiber and thus its lower δ_b and G .

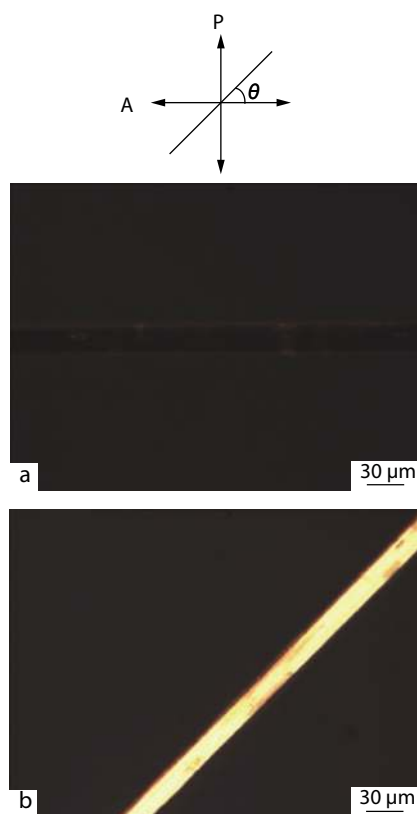


Fig. 5 POM texture images of one representative Azo-MP6 fiber taken at room temperature with sample angle to the analyzer: $\theta = 0^\circ$ (a) and $\theta = 45^\circ$ (b).

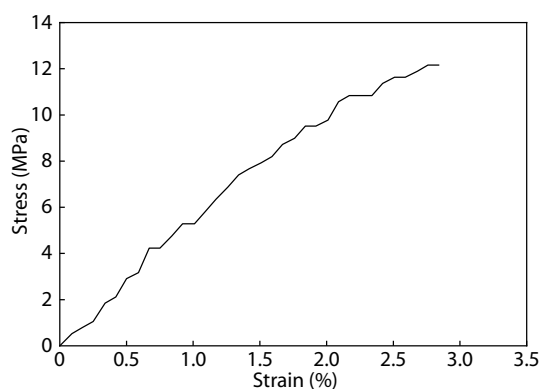


Fig. 6 Stress-strain curve of one representative Azo-MP6 fiber (size: 10 mm × 21 μm) measured at 25 °C.

The photodeformation behaviors of one representative Azo-MP6 fiber were then studied. Part of the azo polymer fiber was pasted onto an aluminum block and the temperature was kept at 40 °C by using a hot stage (Fig. 7a). The experimental results demonstrated that the azo polymer fiber could exhibit photoinduced “reversible” bending upon irradiation with 365 nm UV light from its right and left sides. The fiber bent to the right side along the fiber axis upon its exposure to UV light from the right side of the sample, and the subsequent irradiation with the same UV light from the left side led to bending of the fiber to the left side. The bending time from the right side to the left side was about 120 s. Almost constant bending time and bending angle were observed for the photodeformation of the fiber over 15 cycles (Fig. 7b; such “reversible” photodeformation is also presented in Fig.

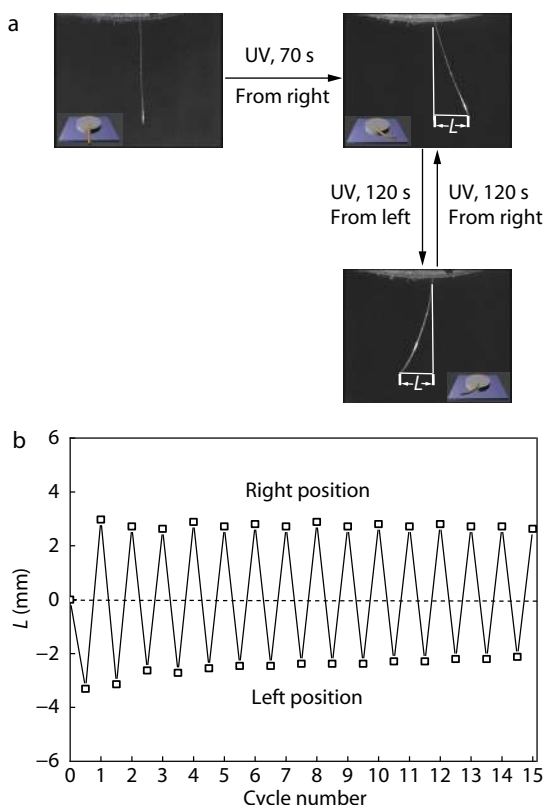


Fig. 7 (a) Photographs of one representative Azo-MP6 fiber that exhibited photoinduced bending behaviors upon irradiation with 365 nm UV light ($150 \text{ mW}\cdot\text{cm}^{-2}$) at 40°C (the size of the fiber is $9 \text{ mm} \times 17 \mu\text{m}$); (b) “Reversible” photodeformation of the representative Azo-MP6 fiber characterized by tracing the bent distance from its straight state at 40°C .

S4 in ESI by changing the bent distance (L) in Fig. 7b to the displacement angle (θ) for the y axis^[22], revealing its good fatigue resistance. Such photoinduced bending toward the incident UV light can be attributed to the switch of the rod-like *trans*-azo isomer aligned parallel to the fiber axis to the bent-shaped *cis*-azo isomer only in the surface region of the azo polymer fiber because of the high concentration of azo groups in the azo polymer fiber and their high UV absorbance (more than 99% incident photons could be absorbed by the irradiated top surface (thickness of less than $1 \mu\text{m}$ below)), and such a gradient in the extent of photoisomerization on azo polymer fiber surface thus led to the reduction of order parameter on the photoirradiated side of the azo polymer fiber surface and the contraction of the irradiated part of the fiber.^[18,23,24] In addition, the occurrence of “reversible” photoinduced bending under the irradiation of UV light alone suggests that the *cis*-azo isomer (formed during the UV light illumination) simultaneously switched back to its *trans* form from the opposite side of the fiber during its photodeformation process. Note that such a unusual “reversible” photodeformation behavior induced by using UV light alone was also previously reported by Peng and co-workers for an azo-containing LCP/carbon nanotube composite system, where the strong interaction between the aligned carbon nanotubes and azo units was found to induce the conformation

change of azo units from their *cis* form to *trans* form when the nanotubes were recovered by the expansion of the opposite side under UV irradiation in structure and shape.^[21] In our case, it might be the combined effect of the main-chain characteristics of Azo-MP6 (the azo units are situated in the polymer backbones) and the presence of both the physically crosslinked supramolecular hydrogen-bonded network and the physical crosslinking network formed by microcrystals in the fiber that induced the rapid switching back of *cis*-azo isomer to *trans*-azo isomer during the expansion of the opposite side of the fiber under UV irradiation.

In this context, it should be interesting to compare the photodeformation properties of this physically crosslinked main-chain azo crystalline polymer with those of our previously reported supramolecular hydrogen-bonded main-chain azo LCPs (with either amide^[9] or secondary amino^[8] groups in their backbones). The fibers prepared from the main-chain azo LCPs exhibited more rapid UV-induced bending than that prepared from the main-chain azo crystalline polymer, which suggests that the presence of crystalline structure in such main-chain azo polymers could have negative influence on their photodeformation performance, just as reported previously by others^[25] (note that photoinduced multi-directional deformation of azo molecular crystals was also demonstrated, but under the UV irradiation with a rather high intensity ($500 \text{ mW}\cdot\text{cm}^{-2}$)^[26]). In addition, while the main-chain azo LCP fibers could exhibit reversible deformation upon irradiation with alternative UV light and visible light, this main-chain azo crystalline polymer (Azo-MP6) fiber only showed “reversible” deformation under the irradiation of UV light alone. The real reason for this phenomenon is not very clear yet, but might be related to the presence of crystalline phase in the formed Azo-MP6 fiber.

CONCLUSIONS

We have demonstrated the successful synthesis of a new azo-benzene-containing main-chain crystalline polymer with secondary amino groups in its backbone *via* Michael addition copolymerization method and photodeformation behaviors of its supramolecular hydrogen-bonded fibers. The obtained azo polymer proved to have a linear main-chain structure, good thermal stability, low glass transition temperature, broad crystalline phase temperature range, and obvious photoresponsivity. Its physically crosslinked supramolecular hydrogen-bonded fibers with good mechanical properties and a high alignment order of azo mesogens were readily fabricated by using the simple melt spinning method, and they could exhibit “reversible” photoinduced bending and good anti-fatigue properties under the same UV light irradiation. Such photodeformable main-chain azo polymer fibers can be recycled for reuse due to their physical crosslinking characteristics.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2302-4>.

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