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Synthesis of High Refractive Index Polyamides Containing Thio-ether Units

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Two kinds of new aromatic diamine monomer containing thio-amide unit, bis[4-(p-aminothiophenyl)benzoyl]diamine (ATPBA), were synthesized in two steps, which was reacted with 4,4′-(sulphonyl-bis(p-phenylthio)) dibenzoyl chloride (S-DC) to prepare a new polyamide containing high quantity thio-ether unit. The intrinsic viscosity of PASSA was 0.81–0.93dl/g obtained with optimum synthesis conditions. The polymers were found to have excellent thermal performance with glass transition temperature (T_g) of 245.3–265.8°C, initial degradation temperature (T_d) of 446.9–441.6°C. They showed improved solubility in polar aprotic solvents. The optical transmittance of the aromatic polyamide (**PA-3a** and **PA-3b**) film at 450 nm is higher than 80%. The thio-ether unit provided the **PA-3a** and **PA-3b** with a much higher refractive index ranging from 1.699 to 1.701, and low birefringence between 0.006 and 0.007.

Keywords: 4,4′-(sulphonyl-bis(p-phenylthio)) dibenzoyl chloride, polyamide, heat-resistant, optical transmittance, birefringence

1 Introduction

In recent years, there has been strong demand to develop high-refractive-index polymers for optical application, such as components for charge coupled devices, complementary metal oxide semiconductor image sensors etc. (1–4). High-refractive index, optical transparency and low birefringence are the most important factors in optical applications. According to the Lorentz-Lorenz equation, the introduction of substituents with high-molar refractions and low-molar volumes can efficiently increase the refractive index of polymers (5–9). Among the various substituents, the sulfur atom, which has high atomic refraction, is one of the most effective candidates. Recently, much attention has been paid to sulfur-containing polymers such as polyurethane, polymethacrylate, poly(arylenethioether)s and polyimide, to improve their refractive index with high transparency in optical device applications (10–14). Among them, polyimide (PI) is a promising candidate for advanced optical applications. The aromatic polyamide has good thermal and physical properties, excellent mechanical properties and solubility. At the same time, it has a similar rigid structure with PI, so we hope we can produce polyamide with high refractive index as PI.

Here, we describe the synthesis of two kinds of novel diamine with special structural features including amide group and thio-ether unit. Polycondensation reactions of this diamine with 4,4′-(sulphonyl-bis(p-phenylthio)) dibenzoyl chloride (S-DC) in the presence Me_3SiCl (TMSCl) as catalyst resulted high quantity thio-ether units and amide-containing polyamides which was found to have high refractive index, low birefringence while maintain high optical transparency.

2 Experimental

2.1 Materials

Commercially available 4,4′-diaminobenosulfone (DABS), 4,4′-dichlorobenzene sulfone(DCDPS) (AR, JiangSu YangZhong Synthesis Chemical industry Company), m-phenylenediamine (m-PDA) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company), 4-flurobenzoyl chloride (p-FBC) (AR, JiangSu JinTan LanLing Chemical Industry Ltd. Company), 4-aminobenzenthiol(AR, Zhe Jiang Shou Er Fu Chemical Industry Group Co., Ltd.), sodium hydroxide (NaOH) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company), N-methyl-2-pyrrolidone (NMP) (JiangSu NanJing JinLong Chemical

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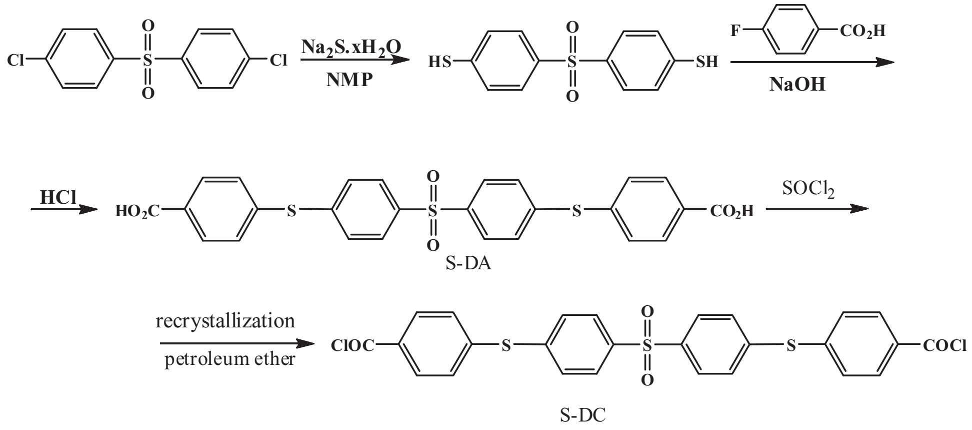


Sch. 1. Synthesis route of 4,4′-(sulphonyl-bis(p-phenylthio)) dibenzoyl chloride (S-DC).

Industry Company), Me_3SiCl (TMSCl) (AR, Aladdin-Reagent Company), all of them were used without further purification. Tetrahydrofuran (THF) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company) was purification by reduced pressure distillation. 4-flurobenzoic acid (4-FBA), Catalysts A and B were made in our lab. Other reagents and solvents were obtained commercially.

2.2 Monomer Synthesis

2.2.1. *4,4′-(sulphonyl-bis(p-phenylthio)) dibenzoic acid (S-DA) (shown as Scheme 1)*

S-DA was prepared according to the following procedure: In a 500 ml three-necked flask equipped with water segregator, reflex condenser, mechanical stirrer, and thermometer was added 150 ml of NMP, 30 ml toluene ,14.3 g (0.11 mol) of sodium sulfide, 4 g (0.10 mol) of sodium hydroxide, 1.5 g of Cat.A, 2.6 g of Cat. B (15,16), then the reactor was heated to 180°C within 35 min and kept for 2 h; during this course, 40.2 ml liquid was removed. When the above reaction vessel was cooled to 110°C, 100 ml of NMP solution containing 28.7g (0.1mol) of 4,4′-dichlorobenzene sulfone was added to the reactor dropwise within 3 h, and kept at 130°C for 6 h to prepare bis(4-mercaptophenyl)sulfone (the solution color changed from blue to pale-yellow). Then, 7.6 g sodium hydroxide and 26.6 g (0.19 mol) 4-FBA was added into the reaction solution, heated to 160°C and maintained for 8 h. The reaction-solution was poured into deionized water and filtrated. The filter liquor was acidified with 1 mol/L HCl to precipitate a cottony crude product under stirring conditions. The crude product was then washed several times with hot water to remove possible residual salt. After the purified product was filtered, it was dissolved in a solution of $NaHCO_3$. The solution was then filtrated to obtain the filter liquor, the filter liquor was acidified to separate precipitation. We then gathered the precipitation with filtration. The above purity procedure was repeated 3 times. The product was further dried at 110°C in vacuum for more than 12 h to yield a white powder."

Yield: 39.8 g, 76.3%. m.p.: 259–260°C. Elemental analysis (%): Found: C, 59.70; H, 3.52; Calculated: C, 59.75; H, 3.47.

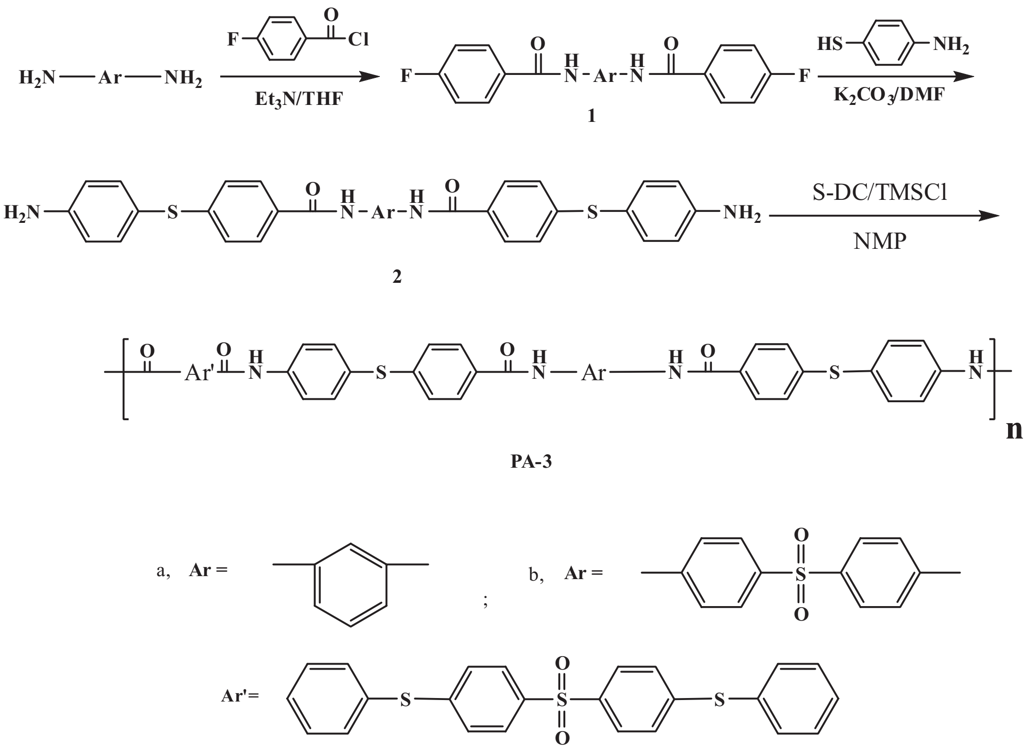
2.2.2. *4,4′-(sulphonyl-bis(p-phenylthio)) dibenzoyl chloride (S-DC)*

A mixture of 13.1 g (0.025 mol) S-DA, 70 ml of thionyl chloride ($SOCl_2$), 0.4 ml of dry pyridine were added and stirred in a round-bottom flask at room temperature under N_2atmosphere in darkness for 3 h and then refluxed for 12 h. The mixture was distilled to dryness under reduced pressure. The residue was extracted repeatedly at 70°C with dry petroleum ether (b.p. 60–90°C). The solvent was evaporated under reduced pressure and the product was dried under vacuum at 56°C.

Yield: 12.6 g, 90.6%, m.p.: 196–198°C, m/z (M^+): 559.46. ^{1}H-NMR (600 MHZ, $CDCl_3$, ppm): $\delta = 8.053$–8.071 (d, 4H), 7.916–7.930 (d, 4H), 7.501–7.519 (d, 4H), 7.400–7.418 (d, 4H). FT-IR: -COCl-: 1768 cm^{-1}, 1728 cm^{-1}, -S-: 1076 cm^{-1}.

2.2.3. *1,3–bis(4-diflurobenzoyl) diaminobenzene (1a) (shown as Scheme 2) (17)*

1a was prepared as Scheme 2 using the following procedure: to a 250 ml round bottom three-necked flask was added 10.8 g (0.1 mol) of m-phenylenediamine, 20.2 g (0.2 mol) of Et_3N, and 300 ml of THF. The mixture was stirred under nitrogen until the solids dissolved, then cooled in an ice bath, and 31.7 g (0.2 mol) of p-FBC was added dropwise. The mixture was stirred for 1 h in ice bath, 24 h at room temperature. Then the reaction solution was poured into water. The resulting solid was filtered, washed with hot water and methanol, dried, recrystallized from the mixture of DMF and water (3:1). That afforded **1a** as white sheet crystal.



Sch. 2. Synthesis route of PASSA (**PA-3a** and **PA-3b**).

Yield: 29 g, 82.3%. m.p.: 265–267°C; Element analysis: Found: C, 68.22; H, 4.09; N, 7.99; Calculated: C, 68.18; H, 4.01; N, 7.95.

2.2.4. *4,4′-bis (4-diflurobenzoyl) diaminophenyl sulfone (1b)*

1b was prepared as**1a**. The crude product of **1b** was recrystallized from pyridine. That afforded **1b** as white needle crystal.

Yield: 40.6 g, 82.5%. m.p.: >300°C. Element analysis: Found: C, 63.42; H, 3.74; N, 5.66; Calculated: C, 63.4; H, 3.68; N, 5.69.

2.2.5. *Bis[4-(p-aminothiophenyl)benzoyl]diamine (ATPBA) (18–19)*

Then, **1** was converted to ATPBA **2** through nucleophilic etherification of 4-aminobenzenethiol in DMF at 155°C kept for 4 h as shown in Scheme 2. Finally, corresponding diamine monomer (ATPBA) was synthesized. **2a**–**2b** was cleaned with water and methanol, and then was recrystallized from the mixture of water and DMF (1:1), that afforded **2a**–**2b** as a yellow sheet crystal.

2a Yield: 83.4%. m.p.: 157–159°C, m/z (M$^-$): 561.35.^{1}H-NMR (600 MHZ, DMSO-d6, ppm): $\delta = 10.152$ (s, 2H), 8.232 (s, 1H), 7.820–7.841 (d, 4H), 7.433–7.457 (d, 2H), 7.251–7.271 (t, 1H), 7.207–7.235 (d, 4H), 7.075–7.096 (d, 4H), 6.649–6.670 (d, 4H), 5.592 (d, 4H), FT-IR: -NH$_2$-: 3429 cm^{-1}, 3352 cm^{-1}, -CONH-: 3390 cm^{-1}, -S-:1083 cm^{-1}.

2b Yield: 78.6%. m.p.: 262–264°C, m/z (M$^-$): 701.26. ^{1}H-NMR (600MHZ, DMSO-d6, ppm): $\delta = 10.514$ (s, 2H), 7.973–7.995(d, 4H), 7.895–7.917 (d, 4H), 7.809–7.830 (d, 1H), 7.203–7.224 (d, 4H), 7.084–7.105 (d, 4H), 6.651–6.672 (d, 4H), 5.617 (d, 4H), FT-IR: -NH$_2$-: 3435 cm^{-1}, 3337 cm^{-1}, -CONH-: 3392 cm^{-1}, -S-:1076 cm^{-1}.

2.3 Polymer Synthesis

2.3.1. *Synthesis of PASSA (shown as Scheme 2)*

A typical polymerization was prepared as shown in Scheme 2. In a 100 ml three-necked flask equipped with mechanical stirrer and thermometer, 2.81 g (0.005 mol) bis[4-(p-aminothiophenyl)benzoyl] meta-phenylene diamine (**2a**) and 0.33 g (0.003 mol) Me$_3$SiCl (TMSCl) was dissolved in 60 ml NMP. After **2a** was dissolved completely, 2.8 g (0.005) S-DC was added. The mixture was stirred at 0°C for 2 h, then at room temperature for about 8 h to afford a viscous pale-yellow solution. Then it was poured into water to obtain a fibrous precipitate, washed with ethanol and water, and dried in a vacuum oven. The fibrous precipitate was pulverized to a powder and washed with ethanol and water and dried in a vacuum oven at 100°C for 12 h to give m-PASSA (**PA-3a**) 4.92 g (yield: 94%). PASSA (**PA-3b**) (5.71 g, yield: 96%) was prepared with a similar procedure.

2.4 Characterizations

2.4.1. *Intrinsic Viscosity and Gel Permeation Chromatography (GPC)*

Intrinsic viscosity of PASSA was obtained in NMP at 30 ± 0.1°C with 0.500 g of polymer dissolved in 100 ml NMP, using a Cannon-Ubbelodhe viscometer. The resulting values were obtained by a one-point method (or Solomon–Ciuta equation) as follows (20):

$$\eta_{\text{int}} = \frac{\sqrt{2\left(\eta_{sp} - \ln \eta_r\right)}}{C}$$

where $\eta_r = \eta/\eta_0$, $\eta_{sp} = \eta/\eta_0 - 1$.

Number-average molecular weights (Mn's) and weight-average molecular weight (Mw's) were obtained via GPC performed with a set of a Water 1515 performance liquid chromatography pump, a Waters 2414 differential refractometer (Waters Co., Milford, MA), and a combination of Styragel HT-3 and HT-4 (Waters Co., Milford, MA), the effective molecular weight ranges of which were 100–10000, 500–30000 and 5000–800000, respectively. N, N-dimethyl formamide (DMF) was used as an eluent at a flow rate of 1.0 ml/min at 35°C. Polystyrene standards were used for calibration.

2.4.2. *Elemental Analysis*

The samples of monomers S-DA, **2a**–**2b** and PASSA were determined by a elemental analyzer (EURO EA-3000)

2.4.3. *Characterization of Chain Structure*

The films of PASSA were prepared. FT-IR spectroscopic measurements were determined by a NEXUS670 FT-IR instrument. Nuclear magnetic resonance (^{1}H-NMR) instrument for the determination of the samples structure were provided with a BRUKER-600 NMR Spectrometer. The samples were dissolved in chloroform or deuterated dimethyl sulfoxide.

2.4.4. *Characterization of Aggregation Structure*

The samples (subsequently dried at 100°C in vacuum oven for 12 h, then heated at 180°C for 10 h) were characterized by X-ray diffraction (XRD) (Philips X'pert Pro MPD).

2.4.5. *Thermal Properties Test*

Differential scanning calorimetry (DSC) was performed with NETZSCH DSC 200 PC thermal analysis equipment, fitted with a cooler system using liquid nitrogen. It was operated at a gas rate of 10 ml/min under nitrogen atmosphere. The heating rate of DSC measurement was 10°C/min. Thermogravimetric analysis (TGA) measurement was conducted using TGA Q500 V6.4 Build 193 thermal analysis equipment with a heating rate of 10°C/min under nitrogen atmosphere.

2.4.6. *Tensile Properties*

An Instron Corporation 4302 was used to study the stress-strain behavior of films

2.4.7. *Optical Properties*

The transmittance of the films was determined by UV-Visible spectra (U-200A); The out-of plane (n_{TM}) and in-plane (n_{TE}) refractive indices of PA films were measured with a prism coupler SPA-Lite (SPA-4000) equipped with a He-Ne laser light source (wavelength: 632.8 nm). The in-plane (n_{TE})/out-of-plane (n_{TM}) and birefringence (Δn) were calculated as equation: $\Delta n = n_{TE} - n_{TM}$. The average refractive index was calculated according to equation: $n_{AV} = [(2\,n_{TE}^2 + n_{TM}^2)/3]^{1/2}$ (21).

2.4.8. *Solubility*

The solubility of polymers in various solvents such as: N, N-dimethyl formamide (DMF), N, N-dimethyl acetamide (DMAC), dimethyl sulfoxide (DMSO), NMP and normal solvents were determined at room temperature and the temperature of solvent boiling temperature.

3 Results and Discussion

3.1 Monomers

3.1.1. *Synthesis of S-DC*

The synthetic routes of S-DC were shown in Scheme 1. S-DC was prepared by a three-step procedure with 4,4′-dichlorobenzene sulfone (DCDPS) and 4-FBA. First, DCDPS reacted with sodium sulfide to provide bis(4-mercaptophenyl) sulfone (22–24), which was reacted with 4-FBA under nitrogen to give S-DA. Then S-DA was changed into S-DC which reacted with $SOCl_2$ (25–27). This procedure must be anhydrous or the yield would be very low.

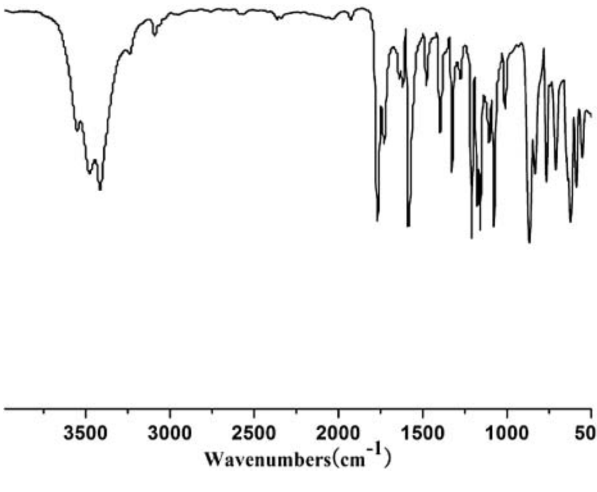


Fig. 1. FT-IR spectrum of S-DC.

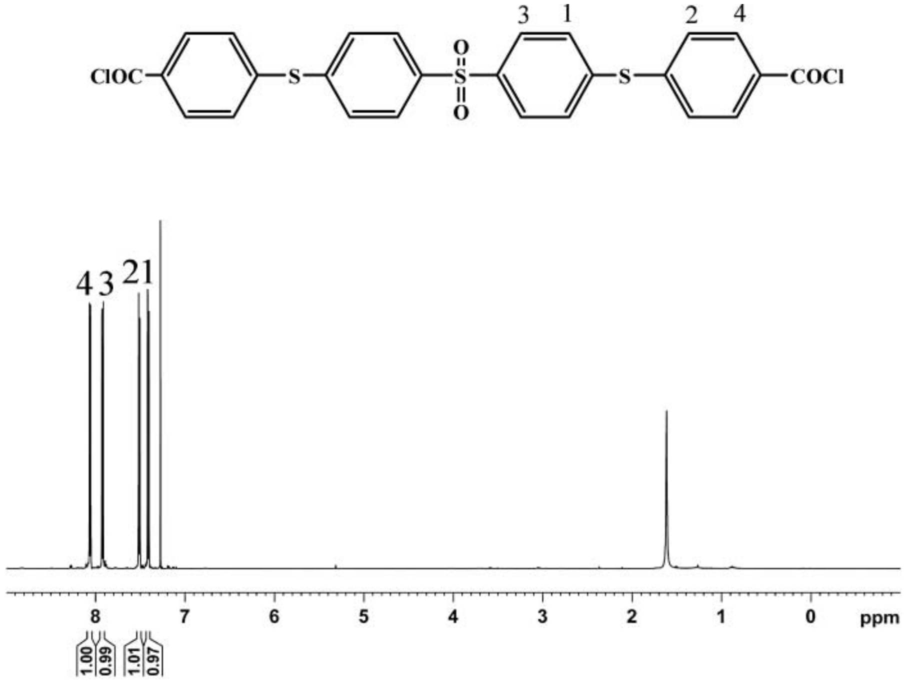


Fig. 2. ^{1}H-NMR spectrum of S-DC.

3.1.2. *The Chain Structure of S-DC*

Figure 1 showed the FT-IR spectrum of **S-DC**. The absorption of 1768 cm^{-1} and 1728 cm^{-1} suggested the formation of -COCl-. We observed the benzene rings absorption: 1579 cm^{-1} and 1478 cm^{-1}, the absorption of-SO_2-: 1326 cm^{-1}, 1158 cm^{-1}, the absorption of -S-: 1076 cm^{-1}, the absorption of benzene ring para-substituted 833 cm^{-1}. Figure 2 was the ^{1}H-NMR spectrum of **S-DC**. Four groups of peaks were appeared in the ^{1}H-NMR spectrum of **S-DC** which was consistent with the expected structure. The chemical shifts (δ) of **S-DC** (H1-H4) were listed in Table 1.

3.1.3. *Synthesis of 1a-1b*

1a-1b was prepared by the reaction of DABS/m-PDA, Et_3N and 4-flurobenzoyl chloride at 0–5°C in THF. 4-flurobenzoyl chloride was kept a little excessive.

3.1.4. *Elemental Analysis of Monomers*

Elemental analysis showed that the experimental results were similar with the calculated results. It suggested the monomers were synthesized as Scheme 2.

Table 1. Chemical shifts (δ) of S-DC

Chemical shift δ(ppm)	H_1	H_2	H_3	H_4
S-DC	7.400–7.418	7.501–7.519	7.916–7.930	8.053–8.071

3.1.5. *Synthesis of 2a-2b and Analysis of Their Chain Structure*

2a-2b was synthesized through nucleophilic etherification of 4-aminobenzenethiol in DMF at 155°C with the N_2 atmosphere. Figure 3 showed the FT-IR spectrum of **2a-2b**. **2a**: the absorption of 3429 cm^{-1} and 3352 cm^{-1} was the -NH_2 stretching vibration absorption, 3390 cm^{-1} was the

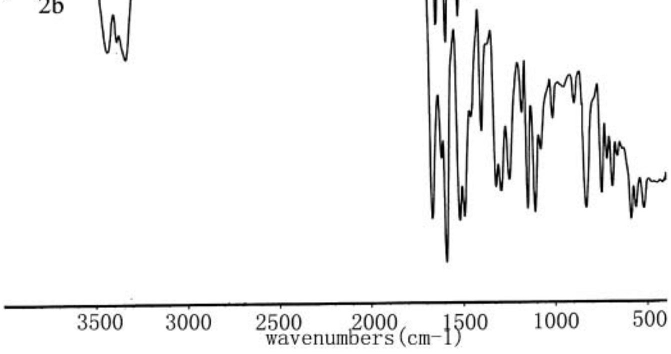


Fig. 3. FT-IR spectrum of **2a-2b.**

Table 2. Chemical shifts (δ) of **2a-2b**

2a	H_1	H_2	H_3	H_4	H_5
Chemical shifts δ(ppm)	5.592	6.649–6.670	7.075–7.096	7.207–7.235	7.251–7.271
2a	H_6	H_7	H_8	H_9	
Chemical shifts δ(ppm)	7.433–7.457	7.820–7.841	8.232	10.152	
2b	H_1	H_2	H_3	H_4	H_5
Chemical shifts δ(ppm)	5.617	6.651–6.672	7.084–7.105	7.203–7.224	7.809–7.830
2b	H_6	H_7	H_8		
Chemical shifts δ(ppm)	7.895–7.917	7.973–7.995	10.514		

N-H stretching vibration absorption. The absorption of 1649 cm^{-1}, 1528 cm^{-1} suggested the formation of -CO-NH-. We observed the benzene rings absorption:1595 cm^{-1}and 1489 cm^{-1}, the -S- absorption of 1083 cm^{-1} and the absorption of benzene meta-substitute: 784 cm^{-1} was also present. **2b**: the absorption of 3435 cm^{-1} and 3337 cm^{-1} was the -NH_2 stretching vibration absorption, 3392 cm^{-1} was the N-H stretching vibration absorption. The absorption of 1667 cm^{-1}, 1526 cm^{-1} suggested the formation of -CO-NH-. We observed the benzene rings absorption:1590 cm^{-1}and 1492 cm^{-1}, the sulfone group absorption: 1302 cm^{-1}, 1151 cm^{-1} and the -S- absorption of 1076 cm^{-1}. Figure 4 was the ^{1}H-NMR spectrum of **2a**. Nine groups of peaks were appeared in the ^{1}H-NMR spectrum of **2a,** which was consistent with the expected structure. The chemical shifts (δ) of **2a** (H_1-H_9) were listed in Table 2, **2b**: Eight groups of peaks appeared in the ^{1}H-NMR spectrum of **2b** in Figure 5. These eight groups of peak (H_1-H_8) were consistent with the expected structure. The chemical shifts (δ) of **2b** were listed in Table 2.

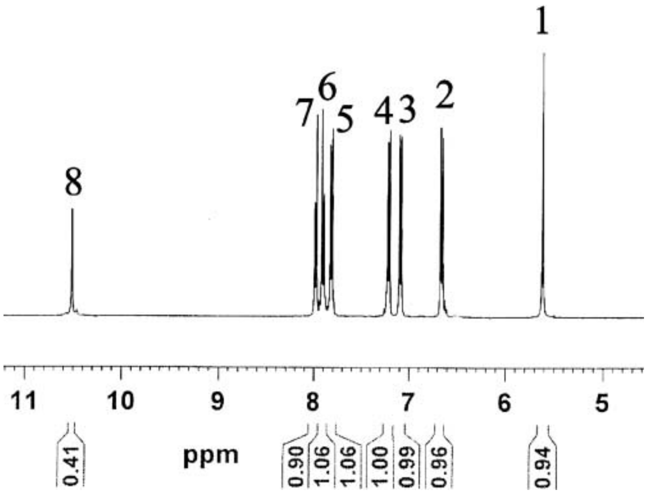


Fig. 5. ^{1}H-NMR spectrum of monomers **2b**.

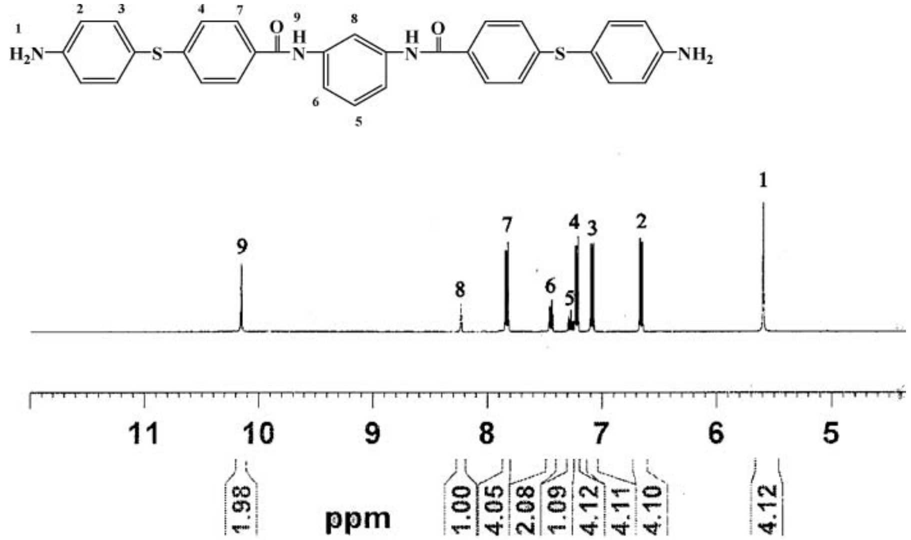
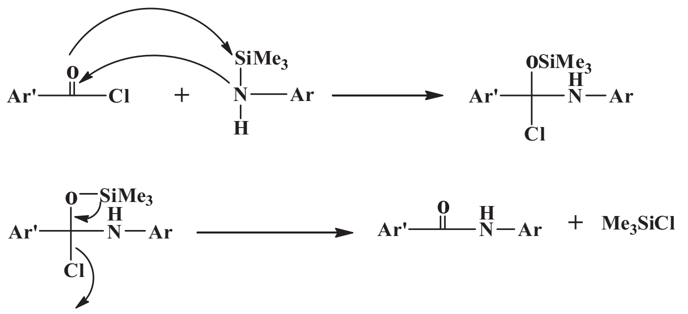


Fig. 4. ^{1}H-NMR spectrum of monomers **2a**.



Sch. 3. Mechanism of polymer formation by silylation.

3.2 Polymers

3.2.1. *Synthesis of PASSA (PA-3a and PA-3b)*

Polycondensation reaction of the diamine with **S-DC** was carried out in the presence of TMSCl as a catalyst in NMP. Silylation of the diamine is an efficient method for activation of diamine to obtain higher molecular weight polymers. According to the literature, the diamine component can be activated by *in situ* addition of TMSCl to the diamine solutions (28–31). As shown in Scheme 3, due to the strong affinity of Si for oxygen, the carbonyl oxygen of the acid chloride is attracted to the Si atom in the amine derivatives, which in turn facilitates the nucleophilic attack of the N atom of the N-silylated amine on the carbonyl carbon. Then, the elimination of chloride ion from the tetrahedral intermediate is enhanced by the presence of the β–silicon through the σ–π effect, rapidly affording the amide product along with TMSCl (as shown in Scheme 3). Another important aspect of using TMSCl was that it could avoid the subsidiary reaction of the small amount of water.

3.2.2. *The Intrinsic Viscosity (η_{int}) and Molecular Weights of PASSA*

The molecular weight of PASSA was determined by η_{int} and GPC as shown in Table 3. The η_{int}'s of **PA-3a** and **PA-3b** were measured in the range 0.81–0.93dL/g. **PA-3a** and **PA-3b** showed Mn values in the range $8.3–9.8\times10^4$, and Mw values in the range $12.7–16.3\times10^4$, respectively. The polydispersity indices (PDIs) of **PA (3a-3b)** ranged from 1.47–1.61.

Table 3. Intrinsic viscosity (η_{int}) and molecular weights of PASSA (**3a-3b**)

Sample	η_{int} *(dL/g)*	*Mn (g/mol)*	*Mw (g/mol)*	*PDI (Mw/Mn)*
PA-3a	0.81	8.3×10^4	1.27×10^5	1.47
PA-3b	0.93	9.8×10^4	1.63×10^5	1.61

Table 4. Elemental analysis results of **PA** (**3a-3b**)

Compound	*C (%)*	*H (%)*	*N (%)*
PA-3a	66.40 (66.39)	3.85(3.84)	5.39 (5.34)
PA-3b	64.98(64.63)	3.79 (3.73)	4.66 (4.71)

*The data in brackets were those calculated.

3.2.3. *Elemental Analysis of PASSA*

Table 4 showed that the experimental results were similar with the calculated results. It suggested that PASSA was successfully synthesized as Scheme 2.

3.2.4. *The Chain Structure of PASSA*

Figure 6 showed the FT-IR spectrum of PASSA (**3a-3b**). When compared with monomer (**2a-2b**), three absorptions of the diamine between 3200 cm^{-1}–3500 cm^{-1} had been changed into single absorption nearby 3350 cm^{-1}, meanwhile, absorption appeared near 1650 cm^{-1}. It suggested the polymers were successfully synthesized.

Figure 7 showed the ^{1}H-NMR spectrum of m-PASSA (**PA-3a**). Nine groups of peaks appeared in the ^{1}H-NMR spectrum of **PA-3a** in Figure 7. The ratio of corresponding integral curves was (H1-H2):(H3-H4):H5:H6: (H7-H9):H10:H11:H12:H13 = 5:6:4:4:12:4:1:2:2. These peaks of H_1-H_{13} were consistent with the expected structure. The chemical shifts (δ) of **PA-3a** were listed in Table 5, **PA-3b**: Nine groups of peaks appeared in the ^{1}H-NMR spectrum of **PA-3b** in Figure 8. The ratio of corresponding integral curves was H1:H2: H3: H4:(H5-H8): (H9-H10):H11:H12 = 2:2:2:2:8:2:2:1:1, These peaks of H_1-H_{12}were consistent with the expected structure. The chemical shifts (δ) of **3b** were listed in Table 5.

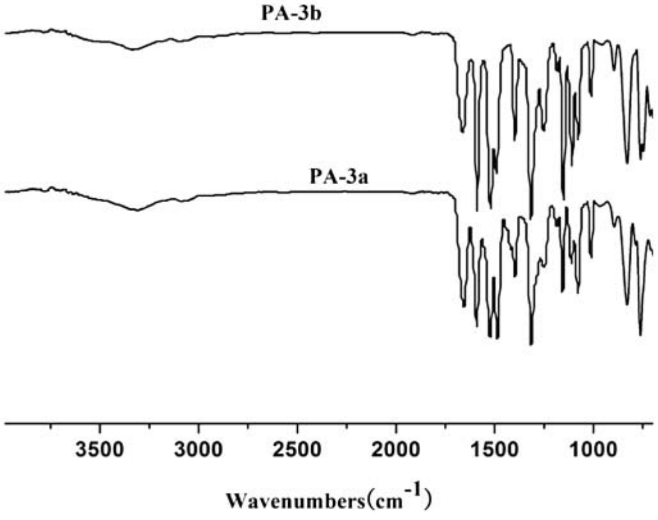


Fig. 6. FT-IR spectrum of **PA** (**3a-3b**).

Table 5. Chemical shifts (δ) of **PA** (**3a-3b**)

PA-3a	*H_1-H_2*	*H_3-H_4*	*H_5*	*H_6*	*H_7-H_9*
Chemical shifts δ(ppm)	7.244–7.279	7.422–7.465	7.521–7.535	7.619–7.632	7.887–7.913
PA-3a	H_{10}	H_{11}	H_{12}	H_{13}	
Chemical shifts δ(ppm)	8.009–8.022	8.276	10.258	10.555	
PA-3b	H_1	H_2	H_3	H_4	H_5-H_8
Chemical shifts δ(ppm)	7.240–7.253	7.421–7.435	7.518–7.531	7.618–7.630	7.862–7.912
PA-3b	H_9-H_{10}	H_{11}	H_{12}		
Chemical shifts δ(ppm)	7.974–8.018	10.555	10.582		

3.2.5. *The Thermal Properties of PASSA*

The thermal properties of PASSA were examined by DSC and TG analysis. The results were displayed in Figures 9 and 10. As shown in Figure 9, the T_g values of **PA-3a** and **PA-3b** were 245.3°C, 265.8°C (Table 6), respectively. The curve of **PA-3a** and **PA-3b** did not show a melting endothermic peak. Thus, DSC measurements also revealed that **PA-3a** and **PA-3b** was amorphous. As manifested in Figure 11, the initial degradation temperature (T_d) of **PA-3a** and **PA-3b** in nitrogen were 446.9°C, 441.6°C, respectively. **PA-3a** and **PA-3b** left more than a 40% char yield at 800°C (in Table 6). The TGA data indicated that these two kinds of polymer had better thermal stability.

3.2.6. *Tensile Properties*

The average tensile strength of PASSA (**PA-3a** and **PA-3b**) casting-film was treated at 120°C–140°C for 10 h in an oven, then 180°C for 10 h were given in

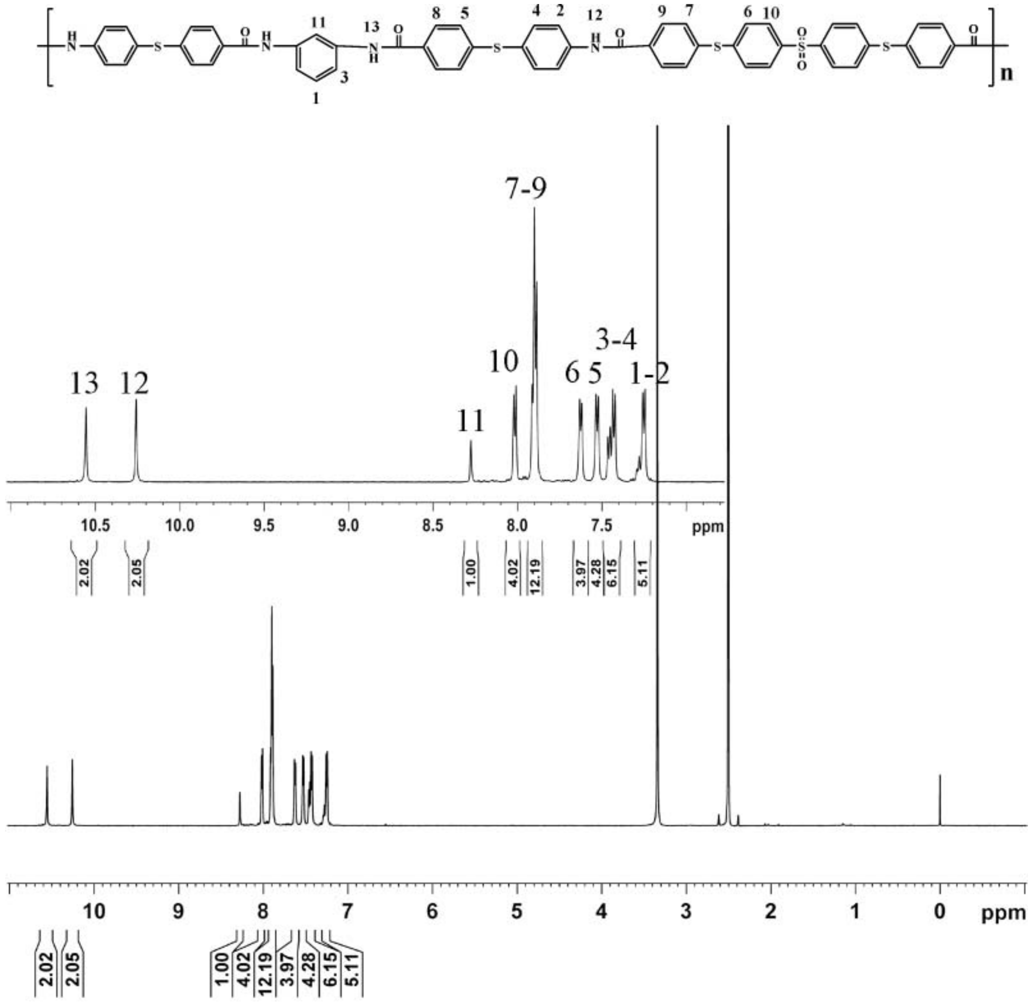


Fig. 7. ^{1}H-NMR spectrum of **PA-3a.**

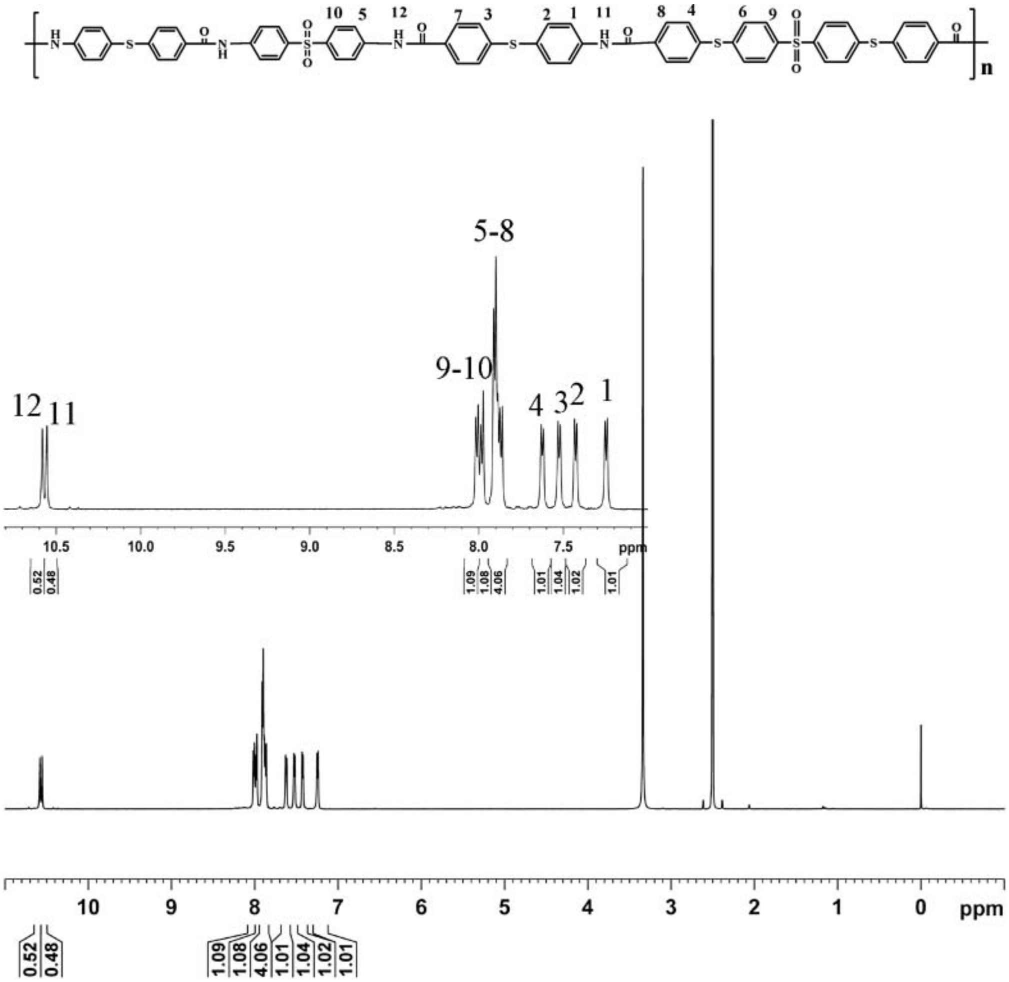


Fig. 8. ^{1}H-NMR spectrum of **PA-3b**.

Table 7. As shown in Table 7, the average tensile strength of the films **PA-3a** and **PA-3b** was 107.3 MPa and 110.8 MPa, respectively. The breakage extensibility was less than 5%, it suggested that the film was brittle fracture.

3.2.7. *Optical properties*

Figure 11 showed the optical transmission spectra of **PA-3a** and **PA-3b**. The cut-off wavelengths (λcutoff) of the

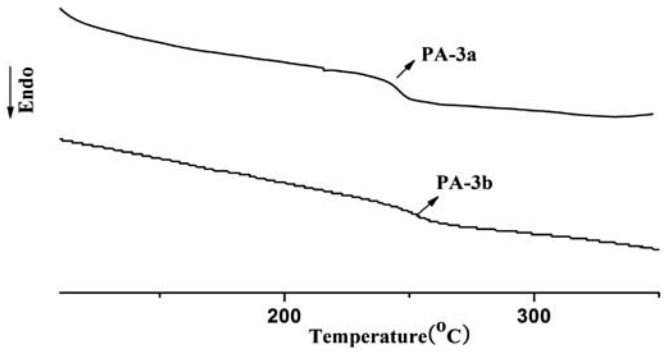


Fig. 9. DSC analysis of **PA** (**3a-3b**) at heating rate of 10°C/min.

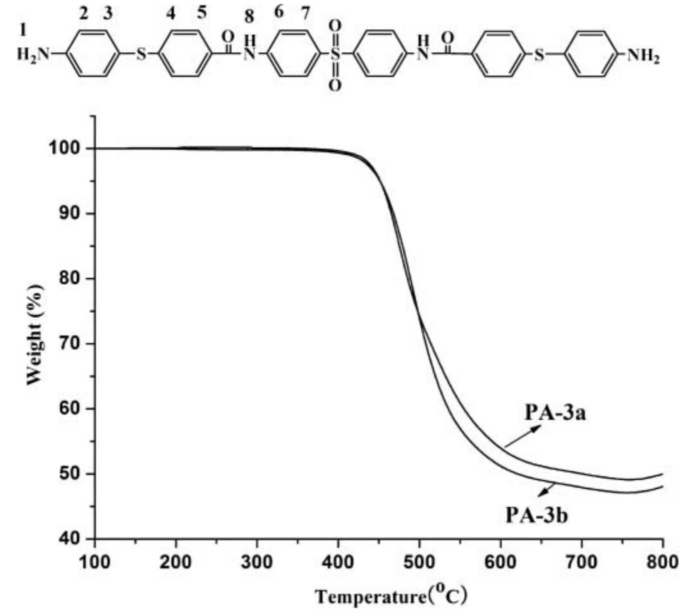


Fig. 10. TGA weight loss behavior of **PA** (**3a-3b**) at heating rate of 10°C/min in N_2.

Table 6. Thermal Properties of PA-3a and PA-3b

Polymer	$T_g(°C)$	$T_d(°C)$	*Char Yield(%)*
PA-3a	245.3	446.9	42.9
PA-3b	265.8	441.6	41.3

Table 7. Tensile properties of PA-3a and PA-3b

Polymer	*Tensile strength (MPa)*	*Breakage extensibility (%)*
PA-3a	107.3	2.6
PA-3b	110.8	4.3

Table 8. Optical properties of the films of PA-3a and PA-3b

Polymer	*Sc (%)*	$\lambda_{cutoff}(nm)$	$T_{450}(\%)$	n_{TE}	n_{TM}	n_{AV}	Δn
PA-3a	15.28	367	85.82	1.701	1.695	1.699	0.006
PA-3b	16.17	364	85.18	1.703	1.696	1.701	0.007

Sc- the content of S; T_{450}- the transmittance of films at 450nm;ε- dielectric constant; n_{TE} - the in-plane refractive index; n_{TM} - the out-of-plane refractive index; Δn – birefringence.

Table 9. Solubility behavior of PA-3a and PA-3b

	Polymer			*Polymer*	
Solvent	*PA-3a*	*3b*	*Solvent*	*PA-3a*	*3b*
Concentrated sulfuric acid	+	+	Chloroform	−	−
formic acid	−	−	DMSO	+	+
NMP	+	+	1, 4−Dioxane	−	−
DMF	+	+	Toluene	−	−
HCl	−	−	DMAC	+	+
acetone	−	−	phenol+ tetrachloroethane**	+	+

*+: soluble at room temperature; −: insoluble with heating.

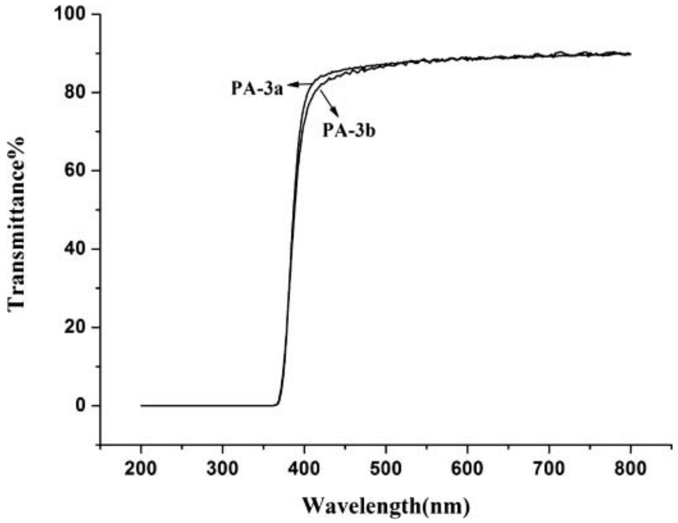


Fig. 11. UV Vis spectra of **PA** (**3a-3b**) films.

PA films were in the range of 364–367 nm. The spectral shapes of **PA-3a** and **PA-3b** were similar to each other, and the transmittance of the films measured at 450 nm was much higher than 80% (film thickness: 13–14μm). These results indicated that sulfur-containing polyamide did not deteriorate the optical transparency. The optical properties of the PA films, such as cut-off wavelengths, in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive index, average refractive indices (nav), and birefringences (Δn) were listed in Table 8. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive index of **PA-3a** and **PA-3b** were in the range of 1.701–1.695 and 1.703–1.696, respectively. The n_{av} value of **PA-3a** and **PA-3b**, measured at 632.8 nm, is from 1.699 to 1.701, although they are not much higher than aromatic PI which contained similar sulfur content because PI had a more rigid imide ring (32). The **PA-3a** and **PA-3b** showed low Δn in the range of 0.006 and 0.007. The high refractive index and low Δn value of **PA-3a** and **PA-3b** can be attributed to the high content of -S-linkages in the main chains.

3.2.8. *Solubility Experiment*

Table 9 showed that PASSA (**PA-3a** and **PA-3b**) had better solubility in polar aprotic solvents. They were soluble in NMP, DMF, DMAC, DMSO and concentrated sulfuric acid etc. at room temperature and showed no tendency to precipitate. So they may be processed by more methods, such as electro-spinning, solution casting etc. But they cannot dissolve in HCl, formic acid, toluene and 1, 4-dioxane, etc. Compared to alkyl-polyamide, PASSA showed a better corrosion resistance.

4 Conclusions

In this paper, high molecular weight PASSA was prepared successfully by polycondensation reaction. PASSA was a kind of thermo-stable resin with higher glass transition temperature and initial degradation temperature. **PA-3a** and **PA-3b** were both amorphous. They had better solubility in polar aprotic solvents, and can be used to prepare films that have better mechanical properties, high transparency, refractive index and low birefringence.

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