Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of Poly(meta-aryl sulfide amide amide)

Gang Zhang[a]; Jing Liu[a]; Mei-Lin Zhang[a]; Sui-Lin Liu[b]; Sheng-Ru Long[b]; Jie Yang[bc]
[a] College of Chemistry, Sichuan University, Chengdu, P. R. China [b] Institute of Materials Science and Technology, Sichuan University, Chengdu, P. R. China [c] State Key Laboratory of Polymer Materials Engineering of China, Sichuan University, Chengdu, P. R. China

To cite this Article Zhang, Gang , Liu, Jing , Zhang, Mei-Lin , Liu, Sui-Lin , Long, Sheng-Ru and Yang, Jie(2009) 'Synthesis and Characterization of Poly(meta-aryl sulfide amide amide)', Journal of Macromolecular Science, Part A, 46: 10, 1015 — 1023

To link to this Article: DOI: 10.1080/10601320903158768

URL: http://dx.doi.org/10.1080/10601320903158768

Journal of Macromolecular Science®, *Part A: Pure and Applied Chemistry* (2009) **46**, 1015–1023
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903158768

Synthesis and Characterization of Poly(meta-aryl sulfide amide amide)

GANG ZHANG[1], JING LIU[1], MEI-LIN ZHANG[1], SUI-LIN LIU[2], SHENG-RU LONG[2] and JIE YANG[2,3,*]

[1] *College of Chemistry, Sichuan University, Chengdu 610064, P. R. China*
[2] *Institute of Materials Science and Technology, Sichuan University, Chengdu 610064, P. R. China*
[3] *State Key Laboratory of Polymer Materials Engineering of China, Sichuan University, Chengdu, 610065, P. R. China*

Received February 2009, Accepted April 2009

Poly(meta-aryl sulfide amide amide) (m-PASAA) was prepared with aromatic nucleophilic substitution reaction: by the step polycondensation of sodium sulfide($Na_2S\cdot xH_2O$) with 3,3′ -bis(4-diflurobenzoyl) aryl diamine between 180–202°C at atmospheric pressure. The polymers were characterized by FT-IR spectrum, ^{1}H-NMR spectrum, ^{13}C-NMR spectrum, X-ray diffraction, element analyzer, DSC, TGA, AFM, instron universal tester and dissolvability experiment. The intrinsic viscosity of m-PASAA was 0.41–0.46 dl/g obtained with optimum synthesis conditions. The polymers were found to have excellent thermal performance with glass transition temperature (T_g) of 233.5–277.8°C, initial degradation temperature (T_d) of 447–456.7°C. They could afford flexible and strong films with tensile strengths 38.4–46.1MPa. At the same time, their solubility was much better than polyphenylene sulfide (polyphenylene sulfide scarcely dissolves in whole organic solvents under 200°C (1)).

Keywords: Polyphenylene sulfide, atmospheric pressure, 3,3′ -bis(4-diflurobenzoyl) aryl diamine, poly(meta-aryl sulfide amide amide), solubility

1 Introduction

A special kind of thermoplastic engineering material poly(arylene sulfide)s (PAS) has received much attention due to its excellent mechanical and thermal properties. A number of available PAS such as polyphenylene sulfide (PPS), poly(phenylene sulfide sulfone) (PPSS), poly(phenylene sulfide ketone) (PPSK), poly(phenylene sulfide amide) (PPSA) etc. (Scheme 1) were synthesized and developed in the last few decades. PPS is a semi-crystalline polymer with T_g and T_m around 8°C, 285°C, respectively, was considered to possess inherent fire resistant and excellent chemical resistance. It can be processed by melting molding (2–9). PPSS is amorphous and soluble, but its solution was unstable and showed a tendency to precipitate (10–18). While PPSA had been reported, it had low molecular weight that limited its application (19–20). In this paper, the normal pressure synthesis method was used to synthesize m-PASAA which reduced the experimental cost and environment pollution. This kind of modified PAS materials combined better qualities of polyamide (PA) and PPS. For the purpose of obtaining a new kind of PAS materials that possessed good qualities of excellent thermal, chemical, mechanical and physical characters, poly(meta-aryl sulfide amide amide) were successfully synthesized by polycondensation under normal pressure. The elemental analyzer was used to examine the constituent of the polymer. The chain and aggregation structure of m-PASAA were characterized by FT-IR spectrum, ^{1}H-NMR spectrum, ^{13}C-NMR spectrum and X-ray diffraction. Differential scanning calorimetry (DSC) and thermogravimetic analysis (TGA) were employed to understand the thermal properties of m-PASAA. The micro-structure of the polymer films' surface was detected by atomic force microscopy (AFM), the instron universal tester and electrical insulation detector equipment were employed to study the films' mechanical performance and electrical insulation. The dissolvability experiment was employed to study their solubility.

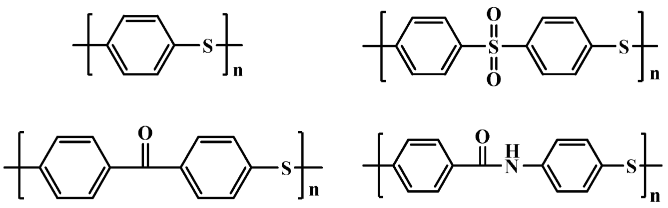
2 Experimental

2.1 Materials

Commercially available 3,3′ -diaminobenosulfone (DABS) (AR, JiangSu YangZhong Synthesis Chemical Industry

---

*Address correspondence to: Jie Yang, Institute of Materials Science and Technology, Sichuan University, Chengdu 610064, P. R. China or State Key Laboratory of Polymer Materials Engineering of China, Sichuan University, Chengdu, 610065, P. R. China. Fax: 86-28-8541-2866; E-mail: ppsf@scu.edu.cn



Sch. 1. Four kinds of available poly(arylene sulfide).

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), sodium sulfide ($Na_2S\cdot xH_2O$ $Na_2S\%$ ≈60%) (Nafine Chemical Industry Group Co., Ltd.), sodium hydroxide (NaOH) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company), N-methyl-2- pyrrolidone (NMP) (JiangSu NanJing JinLong Chemical Industry Company), triethylamine (Et_3N) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company), all of them were used without further purification. Tetrahydrofuran (THF) (AR, SiChuan ChengDu ChangLian Chemical Reagent Company) was purified by reduced pressure distillation. Catalyzers A and B were made in our lab. Other reagents and solvents were obtained commercially.

2.2 Monomer Synthesis

2.2.1. *3,3′ -bis(4-diflurobenzoyl) diaminobenzene (1a) (Scheme 2)* (21)

1a was prepared as Scheme 2 using the following procedure: to a 250 ml round bottom three-necked flask was added 24.8 g (0.1mol) of 3,3′ -diaminobenosulfone, 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 an 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); this afforded **1a** as a white sheet crystal.

Yield: 29 g, 82.3%. m.p.: 265–267°C.

2.2.2. *3,3′ -bis (4-diflurobenzoyl) diaminophenyl sulfone (1b)*

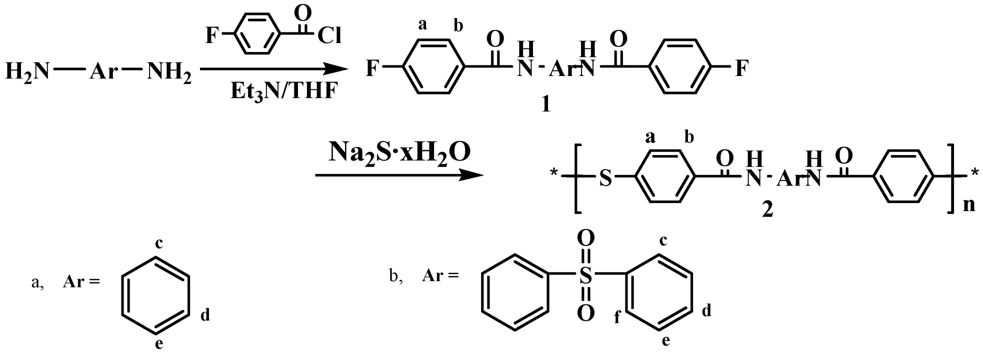
1b was prepared as **1a**. The crude product of **1b** was recrystallized from acetone; this afforded **1b** as a white needle crystal.

Yield: 38.7 g, 78.6%. m.p.: 254–256°C.

2.3 Polymer Synthesis

2.3.1. *Synthesis of poly(meta-aryl sulfide amide amide) (m-PASAA) (Scheme 2)*

m-PASAA was synthesized by an aromatic nucleophilic substitution reaction of **1a** or **1b** with sodium sulfide in NMP at atmospheric pressure as depicted in Scheme 2. A typical polymerization of m-PASAA (**2a**) was carried out as follows. In a 250 ml three-necked flask equipped with water segregator, reflex condenser, mechanical stirrer, and thermometer was added 100 ml of NMP, 13.00 g (0.10 mol) of sodium sulfide, 4 g (0.10 mol) of sodium hydroxide, 1.7 g of Cat.A, 2.3 g of Cat. B (22), then the reactor was heated to 180°C in 35 min and kept for 20 min; during this course, 6.2 ml liquid was removed. When the above reaction vessel was cooled to 110°C, 35.2 g (0.1 mol) of **1a** was added into the reactor, kept for 1 h at 180°C, then the reactor was heated to 200°C and maintained for 4 h. The reaction-solution was then poured into water to precipitate a fibrous polymer under stirring conditions. The crude product was then pulverized and washed several times with hot water to remove possible residual salt. After the purified polymer was filtered, the polymer was extracted with water and acetone, respectively, then further vacuum-dried at 100°C for more than 12 h to yield 36 g (yield: 92%) of a greyish white powder.



Sch. 2. Synthesis route of polymer (**2a**–**2b**).

Table 1. Elemental analysis results of *1a–1b*

Compound	*C(%)*	*H (%)*	*N(%)*
1a	68.22 (68.18)	4.09(4.01)	7.99 (7.95)
1b	63.47 (63.4)	3.71 (3.68)	5.68 (5.69)

The data in brackets were those calculated.

2.4 Characterizations

2.4.1. *Intrinsic viscosity and gel permeation chromatography (GPC)*

Intrinsic viscosity of m-PASAA 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: (23):

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

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 (**2a**–**2b**) and m-PASAA were determined by elemental analyzer (EURO EA-3000)

2.4.3. *Characterization of chain structure*

The samples of m-PASAA casting films were prepared. FT-IR spectroscopic measurements were determined by NEXUS670 FT-IR instrument. Nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR) instrument for the determination of the samples structure were provided with a BRUKER-400 NMR Spectrometer. The samples were dissolved in deuterated dimethyl sulfoxide.

2.4.4. *Characterization of aggregation structure*

The samples (subsequently dried at 110°C in vacuum oven for 24 h, then annealed at 240–280°C for 4 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. *Characterization of the film-surface micro-structure*

The samples were characterized by atomic force microscopy (AFM-SPA-400 SPM UNIT). Films were prepared by casting NMP solution on microscopy slide glass. Samples were subsequently dried at 100°C, 120°C, 140°C, 170°C for 10 h in an oven, then annealed for 4 h at 240 and 280°C, respectively.

2.4.7. *Tensile properties*

An Instron universal tester model JG-4000 with a load cell of 5 kg was used to study the stress-strain behavior of m-PASAA film samples, and the tensile strength was detected according to GB/T 13022-1991.

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 monomers (1a–1b)*

The monomer 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 disproportionate.

Table 2. Chemical shifts (δ) of **1a**–**1b**

1a	H_a	H_b	H_c	H_d	H_e	H_f
Chemical shifts δ (ppm)	7.392–7.370	8.063–8.041	8.318	7.506–7.486	7.342–7.322	10.332
1b	H_a	H_b-H_c	H_d-H_e	H_f	H_g	
Chemical shifts δ (ppm)	7.369–7.413	7.638–7.689	8.037–8.084	8.464–8.474	10.631	

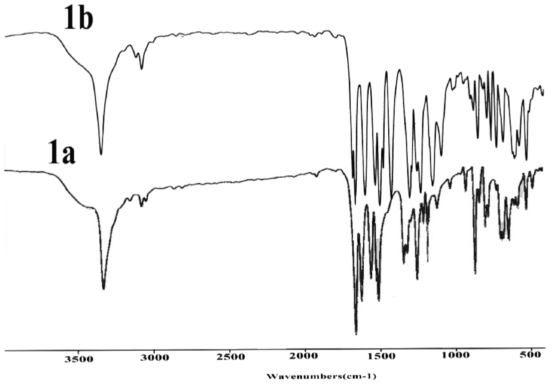


Fig. 1. FT-IR spectrum of monomers **1a**–**1b**.

3.1.2. *Elemental analysis of monomers*

Table 1 showed that the experimental results were similar to the calculated results. It suggested the monomers were synthesized as Scheme 2.

3.1.3. *The chain structure of 1a–1b*

Figure 1 showed the FT-IR spectrum of **1a**–**1b**. **1a**: the absorption of 3322 cm^{-1} was the N-H stretching vibration absorption. The absorption of 1644 cm^{-1}, 1540 cm^{-1} suggested the formation of -CO-NH-. We observed the benzene rings absorption:1604 cm^{-1}, 1506 cm^{-1} and 1489 cm^{-1} and the absorption of benzene meta-substitute: 778 cm^{-1} was also present. **1b**: the absorption of N-H: 3346 cm^{-1}, the absorption of -CO-NH-: 1678 cm^{-1}, 1530 cm^{-1}, the benzene rings absorption: 1597 cm^{-1}, 1500 cm^{-1} and 1475 cm^{-1}, the typical absorption of sulfone group: 1302 cm^{-1}, 1151 cm^{-1} and the absorption of benzene meta-substitute: 785 cm^{-1}. Figure 2 was the ^{1}H-NMR spectrum of **1a**–**1b**. Six groups of peaks appeared in the ^{1}H-NMR spectrum of **1a** in Figure 2. The ratio of corresponding integral curves was about 1:4:2:4:1:2. Combining the results of FT-IR, these five groups of peaks were ascribed to the construction units of Ha, Hb, Hc, Hd, He, and Hf. The chemical shifts (δ) of **1a** were listed in Table 2. **1b**: Five groups of peaks appeared in the ^{1}H-NMR spectrum of **1b** in Figure 2. The ratio of corresponding integral curves was 1:1:3:2:2. The calculated result should have seven group peaks and the ratio of corresponding integral curves was 1:1:1:2:1:1:2, but the chemical shift of Hd-He and Hc-Hb is so approximate that it cannot be split. Combining the results of FT-IR, these five groups of peaks were ascribed to the construction units of Ha, Hb, Hc, Hd, He, Hf, and Hg. The chemical shifts (δ) of **1b** were listed in Table 2.

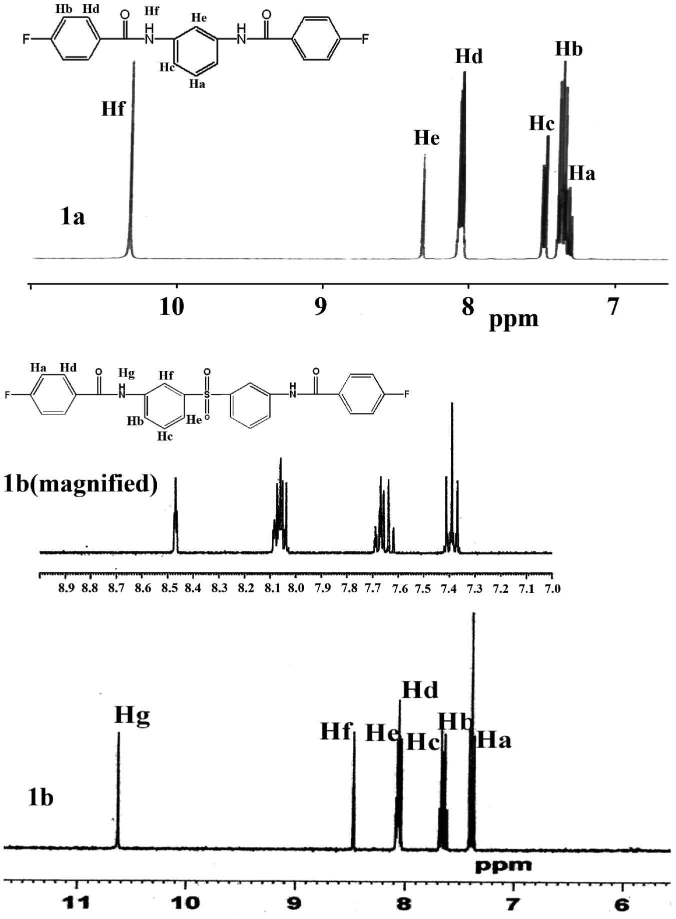


Fig. 2. ^{1}H-NMR spectrum of monomers **1a**–**1b**.

Table 3. Intrinsic viscosity (η_{int}) and molecular weights of m-PASAA (**2a**–**2b**)

Sample	η_{int} *(dL/g)*	*Mn (g/mol)*	*Mw (g/mol)*	*PDI (Mw/Mn)*
2a	0.41	4.50×10^4	7.13×10^4	1.57
2b	0.46	4.91×10^4	8.74×10^4	1.78

3.2 Polymers

3.2.1. *Synthesis of m-PASAA (2a–2b)*

At present, the mechanism about the synthesis process of m-PASAA has not been reported. However, the mechanism of the synthesis process of PPS had been discussed by many researchers in detail (24). The difference in the synthesis process between m-PASAA and PPS was that the monomer (**1a**–**1b**) acted as the activated aromatic halide in synthesis of m-PASAA, while 4,4′ -dichlorobenzene acted as inactivated aromatic halide in that of PPS (25–27). Before adding the second monomer, the two processes were congruous. Based on the results of Darryl et al. about

Table 4. Elemental analysis results of m-PASAA (**2a**–**2b**)

Compound	*C(%)*	*H (%)*	*N(%)*	*S(%)*
2a	69.28 (69.35)	4.03 (4.07)	8.06 (8.09)	9.19 (9.26)
2b	64.02 (64.18)	3.75 (3.73)	5.66 (5.76)	13.25 (13.18)

The data in brackets were those calculated.

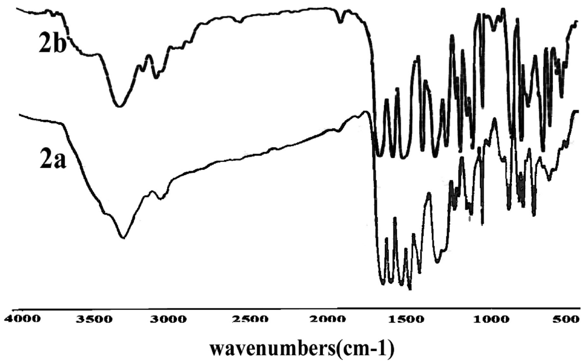


Fig. 3. FT-IR spectrum of m-PASAA (**2a**–**2b**).

synthesis mechanism of PPS, the conclusion is that the $Na_2S\cdot xH_2O$ reacted with the solvent and produced a kind of new complex compound which can be denoted as $Na_2S\cdot NMP\cdot H_2O$. The mechanism process followed that of S_NAr, which can be accelerated by NMP. Some experiments have proved that NMP can accelerate the reaction of m-PASAA by promoting the reactivity of S^{2-} (28–30). However, further work would be necessary to confirm the synthesis mechanism of m-PASAA.

3.2.2. *The intrinsic viscosity (η_{int}) and molecular weights of m-PASAA*

The molecular weight of m-PASAA was determined by GPC and η_{int} as shown in Table 3. **2a** and **2b** showed Mn values in the range 4.50–4.91 × 10^4, and Mw values in the range 7.13–8.74 × 10^4, respectively. The η_{int}'s of **2a**–**2b** were measured in the range 0.41–0.46 dL/g. The polydispersity indices (PDIs, PDI=Mw/Mn) of **2a**–**2b** ranged from 1.57–1.78. The molecular weight of **2a** was less than that of **2b** because the reactivity of **1a** was lower than that of **1b**.

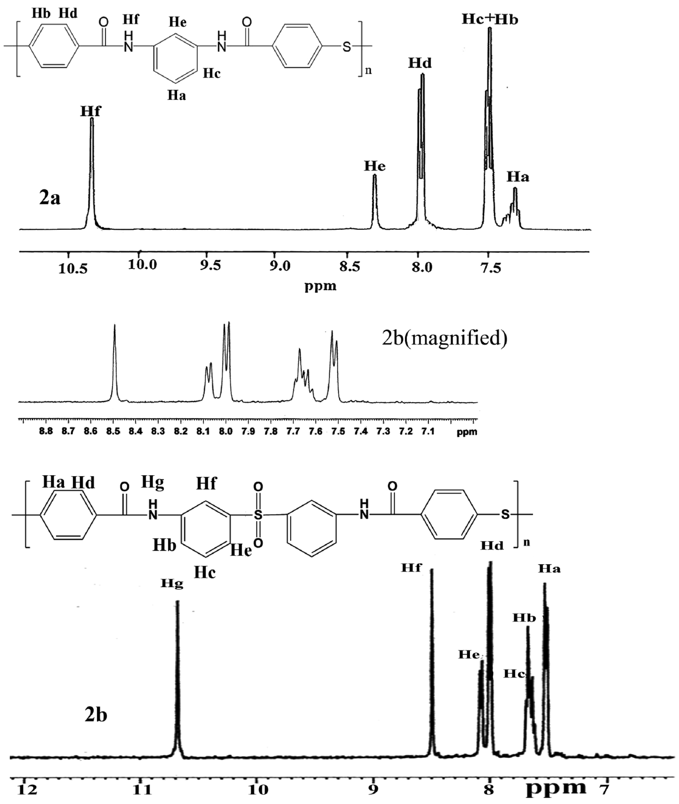


Fig. 4. ^{1}H-NMR spectrum of m-PASAA (**2a**–**2b**).

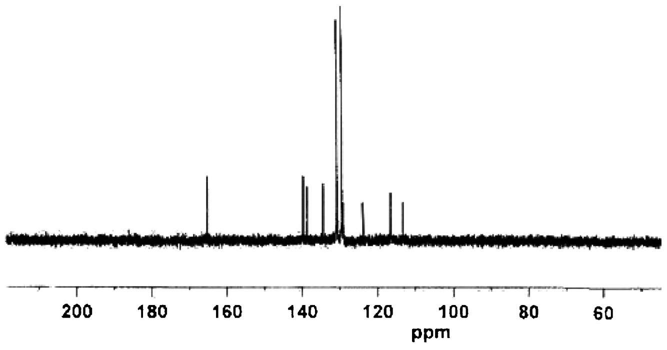


Fig. 5. ^{13}C-NMR spectrum of **2a**.

3.2.3. *Elemental Analysis of m-PASAA*

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

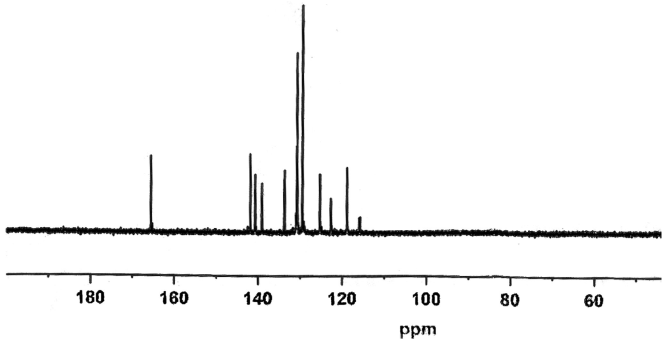


Fig. 6. ^{13}C-NMR spectrum of **2b**.

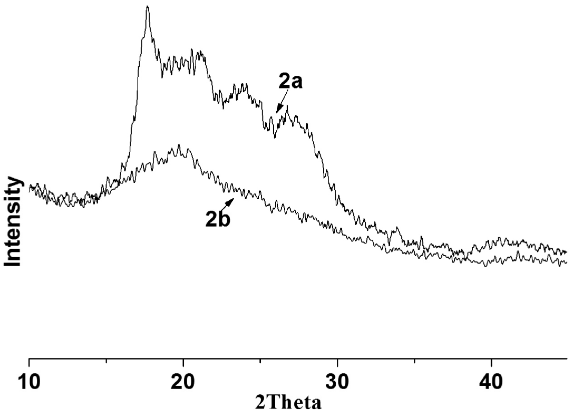
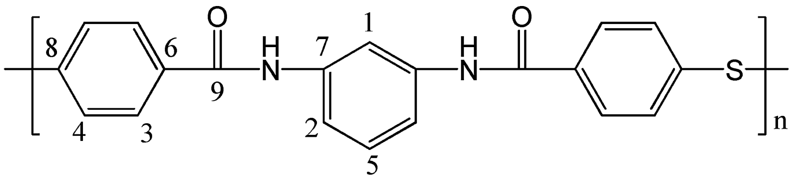
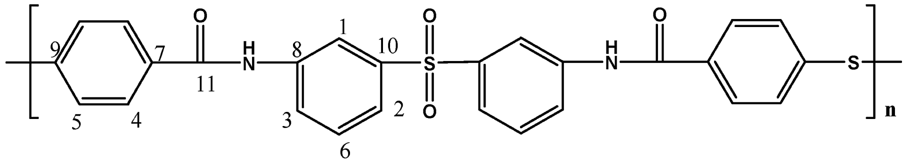


Fig. 7. XRD spectra of m-PASAA annealed (**2a**–**2b**).





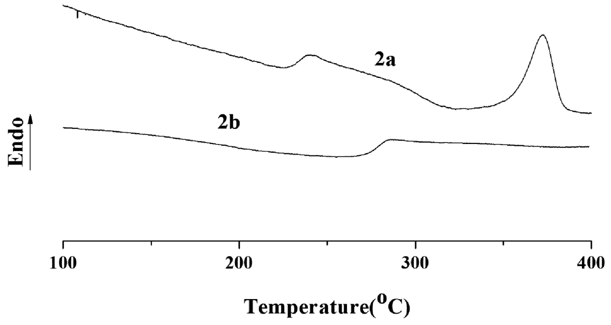


Fig. 8. DSC analysis of m-PASAA (**2a**–**2b**) at heating rate of 10°C/min.

3.2.4. *The chain structure of m-PASAA*

Figure 3 showed the FT-IR spectrum of m-PASAA (**2a**–**2b**). When compared with monomer (**1a**–**1b**), the strong absorption of the thio-ether bond near 1080 cm^{-1} could be identified in the spectrum of **2a** or **2b** in Figure 3. It suggested the polymers were successfully synthesized.

Figure 4 showed the ^{1}H-NMR spectrum of m-PASAA (**2a**–**2b**). Six groups of peaks appeared in the ^{1}H-NMR spectrum of **2a** in Figure 4. The ratio of corresponding integral curves was about 1:4:2:4:1:2. Combining the results of FT-IR, these six groups of peaks were ascribed to the construction units of Ha, Hb, Hc, Hd, He and Hf. The chemical shifts (δ) of **2a** were listed in Table 5. **2b**: Six groups of peaks appeared in the ^{1}H-NMR spectrum of **2b** in Figure 4. The ratio of corresponding integral curves was 1:1:1:2:2:2, the calculated result should have seven groups peeks and the ratio of corresponding integral curves was 1:1:1:2:1:1:2., but the high viscosity of the solution restrained molecule oscillation, and the chemical shift of Hb, Hc is so approximate that the weak split signal was shielded. Combining the results of FT-IR, these six groups of peaks were ascribed to the construction units of Ha, Hb, Hc, Hd, He, Hf and Hg. The chemical shifts (δ) of **2b** were listed in Table 5. Figure 5 showed the ^{13}C-NMR spectrum of **2a**. Nine groups of peaks C1-C9 were 113.35, 116.61, 123.46, 129.47, 130.79, 134.42, 138.68, 139.73 and 165.24. Figure 6 showed the ^{13}C-NMR spectrum of **2b**. Eleven groups of peaks C1-C11 were 115.99, 118.86, 122.71, 125.32, 129.52, 130.73, 133.76, 139.11, 140.69, 141.88 and 165.6 respectively.

3.2.5. *The aggregative structure of m-PASAA*

X-ray diffraction of m-PASAA (**2a**–**2b**) annealed was listed in Figure 7. As manifested in Figure 7, the polymer of **2a** had a partial regular structure. But **2b** was amorphous,

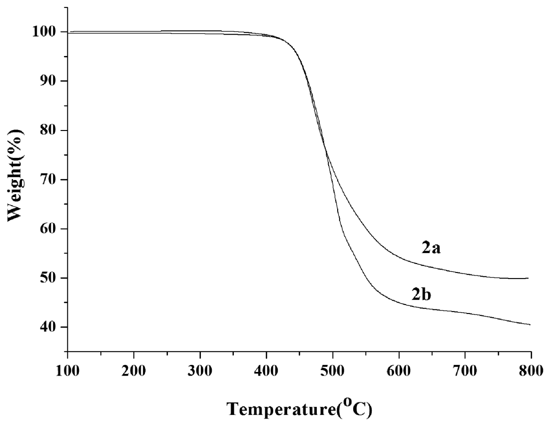


Fig. 9. TGA weight loss behavior of m-PASAA (**2a**–**2b**) at heating rate of 10°C/min in N_2.

Table 5. Chemical shifts (δ) of m-PASAA (**2a**–**2b**)

2a	H_a	H_b	H_c	H_d	H_e	H_f
Chemical shifts δ (ppm)	7.395–7.375	8.075–8.055	8.509	7.509–7.490	7.690–7.672	10.373
2b	H_a	H_b-H_c	H_d	H_e	H_f	H_g
Chemical shifts δ (ppm)	7.508–7.527	7.634–7.690	7.987–8.007	8.066–8.0846	8.494	10.677

the probable reason was the existence of a strong polarity sulfone group and the asymmetry of the molecular chain. The molecule chain locomotion was limited by the sulfone group so it could not arrange in order.

3.2.6. *The thermal properties of m-PASAA*

The thermal properties of m-PASAA were examined by DSC and TG analysis. The results were displayed in Figures 8 and 9. As shown in Figure 8, the T_g values of **2a** and **2b** were 233.5°C, 277.8°C (Table 6), respectively. The curve of **2a** showed a melting endothermic peak at 375°C before decomposition of the polymer, but **2b** showed no melting endothermic peak. Thus, DSC measurements also revealed that **2a** was semi-crystalline, the amorphous nature of **2b**, and this agreed with the results of X-ray diffraction. As manifested in Figure 9, the initial degradation temperature (T_d) of **2a** and **2b** in nitrogen were 447°C, 456.7°C, respectively. **2a** and **2b** left more than a 50% and 40% char yield, respectively at 800°C (Table 6). The TGA data indicated that these two kinds of polymer had better thermal stability.

3.2.7. *Characterization of the film-surface micro-structure*

The film-surface micro-structure of **2a** and **2b** were detected with AFM. As shown in Figure 10, it could be found that the surface of the film (**2b**) had some nodular structure. At the same time, these nodular structures distributed more were less with increasing the treated temperature. It can be explained with the research of X. J. Wang et al. (31). The appearance of this structure may be ascribed to the influence of a casting-film procedure and solvent. This nodular structure was formed by a certain amount of solvent remaining in the film due to glass transition of the surface layer. The remainder solvent molecules and polymer molecule chains could form paracrystallines with high surface energy. During the annealing process, the paracrystallines aggregated on the surface of the film and formed the nodules, so, the higher quantity remainder solvent in the film with the more

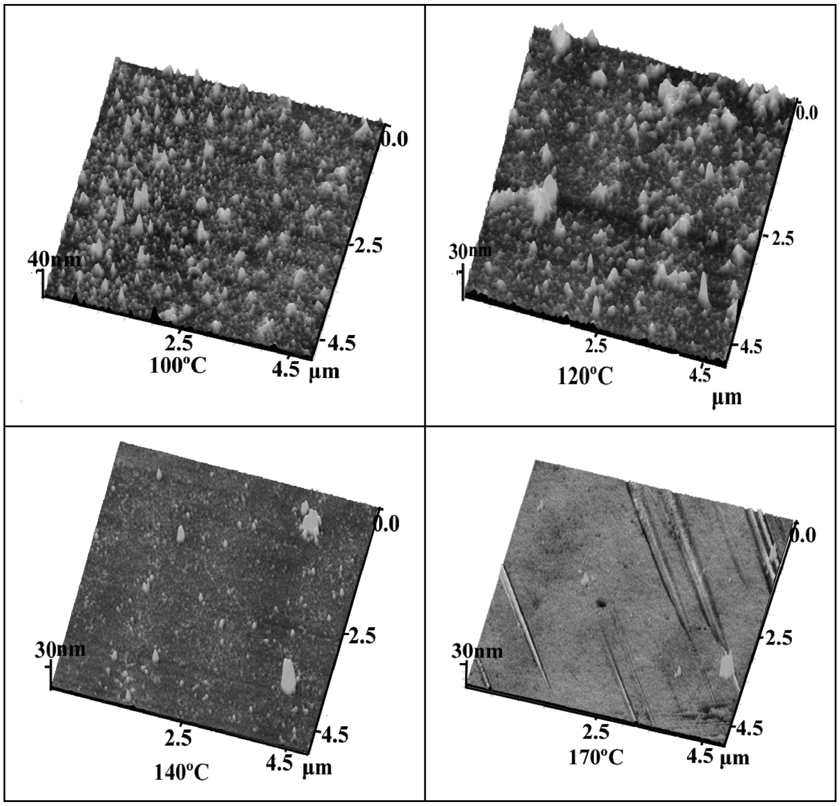


Fig. 10. The atomic force microscopy of the films (**2b**) treated at different temperatures.

Table 6. Thermal Properties of m-PASAA (**2a**–**2b**)

Polymer	T_g (°C)	T_m(°C)	T_d(°C)	*Char Yield(%)*
2a	233.5	375	447	51.2
2b	277.8	–	456.7	40.3

nodular structure; it was then not hard to understand the above phenomenon. However, the last picture treated at 170°C showed some pores on the film surface, and it was maybe ascribed to the high treated temperature, the solvent volatilized too fast and the polymer molecule chain could not move as fast as the solvent molecule below its glass transition temperature, so it formed some holes.

3.2.8. *Tensile properties*

The average tensile strength of m-PASAA (**2a**–**2b**) casting-film treated at different temperature (dried at 100°C, 120°C, 140°C, 170°C for 10 h in an oven, then annealed for 4 h at 240 and 280°C, respectively) were given in Figure 11. As shown in Figure 11, the tensile strength of **2a** and **2b** presented a tendency of first increasing and then decreasing with the treated temperature from 100°C to 170°C. The best treated temperature was 120°C–140°C, with the optimum condition the average tensile strength of the films 2a and 2b was 38.4MPa and 46.1MPa, respectively. We ascribed this phenomenon to the procedure of casting-film. The lower treated temperature, the more quantity of solvent in the films, then it formed a great deal more nodules and decreased the film's smoothness (manifested in Figure 10). On the other hand, it caused the solvent to volatilize quickly under higher treated temperature and it may result in forming flaws on the film's surface. Therefore, it was not good to treat the film under lower or higher temperatures.

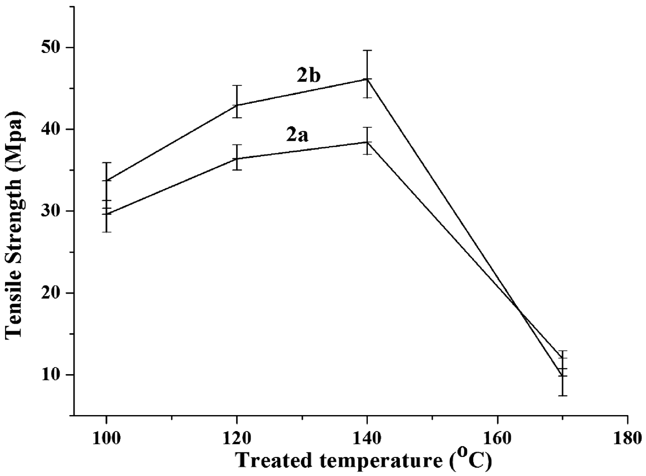


Fig. 11. The tensile strength of m-PASAA (**2a**–**2b**).

Table 7. Solubility behavior of m-PASAA

	Polymer			*Polymer*	
Solvent	*2a*	*2b*	*Solvent*	*2a*	*2b*
Concentrated sulfuric acid	++	++	Chloroform	–	–
formic acid	–	–	DMSO	++	++
NMP	++	++	1, 4-Dioxane	–	–
DMF	++	++	Toluene	–	–
HCl	+−	+−	DMAC	++	++
acetone	–	+−	phenol+tetra-chloroethane	++	++

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

3.2.9. *Solubility experiment*

Table 7 showed that m-PASAA (**2a**–**2b**) had better solubility than PPS and PPSS. They were soluble in NMP, DMF, DMAC, DMSO and concentrated sulfuric acid etc. at room temperature and showed no tendency to precipitate, so they could be processed by more methods than PPS, such as electro-spinning, solution casting etc. But they cannot dissolve in HCl, formic acid, chloroform, toluene and 1, 4-dioxane etc. Compared to polyamide, m-PASAA showed a better corrosion resistance.

4 Conclusions

In this paper, higher molecular weight m-PASAA (**2a**–**2b**) was prepared successfully by polycondensation reaction at atmosphere pressure. m-PASAA was a type of thermostable resin with higher glass transition temperature and initial degradation temperature. **2a** was semi-crystalline, but **2b** was amorphous. The best treated temperature of casting-film was 120–140°C. Under these conditions, they could afford flexible and strong films; they had better solubility than PPS and PPSS. Their solution was stable and had no precipitation tendency. They can be used in some fields such as the electron-spinning, separation membrane etc.

Acknowledgments

This work was supported by research grants from the National High Technology Foundation of China (863 program, Grant No.: 2007AA03Z561).

References

1. Yang, J. (2006) PAS resin and its application. Chemical Industry Press: *China*.

2. Bailey, G.C. and Hill, J.H.W. (1974) Polyphenylene Sulfide: A New Industry Resin. *American Chemical Society, Division of Organic Coatings and Plastics Chemistry, Preprints,* 34(1), 156–161.
3. Park, L.S., Lee, T. H. and Lee, S.C. (1999) *J. Polym. Sci. Part. A: Polymer Chemistry,* 37(14), 2311–2317.
4. Kiyoshi, S., Kohji, N. and Tetsuro, T. (1998) *US Patent 5756654*.
5. Miyahara, M., Sato, H. and Satake, Y. (1996) *EP Patent 0720998*.
6. Michael, H., Bad, K., Wagener, R. and Florsheim. (1999) *US Patent 5894072.*
7. Machida, T., Ohkura, M., Imanishi, Y. and Higashioji, T. (2007) *WO2007129721*.
8. Yang, J., Long, S.R., Tong, W. and Li, G.X. (2003) *CN Patent 1425715*.
9. Yang, J., Du, Z.Y., Long, S.R., Wang, X.J., Yang, Z., Yang, Q. and Huang, R. (2003) *CN Patent 1464008*.
10. Wang, H.D., Yang, J., Long, S.R., Du, Z.Y. and Chen, Y.R. (2003) *Polymer Materials Science and Engineering* (Chinese), 19(3), 54–57.
11. Liu, Y., Bhatnagar, A., Ji, Q., Riffile, J.S., McGrath, J.E., Geibei, J.F. and Kashiwagi, T. (2000) *Polymer,* 41, 5137–5146.
12. Campbell, R.W. and Bartlesville, O. (1978) *US Patent 4125525*.
13. Bobsein, R.L. and Clark, J.E. (1989) *US Patent 4808698*.
14. Campbell, R.W. and Bartlesville, O. (1978) *US Patent 4102875*.
15. Campbell, R.W. and Bartlesville, O. (1977) *US Patent 4016145*.
16. Campbell, R.W. and Bartlesville, O. (1981) *US Patent 4301274*.
17. Yang, J., Chen, Y.R., Wang, H.D. and Long, S.R. (2003) *CN Patent 1461763*.
18. Yang, J., Wang, H.D., Xu, S.X., Li, G.X. and Huang, Y.J. (2005) *J. Polym. Research,* 12, 317–323.
19. Wu, Q.X., Chen, Y.R. and Zhou, Z.W. (1995) *Chinese Journal of Polymer Science,* 13(2), 136–143.
20. Zhou, Z.W. and Wu, Q.X. (1997) *Journal of Applied Polymer Science,* 66, 1227–1230.
21. Lucas, M., Brock, P. and Hedrick, J.L. (1993) *J. Polym. Sci. Part. A: Polymer Chemistry,* 31, 2179–2185.
22. Yang, J., Zhang, G., Long, S.R., Wang, X.J., Liu, J. and Chen, Y.R. (2008) *CN Patent 101215379.*
23. Xu, S.X., Yang, J., Long, S.R., Chen, Y.R. and Li, G.X. (2005) *Polymer Bulletin,* 54(4-5), 251–261.
24. Darryl, R.F.and Carlton, E.A. (1991) *Macromolecules,* 24(15), 4242–4249.
25. Angel, E.L., Jimeno, M.L., Javier, D.A., Jose and Campa, G.D. (1994) *Macromolecules,* 27, 7164–7170.
26. Hilborn, J.G., Labadie, J.W. and Hedrick, J.L. (1990) *Macromolecules,* 23(11): 2854–2861.
27. Hedrick, J.L. (1991) *Macromolecules,* 24(3), 812–813.
28. Cox, B.G. and Parker, A.J. (1973) *J. Am. Chem. Soc.,* 95(2), 408–410.
29. Miller, J. and Parker, A.J. (1961) *J. Am. Chem. Soc.,* 83(1), 117–123.
30. Campbell, J.R. (1964) *J. Org. Chem.,* 29(7), 1830–1833.
31. Wang, X.J. (2008), A Study on Solution Behaviors and Applications of Polyarylene Sulfide Sulfone. *http://dlib.edu.cnki.net/kns50/detail.aspx?QueryID=6&CurRec=1* (accessed 2008).