Liquid-Crystal Aromatic Polyesters Containing Azo and Sulfone Units

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Two novel aromatic polyesters containing azo and sulfone units were synthesized by poly-condensation of 4,4'-azobenzene-dicarbonyl chloride with dihydroxydiphenyl sulfones at low temperature. The synthesized polymers exhibited good solubility, inherent viscosity (reaches 1.05 dL g^{-1}), high glass transition temperature (above 200 °C) and thermal stability ($\leq$ 5 % weight loss at 348 °C), which were characterized by Fourier transform infrared spectroscopy. The liquid crystalline and photoisomerization properties were observed by polarizing optical microscope and an ultraviolet-visible spectrophotometer.

Keywords: Azo-polyesters, Soluble properties, Photoisomerization, Liquid-crystal polymers.

INTRODUCTION

Aromatic polyesters have been widely used as engineering thermoplastic materials in electronic industries, medical equipment and other high technology fields due to their outstanding mechanical properties, excellent thermal stability and enhanced environment resistance[1-3]. However, most of them are neither soluble nor fusible because of the high rigidity of their backbone. High rigidity of aromatic polyesters is responsible for high chemical and thermal stability and high glass transition temperature, but at the same time, these aspects contribute to poor solubility in common solvents[4-7]. For real application purpose, major effort has been devoted to overcome the issues related to solubility and processability of polyesters. The introduction of flexible units in main chain is some of the approaches generally adapted to improve solubility of polymers without sacrificing the thermal stability[8-14]. Therefore, introducing sulfonic units into polymer chains could probably create the aromatic polyesters with favorable properties.

Azobenzene as a chromophore has attracted considerable attention owing to their potential application in optical data storage, optical switching and nonlinear optical materials[15-23]. Because of the unique reversible photoisomerization and photoinduced anisotropy azobenzene chromophores, azo polymers possess some interesting properties such as holographic optical memories[24], the photo-controlled release of drugs[25], the preparation of polymeric dyes[26-28]. However, their application is limited due to their poor thermal stability, liquid crystal and viscosity properties.

To develop new high performance materials, the flexible sulfone and azo groups were introduced to the backbone of aromatic polyesters, which was a viable method to improve the thermal stability, solubility and liquid crystalline properties of aromatic polyesters. Two azo-containing aromatic polyesters were prepared by the low temperature poly-condensation of 4,4'-dihydroxydiphenyl sulfone (4,4'-DHDPS) or 2,4'-dihydroxydiphenyl sulfone (2,4'-DHDPS) with 4,4'-azobenzene-dicarbonylic chloride, respectively. The chemical structures were confirmed by FTIR and the optical properties, thermal stability and solubility of aromatic polymers were also investigated. To the best of our knowledge, this is one of the first syntheses of an aromatic polyester containing only azo and sulfone groups.

EXPERIMENTAL

All reagents and solvents (> 98 %) were purchased from the Aldrich Chemical Co. and were not purified before use. Distilled water was used in this work.

The contents of dihydroxydiphenyl sulfone were measured on Shimadzu LC-10A High performance liquid chromatography using Shim-Pack VP-ODS column. FTIR spectra were recorded on a FTS-40 spectrophotometer in KBr pellets. UV-visible absorption spectra were recorded on a UV 2501-PC spectrophotometer. ^{1}H NMR spectra were recorded with a Bruker DPX-400M spectrometer using TMS as internal standard and CDCl$_3$ as solvent. Elemental analyses were performed on a PE-2400 CHN elemental analyser. Glass transition temperatures were determined by America Waters DSC Q2000

instrument at a heating rate of 20 °C min⁻¹ under a nitrogen flow of 50 mL min⁻¹. The glass transition temperature (T_g) value was recorded from the second scan after the sample was first heated and then quenched. Thermo-gravimetric analysis (TGA) was performed on DTG-60 analyzer under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Liquid crystalline texture was examined using a Carl Zeiss polarizing optical microscope (POM).

Preparation of 4,4'-dihydroxydiphenyl sulfone (4,4'-DHDPS) and 2,4'-dihydro-xydiphenyl sulfone (2,4'-DHDPS): Dihy-droxydiphenyl sulfone were prepared by a typical procedure (**Scheme-I**)[29,30]. The crude product was obtained with yield of 96.0 %. (56.6 % 4,4'-DHDPS and 37.5 % 2,4'-DHDPS). 4,4'-DHDPS and 2,4'-DHDPS were obtained by separation of crude product using 2 % methanol in *o*-dichlorobenzene mixture. The melting points of 4,4'-DHDPS and 2,4'-DHDPS recrystallized were 248-249 and 185-186 °C, respectively.

Synthesis of 4,4'-azobenzene-dicarbonyl chloride: The synthesis route for the preparation of 4,4'-azobenzene-dicarbonyl chloride was depicted in **Scheme-I**. Suitable preparation for 4,4'-azobenzene-dicarbonyl chloride has been reported in literature[31]. The product was isolated as dark-red needles crystal with an over yield approximate 88.5 %. 4,4'-Azobenzene-dicarbonyl chloride was characterized. ¹H NMR (CDCl₃) δ: 8.06 (d, 4H, ArH), 8.32 (d, 4H, ArH); For $C_{14}H_8N_2O_2Cl_2$: calcd: C, 54.72; H, 2.61; N, 9.12. Found: C, 54.96; H, 2.67; N, 9.48. m.p. 164-165 °C.

Synthesis of polymers: In a typical polymerization reaction as shown in **Scheme-II**, 4,4'-DHDPS (2 mmol), NaOH (0.2 g, 5 mmol), H₂O (40 mL) and tetrabutylammonium bromide (TBAB, 0.06 g) were added to a dry three-neck flask. After the mixture was completely dissolved, 4,4'-azobenzene-dicarbonyl chloride (2 mmol) in 40 mL of 1,2-dichloroethane was added under vigorously stirring. Then mixture was stirred at 10-15 °C for 2 h. The viscous solution was poured into water (250 mL), which afforded a stringy solid. The solid was extracted with ethanol (2 × 100 mL) and acetone (1 × 50 mL) and then dried under vacuum at 60-70 °C for 48 h.

RESULTS AND DISCUSSION

FTIR spectroscopy: The AZO-PSs were synthesized through typitical poly-condensation reaction from 4,4' azoben-
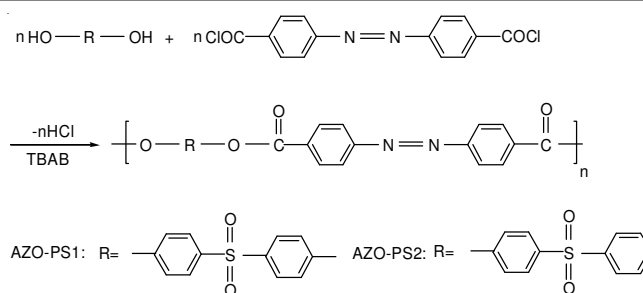
Scheme-II: Synthesis route of polymers

zene-dicarbonylic chloride and dihydroxydiphenyl sulfone monomers, as shown **Scheme-II**. The chemical structure of polymer was confirmed by FTIR spectra (Fig. 1). The AZO-PS1 and AZO-PS2 exhibited the characteristic absorption bands of -COO bond at 1732,1740 cm⁻¹, respectively. Absorption bands lying at 1593-1409 cm⁻¹ can be attributed to the stretching vibration of the skeleton construction of benzene rings. Absorption band of -SO₂- is visible in the spectrum at 1264-1152 cm⁻¹ (AZO-PS1) and 1256-1152 cm⁻¹ (AZO-PS2). The stretching frequencies of N=N in aromatic azobenzene compounds generally fall within the 1650-1380 cm⁻¹ range. However, it should be pointed out that the -N=N- absorption band of the aromatic azobenzene compound is difficult to
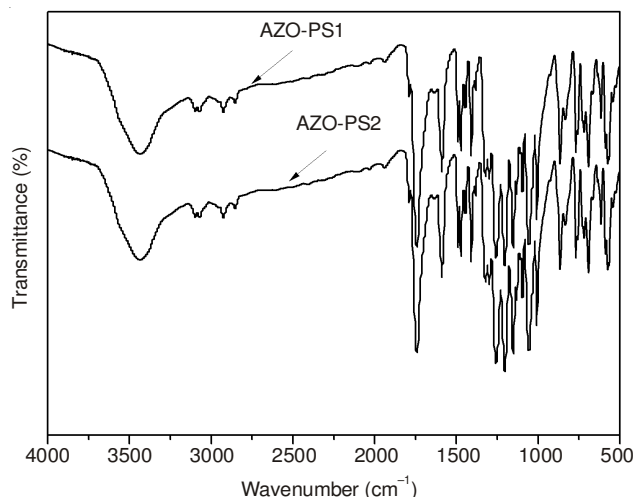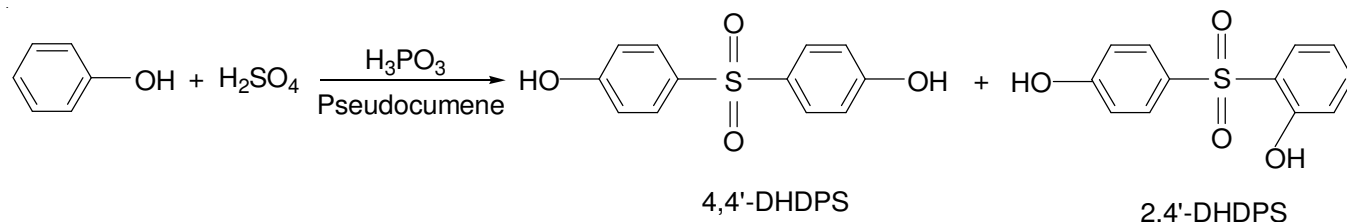

Fig. 1. FTIR spectrum of AZO-PS

4,4'-DHDPS   2,4'-DHDPS

Scheme-I: Synthesis of monomers

identify in the FTIR spectra because of the interference of the C=C ring stretching vibration[32] and the existence of azobenzene can be confirmed by UV-visible spectroscopy.

Thermal properties: The thermal stability of the AZO-PS1 and AZO-PS2 was evaluated under a nitrogen atmosphere by TGA (Fig. 2). The experimental data was illustrated in Table-1. which be observed that the temperature at which a 5 % weight loss ($T_{5\%}$) occurred was over 348 °C. With the increase of temperature, half of the AZO-PS2 mass remained above 730 °C. AZO-PS2 exhibited fairly high thermal stabilities.

TABLE-1
THERMAL PROPERTIES OF POLYMERS

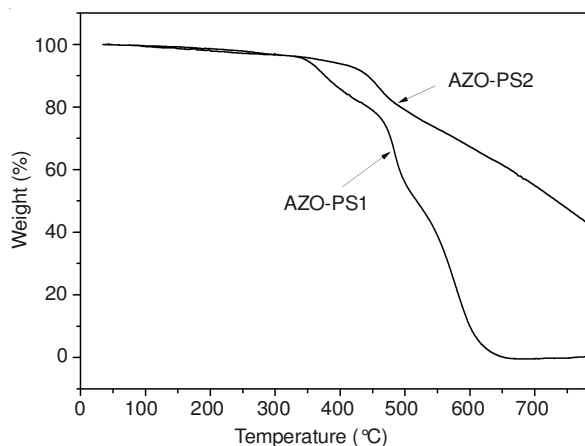| Sample | Onset of weight loss (°C) | | | |
	T_g (°C)	$T_{5\%}$	$T_{10\%}$	$T_{50\%}$
AZO-PS1	204.03	348	372	510
AZO-PS2	202.56	348	440	732

Fig. 2. TGA thermogram of AZO-PS in N_2 atmosphere

The DSC curves of AZO-PS were as shown in Fig. 3 and the experimental results were listed in Table-1. No thermal change except for the glass transition was observed below decomposition temperature indicating amorphous property of the polymers. Glass transition temperature of AZO-PS was high T_g above 200 °C. The existence of azo bond or the intro duction of flexible sulfone units has no sacrificing the thermal stability.
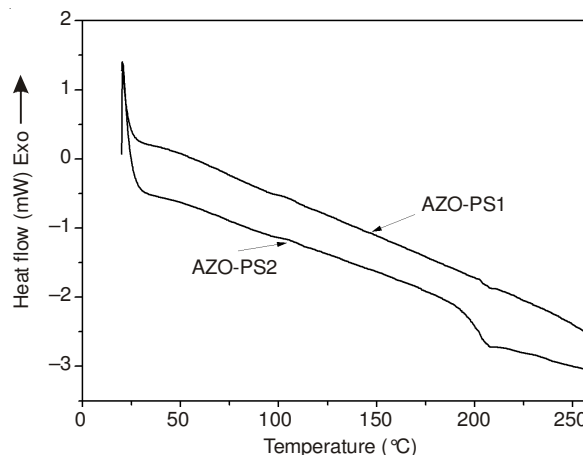

Fig. 3. DSC curves of AZO-PS in nitrogen

Solution properties: The solubility of AZO-PS in various organic solvents was shown in Table-2. The synthesized polyesters are very soluble in H_2SO_4 aqueous solution. Unlike most of the aromatic polyesters which have limited solubility in dimethylacetamide and other aggressive organic solvent media, AZO-PS exhibit excellent solubility in common organic solvents such as dimethylacetamide, *N,N*-dimethyl formamide, N-methyl pyrrolidone and dimethyl sulfoxide. The good solubility of AZO-PS could be attributed to flexible sulfone links which enabled the solvent molecules to diffuse into the polymer chains. Moreover, the asymmetric structure of AZO-PS2 affected the stacking density of the molecule chain, increased the inner free volume among molecules and forced the two phenyl rings into a non-coplanar conformation, which rendered a better solubility. The inherent viscosity of the polyesters are up to 1.05 (AZO-PS1) and 0.95 (AZO-PS2) dL g^{-1} (measured in N-methyl pyrrolidone at 20 °C with c = 0.5g L^{-1}). This indicates that there is a relatively high molecular weight.

Optical properties: The photoisomerization behaviour of AZO-PS in dimethylacetamide solution was investigated by UV-visible spectroscopy upon irradiation of 365 nm UV light. As seen in Fig. 4a and 4b, the UV-visible spectra of AZO-PS were recorded over different time intervals until the stationary state was reached. When the solution was irradiated by 365 nm light, azobenzene chromophores underwent a *trans*-to *cis*- photoiso-merization process. The intensity of the $\pi-\pi^*$ transition band at 332 nm (AZO-PS1) and 320 nm (AZO-PS2)
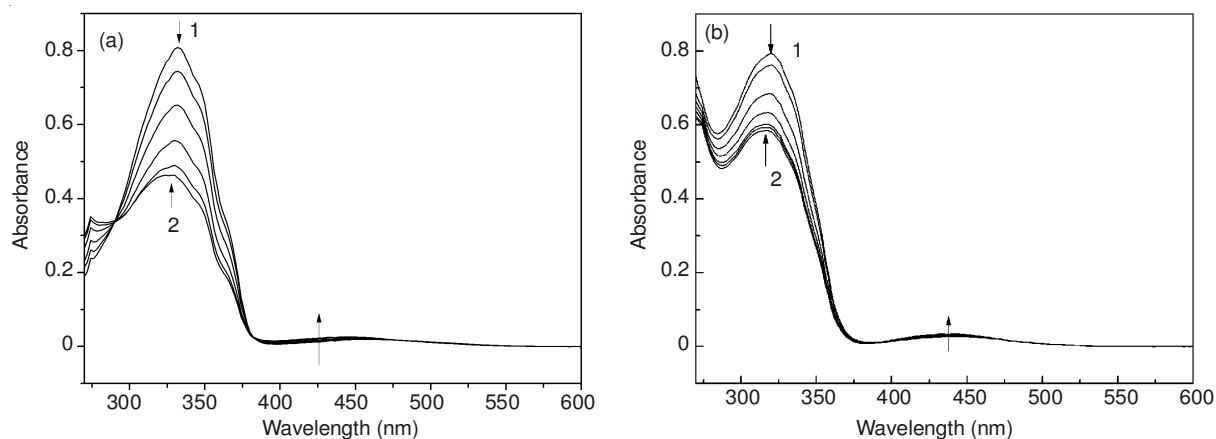

Fig. 4. UV-visible spectra of AZO-PS solution under UV light irradiation, From 1 to 2 (t = 0, 4, 8, 12, 16, 20) (a) AZO-PS1, (b) AZO-PS2

TABLE-2 SOLUBILITY OF AZO-PS[a]							
Sample	H_2SO_4	DMAc	DMF	NMP	DMSO	CH_3COCH_3	C_2H_5OH
AZO-PS1	+++	++	++	++	++	-	-
AZO-PS2	+++	+++	+++	+++	+++	-	-
[a]Qualitative solubility was determined with 0.01 g of polymer in 10 mL of solvent at room temperature. +++ highly soluble; ++ soluble; - insoluble							

decreased gradually and the intensity of the n-π* transition band at 425 nm (AZO-PS1) and 436 nm (AZO-PS2) increased gradually with continued irradiation. Keeping in the dark, the *cis*- form slowly relaxed to the *trans*- form and the spectra gradually recovered to the original curve after 70-75 h. The photo response time is longer in comparison with that of other main-chain azo polymers due to the rigid main chain structure of polyesters. The variation of spectrum confirms the existence and photo response of the azobenzene chromophore.

Liquid crystal properties: The AZO-PS was dissolved in dimethylacetamide with polymer concentration of 0.3 wt. %. The obtained AZO-PS solutions became birefringent and significant liquid crystalline behaviour was also observed. With lower polymer concentration, the macromolecules were well-dispersed in the solvent and no birefringence was observed by polarizing optical microscope. With increased polymer content, there would be enough time and space for polymer segments to rearrange and orient in solution. The liquid crystalline structure was formed because of the symmetrical main-chain and rigid rod-like azobenzene groups. Moreover, the regular and rigid structure of polymer chain induced the formation of dendritic texture of nematic phase of liquid crystalline (Fig. 5). With the microscope stage 45° rotated, the extinction phenomenon could be clearly observed. The interference phenomenon was also revealed in Fig. 5.
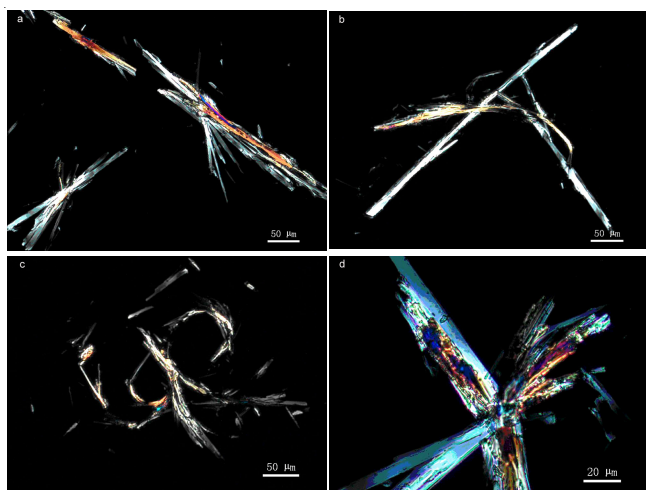

Fig. 5. POM images of different regions of AZO-PS1 (a, b) and AZO-PS2 (c, d)

Conclusion

Aromatic polyesters containing azo and sulfone groups in the main chain have been prepared by poly-condensation of 4,4'-azobenzene-dicarbonylic chloride and dihydroxydiphenyl sulfones at low temperature. The AZO-PS showed good solubility, inherent viscosity (the highest value reaches 1.05 dL g^{-1}), high glass transition temperature (above 200 °C) and thermal stability (up to 348 °C). When the AZO-PS was dissolved in dimethylacetamide, the dendritic texture of the nematic phases was observed by POM. AZO-PS 1 and 2 can undergo typical *trans-cis* photoisomerization of azobenzene with different absorption peaks under successive irradiation of 365 nm UV light. The resulting polymers can be applied in fields of conventional optical techniques and novel anti-ultraviolet and photochromic fibers industry.

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