Liquid–crystal azopolyamides with high thermal stability and inherent viscosity

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Abstract In order to get novel photochromic fiber-forming polyamides with liquid crystal (LC), high inherent viscosity and thermal stability properties, two linear azobenzene polyaramides were synthesized by alternative polycondensation reactions of *trans*-azobenzene-4, 4′-dicarbonyl chloride with various diamine monomers without any substituents under low temperature. As expected, the resulting polyamides exhibit high degree of crystallinity (the highest value reaches 52%), inherent viscosity (the highest value reaches 4.26 dL/g), and thermal stability (≤5% weight loss at 350 °C) due to intensively intermolecular hydrogen bonding and extremely symmetric and rigid molecular structures, which were identified by FT-IR spectroscopy and elemental analysis. Moreover, important liquid crystal and photoisomerization properties for optical devices and photochromics fibers spinning are also observed in N,N-dimethylacetamide (DMAc) solutions due to the regular rigid structure and intermolecular hydrogen bonding. The synthesized azo polyamides are suitable for fiber spinning and can be applied in fields of potential optical techniques and novel anti-ultraviolet and photochromic fibers industry at wide temperature ranges.

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Introduction

Many azobenzene-containing polymers have been studied and applied in optical storage, holographic techniques, and printing and dyeing industry due to their liquid crystalline characteristics, photochromism and chromophoric properties for a long time [1–11]. Further, azobenzene-containing polymer fiber is expected to apply in production of novel anti-ultraviolet and photochromic textile without dyeing, which displays more stable and homogeneous color than conventional product. However, their application is limited due to their poor thermal stability, liquid crystal (LC), and viscosity properties.

High thermal stability and glass transition temperature (T_g) of azo polymers are highly desired in the optical and textile application because their photochromism and photoisomerization properties take place well below decomposed temperature and glass transition temperature [12–14]. Therefore, azobenzene polymers with high thermal stability are urgently required in field of optical devices working at high temperature and wide temperature ranges as well as textile industry.

Aromatic polyamide generally exhibits high thermal stability and T_g as a kind of high-performance fiber-forming polymer in textile industry [14], and a few polyamides bearing azobenzene chromophore have been synthesized so far [15–27]. These polymers are classified into two categories: side-chain-type polymers usually exhibit lower T_g (i.e., 120–180 °C) and amorphous phase due to the steric hindrance of mesogenic moieties in the side chain [12, 23]; main-chain-type polymers demonstrate high thermal stability owing to containing azobenzene mesogenic moieties and some relative rigid groups in macromolecular backbones [16–25]. Although the majority of azo polyamides exhibit excellent photochemical properties under

ultraviolet (UV) irradiation, they are not suitable for fiber spinning due to lack of LC property and high inherent viscosity (>2.0 dL/g).

Liquid crystalline states in polymers are remarkable because of their ability to show spontaneous anisotropy and readily induced orientation, which can be applied in storage of images, electrooptic devices, and even fibers spinning. For example, good quality fibers with a high degree of orientation can be readily obtained from anisotropic solutions due to the natural highly ordered alignment of polyamide chains in the LC state. Moreover, high levels of stiffness and strength of polyamide fibers are also attributed to the high levels of molecular alignment achieved through the spinning of LC solutions of inherently stiff molecules [11]. Therefore, the LC behavior of azobenzene polyamides is of great interest to prepare optical devices and anti-ultraviolet and photochromic fibers. Additionally, high inherent viscosity is also important for electrostatic spinning of polymer fiber in textile industry.

Polymers containing linear rigid-rod mesogenic unit and high-regularity backbone usually possess higher crystallinity, and thermal stability, and are easy to form LC phases [13, 28]. Here we report the synthesis of two azobenzene-containing polyamides by optimal polycondensation between symmetry and rigid monomers. Resulting polyamides exhibit high degree of crystallinity due to molecular structure and intermolecular hydrogen bonding, and hence show higher glass transition temperature and thermal stability when compared with other main-chain azo polymers. Furthermore, as expected, significant lyotropic liquid crystal behaviors of azobenzene polyamides were observed simultaneously in N,N-dimethylacetamide (DMAc) solutions. The synthesized polymers can be applied in field of optical devices working at high temperature and wide temperature ranges due to high thermal stability. Moreover, fairly high inherent viscosity and LC property make it possible to produce novel anti-ultraviolet and photochromic fiber in textile industry by electrostatic spinning technology and a kind of new color fiber without dyeing can be prepared by the process of azobenzene polyamide (AZO-PA).

Experimental

Materials

Anhydrous N,N-dimethylacetamide (DMAc) (Aldrich Chemical Co.) was stored under N_2 over 4A molecular sieves. All other reagents and solvents (>98%) were supplied by Aldrich Chemical Co. and were used without further purification.
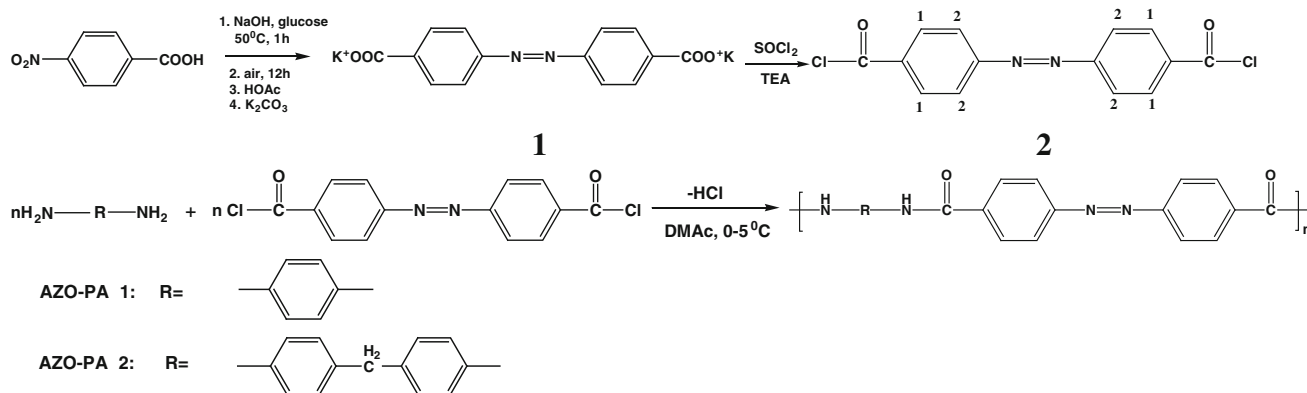
Measurements

Melting points were determined in open capillary tubes with a Kofler melting-point determinator device (China). The heating rate of 2 °C/min was consistently employed. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at 300 MHz on a Bruker DPX-400 instrument (Germany); tetramethylsilane was used as standard and deuterated chloroform ($CDCl_3$) was used as solvent. Infrared (IR) spectra were recorded by a Perkin-Elmer 782 series Fourier transform infrared spectrophotometer (American). Spectra of solids were performed using KBr tablets. UV–visible (UV–Vis) spectra were obtained with a Jin Dao UV-2550 UV–Vis spectrophotometer (Japan). Thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed with a Perkin-Elmer DSC 7E instrument (American). Polymer samples were heated at a rate of 10 °C/min under N_2 atmosphere. Wide-angle X-ray (WAXD) diffraction spectra were collected using a Bruker D8 Diffractometer (Germany), Cu $K\alpha$-radiation ($\lambda = 1.5418$ nm). Optical textures were observed with an Olympus BH-2 (Japan) polarizing optical microscope (POM). The electronic diffraction spectroscopy (EDS) was recorded by an ESCALAB MK II Multi-Technique Electron Spectrometer (U.K.).

Synthesis of monomer

The *trans*-azobenzene-4,4′-dicarboxylic acid-dipotassium salt (**1**) and *trans*-azobenzene-4,4′-dicarbonyl chloride (**2**) was synthesized according to a typical procedure that was shown in Scheme 1 [22–24]. In a magnetically stirred solution of p-nitrobenzoic acid (13.0 g, 77.8 mmol), NaOH (50.0 g, 1250 mmol) and water (225 mL) maintained at 50 °C, the solution of glucose (100 g, 555 mmol) in water (150 mL) was added in 30 min. The reaction mixture was stirred vigorously for 8 h in N_2 atmosphere, ultimately obtaining a viscous, dark brown mixture. On cooling to ambient temperature, the mixture was acidified with glacial acetic acid to pH 6, after which a mud-like precipitate was collected by filtration. The solid was twice recrystallized from hot K_2CO_3 solution, and 8.0 g (59%) of bright orange needles of **1** was obtained.

The *trans*-azobenzene-4,4′-dicarbonyl chloride was prepared by treating **1** with thionyl chloride, the procedure was shown in Scheme 1. Into a 100-mL round-bottomed flask were placed **1** (14.5 mmol), 30 mL thionyl chloride, and 0.2 mL triethylamine. The mixture was refluxed for 12 h, until the suspension mixture was converted into a clear solution. Unreacted thionyl chloride was removed under reduced pressure and the residue was recrystallised from n-heptane and dried below 80 °C in a vacuum to yield the pure products. The product was isolated as dark red

Scheme 1 Synthesis of AZO-PA

needles with an approximate 53% overall yield. Monomer **2** was evidenced by ^{1}H NMR *(CDCl$_3$): δ 8.31(d, H1). 8.06(d, H2); Element analysis (C$_{14}$H$_8$N$_2$O$_2$Cl$_2$) (307.06): Calcd. C 54.72, H 2.60, N 9.12; Found C 54.96, H 2.67, N 9.48.

Synthesis of polymers

In a typical polymerization reaction (Scheme 1), a mechanically stirred solution of *para*-phenylene diamine or 4,4′-diaminodiphenylmethane (3.0 mmol), **2** (3.0 mmol) in DMAc (10–20 mL), LiCl (0.28 g), appropriate pyridine (3.6 mmol), was cooled to 0 °C in 2 h under N$_2$ and then warmed to 45 °C in 2–3 h. The viscous solution was poured into water (250 mL), giving a stringy solid. The solid was vigorously extracted with methanol (2 × 100 mL) and acetone (1 × 50 mL) and then dried under vacuo at 60–70 °C for 48 h. Element analysis: AZO-PA1 (C$_{20}$H$_{14}$N$_4$O$_2$)$_n$ (342.24)$_n$: Calcd. C 70.18, H 4.09, N 16.37; Found C 70.21, H 4.01, N 16.40; AZO-PA2 (C$_{27}$H$_{20}$N$_4$O$_2$)$_n$ (432.29)$_n$: Calcd. C 69.16, H 4.63, N 12.96; Found C 69.14, H 4.53, N 11.85. The NMR of polymer was absence owing to their poor solubility in some solvents, such as, CDCl$_3$ or DMSO-d6.

Results and discussion

The relationship between the primary structure of polyamides and their properties has been studied extensively and reported in the literatures [13, 29]. Azobenzene and benzene ring belong to rigid functional groups, and amide linkage is difficult to rotate in the rigid main chain because of the big conjugated system of electron delocalization. The whole chain is rigid and easy to form LC phase. Especially the hydrogen bond between amide groups can increase the degree of crystal and induced formation of liquid crystal. Therefore, we selected the alternative

polycondensation of azo diacyl chlorides with aromatic diamine groups without any substitutes.

In the FTIR spectrum of the polymers (Fig. 1.), bands of C=O stretching and N–H bending are visible in the spectrum at 1648 (AZO-PA1), 1665 (AZO-PA2) and 1513 (AZO-PA1), 1523 (AZO-PA2) cm^{-1}, respectively. An additional absorption centered at 3336–3356 cm^{-1} due to NH stretching is also apparent. The breadth and position of this third band suggest a considerable degree of hydrogen bonding within the polymer sample [30], as would be expected for IR spectra obtained in the solid state. These data confirm the existence of amide groups and hydrogen bonding which induced the formation of LC phase within the polymer. The notably absence from the IR spectrum are the absorptions specific to the azobenzene chromophore. The nitrogen double bond stretching frequencies for aromatic azobenzene compounds generally fall within the 1650–1380 cm^{-1} range. However, these bands are weak and tend to be obscured by other aromatic absorptions as in
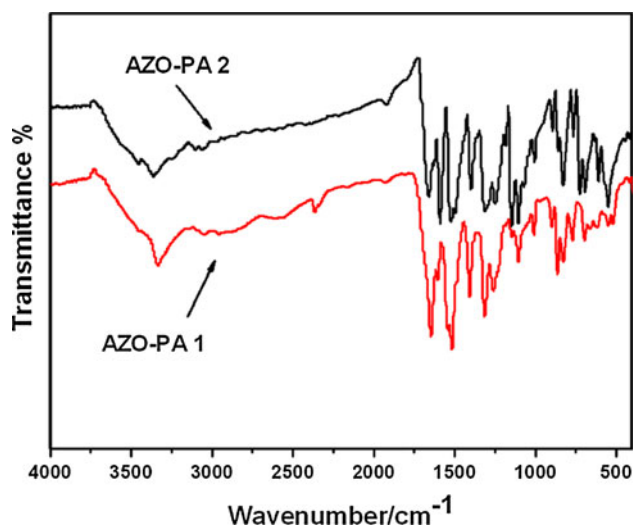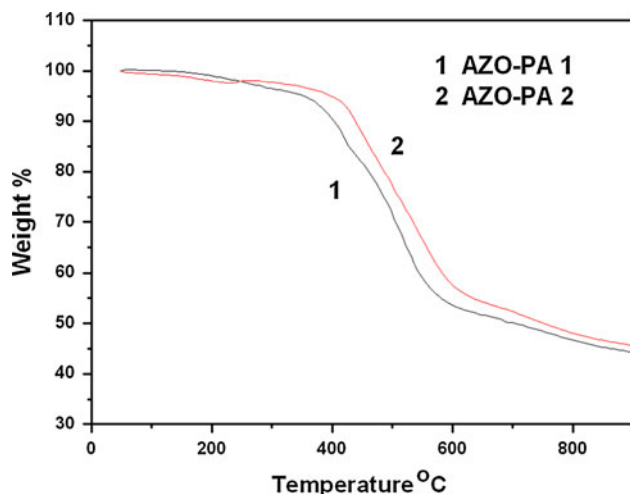

Fig. 1 FTIR spectrum of AZO-PA

Table 1 Polymer thermal properties

Polymer	Onset of weight loss (°C)			
	T_g (°C)	T_{azo} (°C)	5%	50%
AZO-PA 1	252	417.7	350	680
AZO-PA 2	222	412.1	400	739

Fig. 2 Weight loss (TG): temperature profiles for polymers at a rate of 10 °C/min under N_2 atmosphere

the case here, and the existence of azobenzene can be confirmed by UV–vis spectroscopy.

The formation of amide groups and hydrogen bonding can be further confirmed by the presence of high thermal stability. When evaluated under a nitrogen atmosphere, the polymer exhibited good thermal stabilities up to 350 °C, and the results were summarized in Table 1. Weight loss-temperature profiles of the polymers constructed from TGA data are provided in Fig. 2. As can be seen, these materials were quite stabile, with half of the polymers mass remaining above 600 °C. Polymeric residues recovered after heating were highly discolored and insoluble in common solvent. The T_g and thermal decompose temperature of AZO-PA is as high as that of other main-chain azobenzene polyamides (i.e. $T_g > 200$ °C), and is higher than that of side-chain azobenzene polyamides.

It is interesting to note that for the azobenzene-modified polymers described here, the potential loss of the azobenzene groups and the onset of significant weight loss (TGA) both occur in the same temperature window. Polymers containing azobenzene chromophore exhibited an exothermic transition (T_{azo}) at 417.7 °C (AZO-PA 1) and 412.1 °C (AZO-PA 2). Similar observations have been reported for other azobenzene-containing materials [23]. It is inferred that the extrusion of molecular nitrogen from the polymer backbone is responsible for this behavior.

Therefore, the thermal stability of azo-polyamide was limited because of the existent azo bonding, and polyamide without azo usually exhibit higher decomposed temperature above 500 °C [14].

The existence of hydrogen bonding is helpful to crystal behaviors, which is closely related with the thermal stability and LC properties [11]. The XRD (Fig. 3a, b) showed that the original polymer obtained from the synthesis is in a poorly crystallized state. After recrystallizing the precipitated from DMAc, several strong diffraction apexes appeared in XRD patterns showed the formation of AZO-PA crystal, and the degree of crystallinity of AZO-PA 1 and 2 are high up to ca. 52% and 47%, respectively.

Additionally, the diffraction ring and spherocrystal of crystalline AZO-PA1 in EDS and POM (Fig. 3c, d) further indicated the crystal behavior. These results are in good agreement with X-ray diffraction, and show there is preferred tropism in DMAc. Intermolecular hydrongen bonds induce the sufficiently rearrangement of polymer units in a solvent, which makes the existence of LC phase possible.

The resulting polymers are very soluble in H_2SO_4 solution and partially soluble in DMAc, DMF, and NMP. The inherent viscosity data of resulting polyamides are high up to 4.26 (AZO-PA 1) and 2.23 (AZO-PA 2) dL/g (measured in 98% H_2SO_4 at 30 °C with $c = 0.5\%$), and achieve the highest value of other amorphous azo polyamides [24]. When AZO-PA 1 dissolving in DMAc, the AZO-PA solution becomes cloudy and birefringent at 5.3% polymer concentration. Significant liquid crystalline behavior was also observed in the azo-polyamide solution in Fig. 4.

In molecular structure, azobenzene containing a conjugated system bonds with amide bond and forms p–π conjugation among the p-orbit of the nitrogen atom, carbon atom and oxygen atom. The entire chain forms a big conjugated system of electron delocalization and creates a rigid unit in polymer. The high rigidity of chains is advantageous to form LC phase and consequently induce the ordering process at molecular level. In low concentration, macromolecule dissolved in the solvent is dispersed, no birefringence in the field of view of POM. With the increase of the content, rigid-rod chains can link each other due to intermolecular hydrogen bonding; moreover, regular and rigid structure further induces formation of more linkages. Many macromolecular regularly arranged and reoriented, and form the threaded texture of nematic phase of LC. Additionally, an interesting phenomenon was found in POM, the greater the shearing force, the greater is brightness. Shearing leads to a directional alignment and appears optically anisotropism. Although AZO-PA 1 and 2 all show nematic phase of LC, AZO-PA 1 is more facile in forming LC phase than that of AZO-PA 2 due to the relatively rigid structure.

Fig. 3 Characterization of crystal behavior. **a** X-ray diffraction patterns of AZO-PA 1. **b** X-ray diffraction patterns of AZO-PA 2. **c** The electronic diffraction spectroscopy pictures of AZO-PA 1. **d** The pictures with crossed polarizing optical microscope for AZO-PA 1
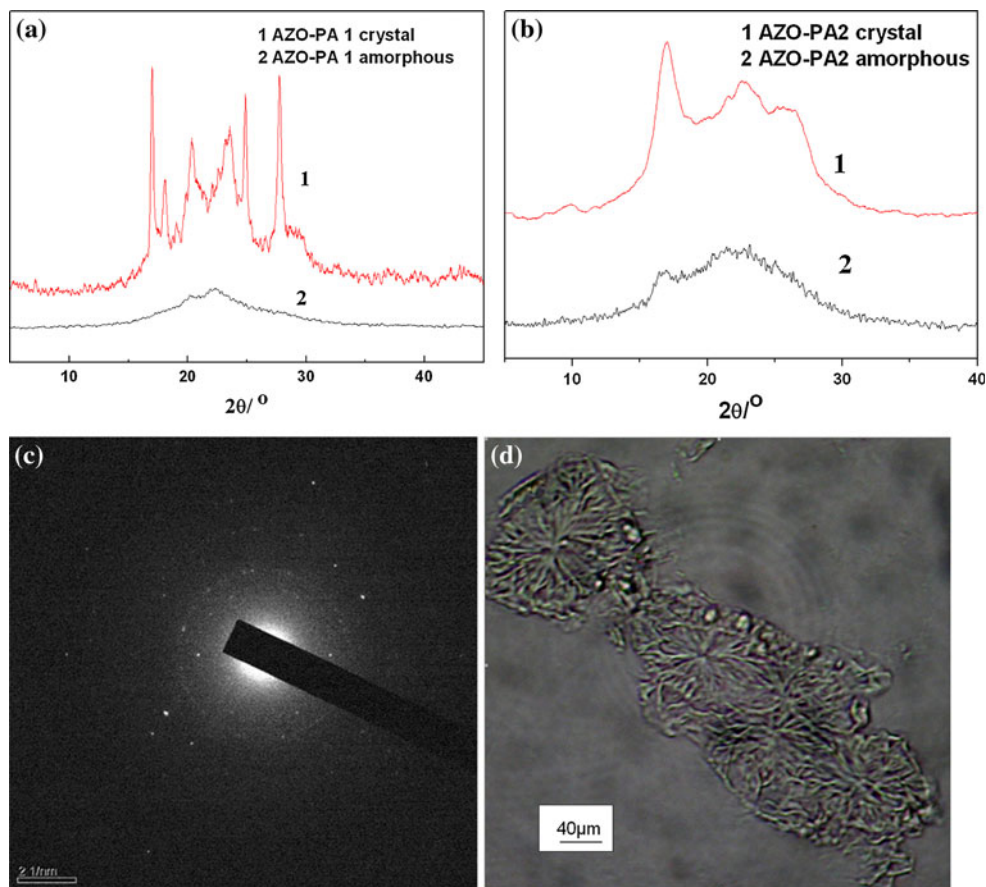

Fig. 4 POM for AZO-PA liquid crystal. **a** AZO-PA 1, **b** AZO-PA 2
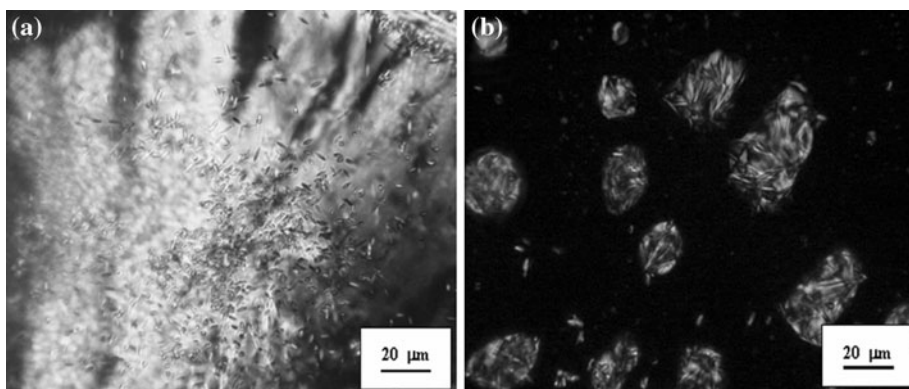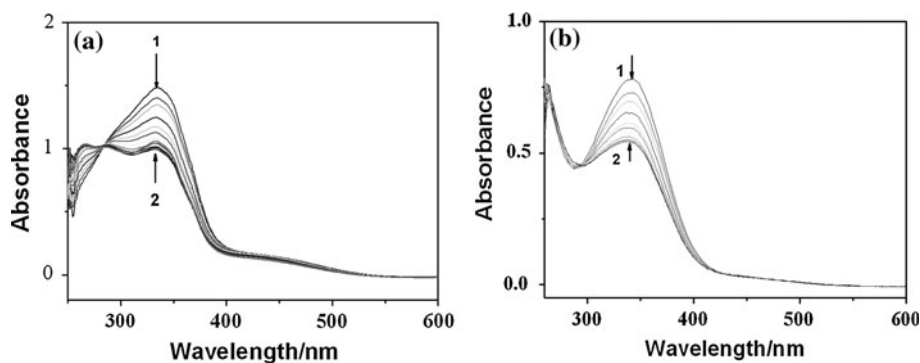

Fig. 5 UV–vis spectra of AZO-PA solution under UV light irradiation, From *1* to *2*: ($t = 0$, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35 min). **a** AZO-PA 1, **b** AZO-PA 2

The characteristic photoresponse of azobenzene in DMAc solutions was studied by UV–vis spectroscopy. The UV spectra of polyamides are shown in Fig. 5 over different time intervals until photostationary states were reached. Upon 365 nm UV irradiation, AZO-PA 1 and 2 exhibit same absorption peak at 345 nm and 450 nm, and the intensity of the π–π^* transition band at 345 nm of *trans*-azobenzene decreased with increase of the intensity of the n–π^* transition band at 450 nm of *cis*-azobenzene at the same time. Kept in the dark, the *cis* form slowly relaxed to the *trans* form, and the spectra gradually recovered to the original curve after 62–70 h. The photoresponse time is longer in comparison with that of other main-chain azo polyamides due to the rigid structure of polyaramides. The variational spectrum confirms the existence and photoresponse of the azobenzene chromophore.

Conclusion

Two novel linear main-chain polyamides containing azobenzene were synthesized by polycondensation of *trans*-azobenzene-4,4′-dicarbonyl chloride with para-phenylene diamine and 4,4′-diaminodiphenylmethane under low temperature. As expected, the resulting AZO-PA display lyotropic LC phases in DMAc solutions, and high T_g (>220 °C) and high thermal stability up to 400 °C under nitrogen because of the intensive intermolecular hydrogen bonding and regular molecular structure. When AZO-PA dissolved in DMAc, the apparent threaded texture of the nematic phases were observed in POM. Under UV irradiation (365 nm), AZO-PA 1 and 2 can undergo typical *trans*–*cis* and *cis*–*trans* photoisomerizations of azobenzene at 345 and 450 nm, showing excellent photochromism. Moreover, polymers possess fairly high inherent viscosity (the highest value reaches 4.26 and 2.23 dL/g, respectively) and high degree of crystallinity (the highest value reaches 52 and 47%, respectively), and is suitable for fiber spinning. The resulting polymers simultaneously exhibit promising LC, high thermal stabilities and photochromism properties and can be applied in fields of conventional optical techniques and novel anti-ultraviolet and photochromic fibers industry.

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