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One-pot Synthesis and Characterization of Poly(meta-aryl sulfide sulfone imide imide)

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Poly(meta-aryl sulfide sulfone imide imide) (m-PASSII) was synthesized by one-pot process using 4-chlorophthalic anhydride, 3,3'-diamino diphenyl sulfone and sodium sulfide ($\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$) as starting materials in N-methyl-2-pyrrolidone at atmospheric pressure. The intrinsic viscosity of m-PASSII was obtained with optimum synthesis conditions is 0.21–0.27 dl/g. The polymer and the separated intermediates which generated during the synthesis process were characterized by elemental analysis, FT-IR spectrum, ¹H-NMR spectrum, X-ray diffraction, DSC, TGA and dissolvability experiment. The polymer is found to have excellent thermal performance with glass transition temperature (T_g) of 224°C and initial degradation temperature (T_d) of 441°C. Moreover, the polymer is dissolvable in strong polar solvents.

Keywords: Poly(arylene sulfide), one-pot synthesis, poly(meta-aryl sulfide sulfone imide imide), intermediates, characterization

1 Introduction

Poly(arylene sulfide)s (PAS) are polymers that have sulfide atoms and different aryl groups in main chains. They have been widely used as heat-resistant and chemical-resistant engineering plastics in aircrafts, electrics, and other high-technology area (1). Poly(phenylene sulfide) (PPS) is the first industrialized product of the PAS family. It is a semi-crystalline polymer and can be easily processed by injection and extrusion (2–3). However, PPS has low glass transition temperature (about 90°C). In order to overcome this shortcoming, many novel kinds of poly(arylene sulfide)s have been synthesized and produced in the last three decades, such as poly(phenylene sulfide sulfone) (PPSS), poly(phenylene sulfide ketone) (PPSK), poly(phenylene sulfide amide) (PPSA) etc. (4–6).

Poly(arylene sulfide)s can be synthesized in many different ways (7–16), among which the sodium sulfide method (polymerization of sodium sulfide and aromatic dihalides at high temperature) had been considered as the most proper method to produce new PASs on large scale. Imide-containing dihalides have been achieved and used for poly-

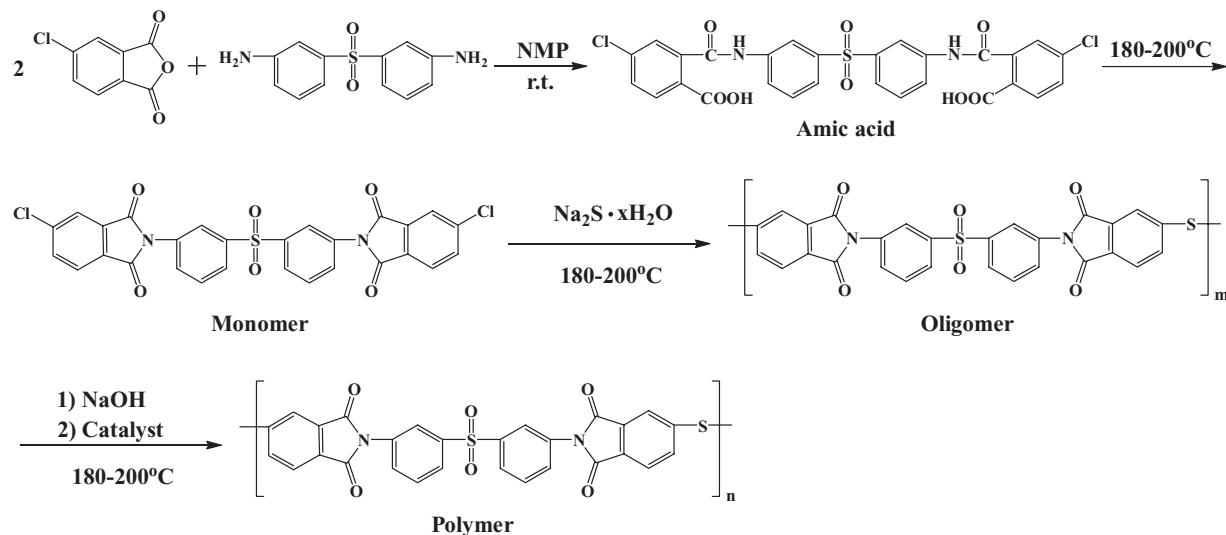
merizing with sodium sulfide at high temperature and high pressure by researchers of General Electric Company and Tonen Sekiyu Kagaku K.K. (17–19). Poly(arylene sulfide sulfone imide) (PASSI) was synthesized by Chen *et al.* using the sodium sulfide method at atmospheric pressure (20). However, in the foregoing processes, the monomers should be prepared before polymerization by other chemical reactions. To avoid these unnecessary reactions, one-pot synthesis process was used and poly(arylene sulfide imide)s were synthesized in our previous work (21). In this paper, the one-pot synthesis method which simplified the experimental operation and reduced the experimental cost and environmental pollution was used to synthesize poly(meta-aryl sulfide sulfone imide imide). Chemical structure and physical properties of the separated intermediates and the achieved polymer were also investigated.

2 Experimental

2.1 Materials

4-Chlorophthalic anhydride (CPA) was purchased from Harbin Times Science & Technology Development Co., Ltd. and was purified by recrystallization from chlorobenzene. Commercially available 3,3'-diamino diphenyl sulfone (m-DDS, AR, JiangSu Yangzhong Synthetic Chemical Factory), N-methyl-2-pyrrolidone (NMP, JiangSu Nanjing Jinlong Chemical Factory), sodium sulfide ($\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$,

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Sch. 1. Synthesis route of *m*-PASSII.

Na_2S ($\approx 60\%$, Nafine Chemical Industry Group Co., Ltd.) and sodium hydroxide (NaOH, AR, SiChuan ChengDu ChangLian Chemical Reagent Company) were used as received. The catalyst was made in our lab (22–23). Other reagents and solvents were obtained commercially.

2.2 Synthesis

m-PASSII was synthesized by a one-pot process using 4-chlorophthalic anhydride, 3,3'-diaminodiphenyl sulfone and sodium sulfide as starting materials in *N*-methyl-2-pyrrolidone at atmospheric pressure as depicted in Scheme 1. A typical synthesis process of *m*-PASSII was carried out as follows. 50 ml of NMP, 18.62 g (102 mmol) of CPA and 12.4g (50mmol) of *m*-DDS were added into a 100ml three-necked flask provided with water segregator, condenser pipe, nitrogen inlet pipe, mechanical stirrer, and thermometer; under the protection of nitrogen, the components were reacted at room temperature for 3 h by stirring, then were processed by the operation of dehydration reaction for 3 h at the temperature from 180 to 200°C; when the temperature was lowered to 100°C, 6.5 g (about 50 mmol) of sodium sulfide was added, and the temperature was raised to 200°C within 40 min; when the temperature was lowered to 160°C, 0.08 g (2 mmol) of NaOH and 2 g of sodium *p*-methylbenzenesulfonate were added, and the temperature was maintained at 180°C for 2 h and another 2 h at 200°C; then the reaction solution was poured into water to separate out the polymer. 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 25 g (yield: 87%) of a brown powder.

2.3 Intermediates

Intermediates display in Scheme 1 were separated and purified as follows. Amic acid was precipitated in 0.01 mol/l hydrochloric acid, washed with ethanol and distilled water, respectively, then oven-dried under vacuum at 50°C for 24 h; the monomer was filtered from the reaction liquid when cooled down to room temperature, washed with acetone and distilled water, respectively, then put on a 100°C oven for 24 h; the oligomer was precipitated in water, washed with distilled water, then put on a 100°C oven for 24 h.

2.4 Characterizations

2.4.1. Elemental Analyses

The samples of amic acid, monomer, oligomer and *m*-PPSSII (polymer) were determined by elemental analyzer (Carlo Erba 1106).

2.4.2. Characterization of Chain Structure

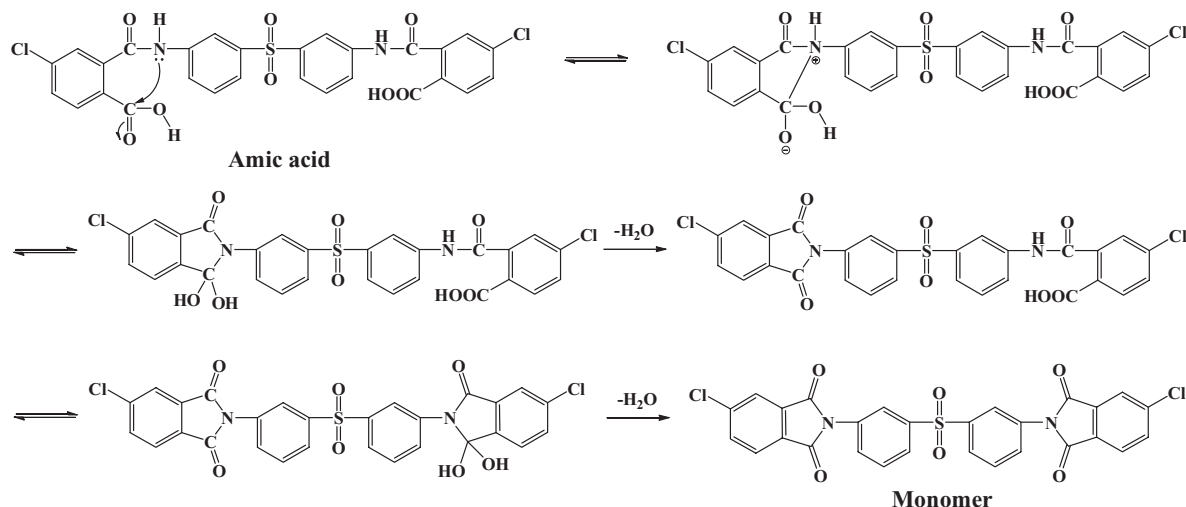
Infrared spectra (FT-IR) were recorded as KBr pellets on a Nicolet Nexus 670 FT-IR spectrophotometer. Proton magnetic resonance ($^1\text{H-NMR}$) instrument for the determination of the samples' structure were provided with a BRUKER-400 NMR Spectrometer. The samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6).

2.4.3. Characterization of Aggregation Structure

The samples of *m*-PPSSII (annealed at 250°C for 5 h and unannealed) were characterized by X-ray diffraction (Philips X'pert Pro MPD).

2.4.4. Intrinsic Viscosity

Intrinsic viscosity of oligomer and *m*-PPSSII were measured in a Cannon-Ubbelohde viscometer at polymer concentration of 0.500 g/dl in NMP at $30 \pm 0.1^\circ\text{C}$. The



Sch. 2. Mechanism of imidization.

resulting values were obtained by a one-point method (or Solomon–Ciuta equation) as follows:

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

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

2.4.5. Thermal Properties Test

Differential scanning calorimetry (DSC) was performed with DSC Q100 V9.4 Build 287 thermal analysis equipment, fitted with a cooler system using liquid nitrogen. It was operated at a gas rate of 50 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. Solubility

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

3 Results and Discussion

3.1 Synthesis

Poly(meta-aryl sulfide sulfone imide imide) was synthesized by a one-pot process. At present, the mechanism about the one-pot synthesis process has not been reported. It probably contains two key mechanisms: heat imidization of amic acid and nucleophilic substitution of monomer. The proposed mechanism is shown in Scheme 2. The mechanism of nucleophilic substitution is similar to polymerization of aromatic difluorides with sodium sulfide (S_NAr mechanism) reported in the literature (24–26). However, further work would be necessary to confirm these mechanisms. Catalyst used in the synthesis process was sodium p-methylbenzenesulfonate, sodium benzoate or other carboxylate reported in literature (22–23). The probable reason is that these salts can improve the solubility of Oligomer and Polymer in NMP. As the products dissolve in solvent, the nucleophilic substitution reacts successfully.

3.2 Characterization of the Intermediates

3.2.1. Elemental Analysis

Table 1 shows that the experimental results are similar to the calculated results (experimental results of oligomer did not fit the calculated value very well. This may be caused by the oligomer's considerable end groups which are not yet

Table 1. Elemental analysis of the intermediates

Compound	Calculated formula	C (%)	H (%)	N (%)	S (%)
Amic acid	C ₂₈ H ₁₈ O ₈ N ₂ SCl ₂	54.81 (54.82)	3.62 (2.96)	5.40 (4.57)	4.99 (5.23)
Monomer	C ₂₈ H ₁₄ O ₆ N ₂ SCl ₂	58.33 (58.24)	2.54 (2.44)	4.70 (4.85)	5.60 (5.55)
Oligomer	(C ₂₈ H ₁₄ O ₆ N ₂ S ₂) _m	58.66 (62.45)	2.67 (2.62)	4.84 (5.20)	11.07 (11.91)

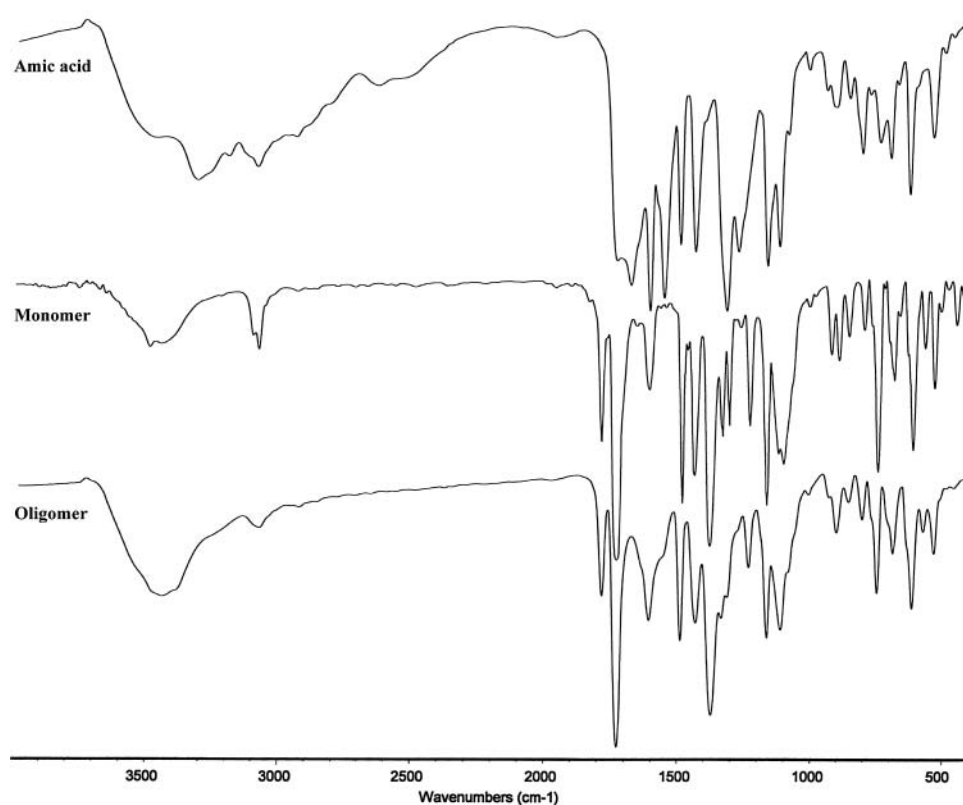


Fig. 1. FT-IR spectra of the intermediates.

calculated in the calculated formula). It suggests the intermediates were synthesized as shown in Scheme 1.

The data in brackets are those calculated.

3.2.2. Infrared Spectra

Figure 1 shows the FT-IR spectra of the intermediates. Amic acid: the absorption of 3303 cm^{-1} is the N-H stretching vibration absorption. The absorption of 1720 cm^{-1} , 1540 cm^{-1} suggest the formation of -CO-NH-, and the absorption of 1664 cm^{-1} suggests the formation of -COOH. Benzene rings absorptions were observed at 1593 cm^{-1} and 1479 cm^{-1} and the absorption of sulfone group: 1304 cm^{-1} and 1151 cm^{-1} are also present. Monomer: the absorption of imide ring: 1779 cm^{-1} , 1724 cm^{-1} and 1374 cm^{-1} , the benzene rings absorption: 1601 cm^{-1} and 1478 cm^{-1} , the typical absorption of sulfone group: 1300 cm^{-1} , 1160 cm^{-1} . Oligomer: The absorption of 1777 cm^{-1} , 1723 cm^{-1} and 1366 cm^{-1} are the absorption of imide ring. We can observe the benzene rings absorption: 1600 cm^{-1} and 1480 cm^{-1} and the absorption of sulfone group: 1156 cm^{-1} is also present.

3.2.3. Proton Magnetic Resonance Spectra

Proton magnetic resonance spectra of the intermediates are shown in Figures 2–4. Six groups of peaks appear in the $^1\text{H-NMR}$ spectrum of Amic acid in Figure 2. The ratio of corresponding integral curves is about 3:1:2:1:1:1.

The calculated result should have nine groups of peaks and the ratio of corresponding integral curves should be 1:1:1:1:1:1:1:1:1. Since the Amic acid has three possible structures (shown in Scheme 3), the chemical shift (δ) of Ha-Hb-Hc and He-Hf are so approximate that the weak split signals are shielded. Along with the foregoing results of FT-IR, it can be deduced that these six groups of peaks are ascribed to the construction units of Ha, Hb, Hc, Hd, He, Hf, Hg, Hh and Hi. The chemical shifts of the intermediates are listed in Table 2. Integral areas and peak ascriptions of monomer and oligomer are shown in Figures 3 and 4, respectively. Combining the FT-IR results, the chain structures of monomer and oligomer can be confirmed.

3.2.4. Thermogravimetric Analysis of Amic Acid

The thermal stability of amic acid was examined by TG analysis. The result is displayed in Figure 5. As shown

Table 2. $^1\text{H-NMR}$ chemical shifts of the intermediates

Amic acid	<i>E</i>	<i>Hc, Hd</i>	<i>He, Hf</i>	<i>Hg</i>	<i>Hh</i>
$\delta(\text{ppm})$	7.57–7.70	7.70–7.79	7.84–7.95	8.37	10.81
Monomer	Ha, Hb	Hc, Hd	He	Hf	Hg
$\delta(\text{ppm})$	7.81–7.87	7.96–8.02	8.03–8.07	8.09	8.16
Oligomer	Ha, Hb	Ha, Hb	He, Hf	Hg	
$\delta(\text{ppm})$	7.73–7.84	7.84–7.96	7.96–8.07	8.15	

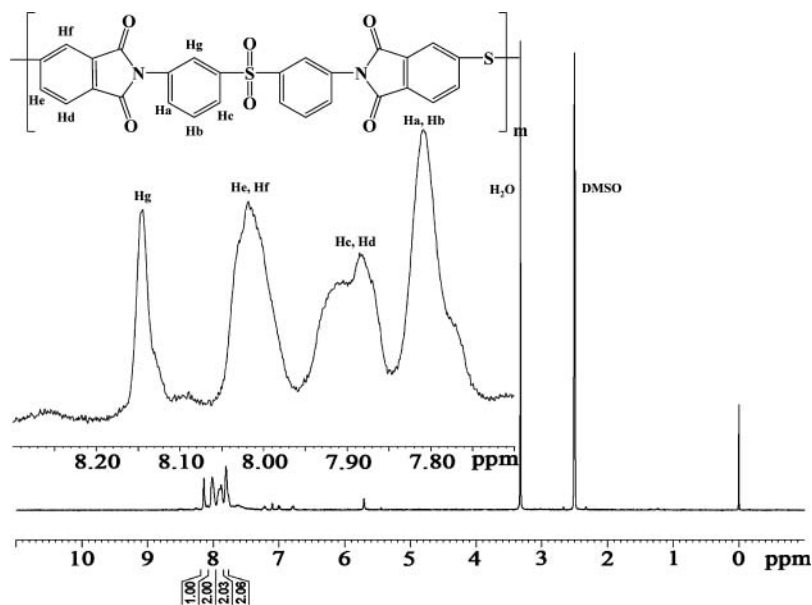


Fig. 4. $^1\text{H-NMR}$ spectrum of oligomer.

in the figure, the initial degradation temperature of the amic acid sample is 129°C . It keeps an invariable weight of about 85% from 200°C to 350°C , and then decomposes for the second time as the temperature rises. It indicates that the degradation product (monomer) is stable below 350°C . However, the calculated weight loss of amic acid to monomer is 5.9% (less than 15%). A probable reason is the sample used for TG analysis test contains impurities (water, NMP and ethanol) which can be identified in proton magnetic resonance spectrum (Fig. 2).

3.2.5. Differential Scanning Calorimetry of Monomer

The melting point of monomer was examined by DSC analysis. As shown in Figure 6, its melting point is 298°C .

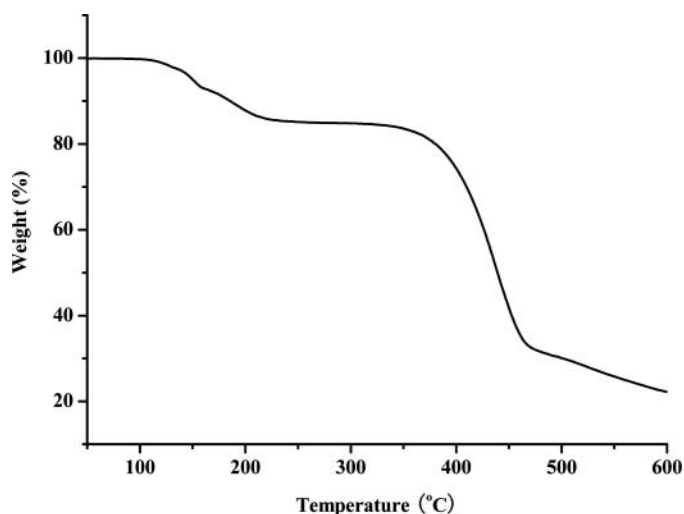


Fig. 5. TGA curve of amic acid.

3.2.6. Intrinsic Viscosity of Oligomer

The intrinsic viscosity of oligomer is 0.13 dl/g.

3.2.7. Thermal Properties of Oligomer

DSC and TG analyses of oligomer are shown in Figures 7 and 8. As manifested in Figure 7, no glass transition step and melting endothermic peak can be found from 10°C to 350°C . The TGA curve of oligomer shows an initial degradation temperature of 396°C .

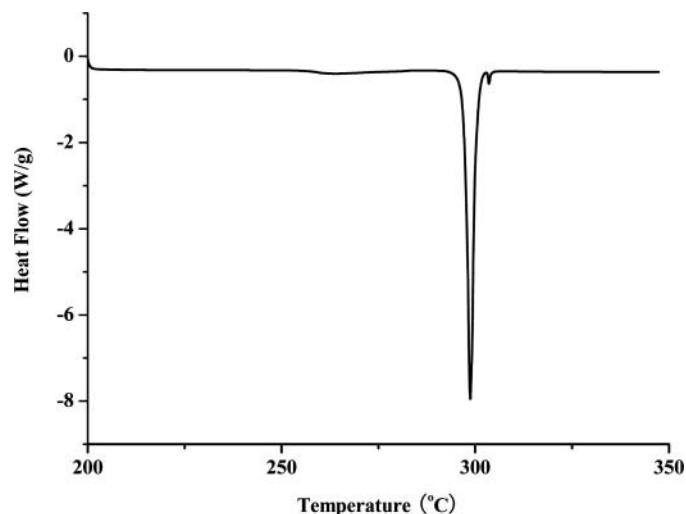


Fig. 6. DSC thermogram of monomer.

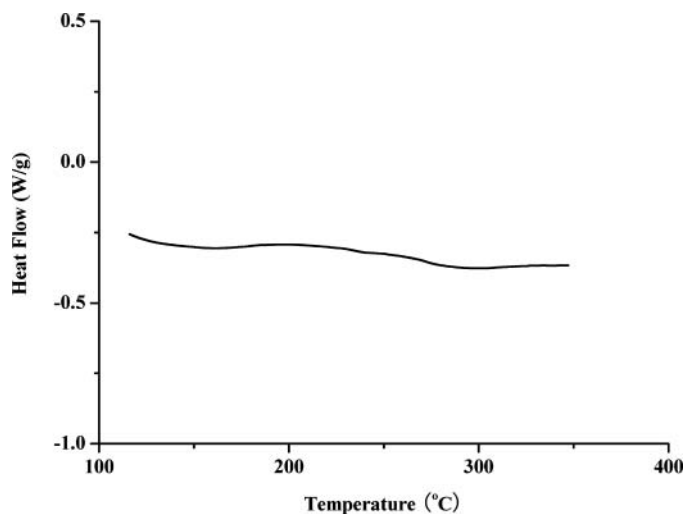


Fig. 7. DSC thermogram of oligomer.

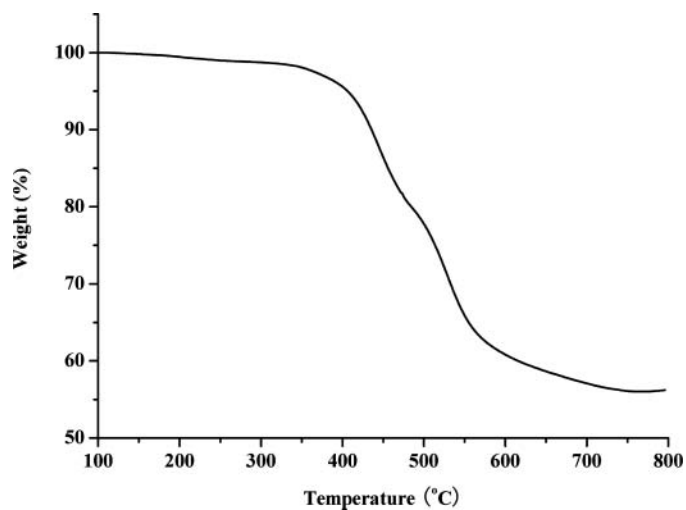


Fig. 8. TGA curve of oligomer.

Table 3. Elemental analysis of m-PPSSII

Compound	Calculated formula	C (%)	H (%)	N (%)	S (%)
m-PPSSII (Polymer)	$(C_{28}H_{14}O_6N_2S_2)_n$	61.26 (62.45)	2.89 (2.62)	5.04 (5.20)	11.20 (11.91)

3.3 Characterization of m-PPSSII

3.3.1. Elemental Analysis

Table 3 shows that the experimental results are similar to the calculated ones. It suggests m-PPSSII was synthesized as Scheme 1.

The data in brackets are those calculated.

3.3.2. Infrared Spectrum

Figure 9 shows the FT-IR spectrum of m-PPSSII. The absorption of 1777 cm^{-1} , 1722 cm^{-1} and 1366 cm^{-1} are the absorption of imide ring. We can observe the benzene rings absorption: 1598 cm^{-1} and 1480 cm^{-1} and the absorption of sulfone group: 1156 cm^{-1} is also present. When compared with monomer, no strong absorption of the thio-ether bond range $1000\text{--}1100\text{ cm}^{-1}$ can be identified in the spectrum of m-PPSSII. The probable reason is the absorption of thio-ether bond is shielded by strong absorption of C=N bond of imide. Along with the elemental analysis results of monomer and m-PPSSII, the rise of sulfide

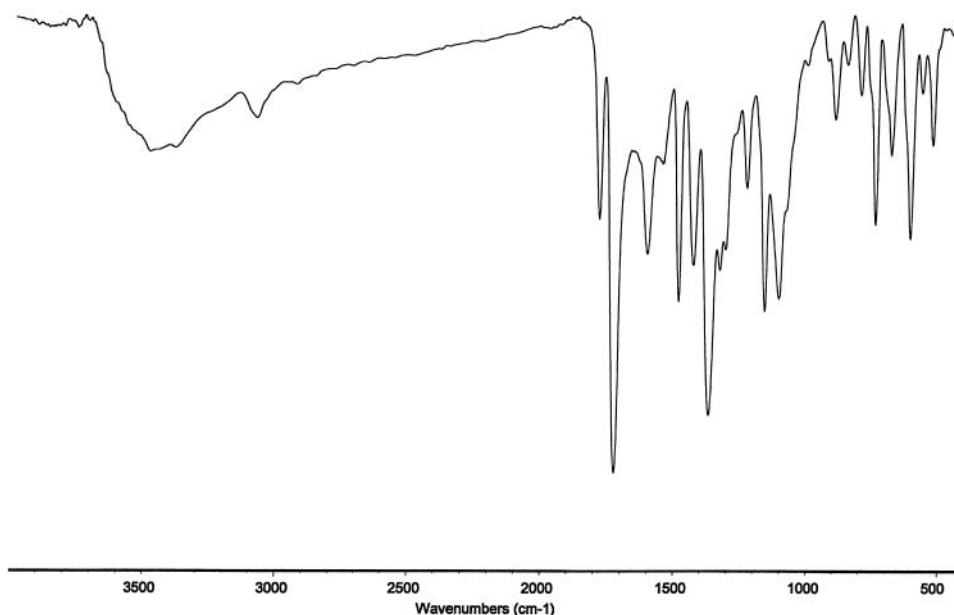


Fig. 9. FT-IR spectrum of m-PPSSII.

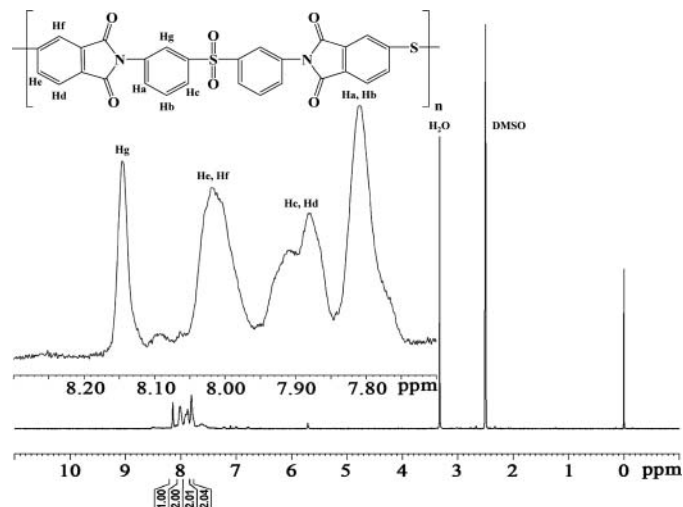


Fig. 10. $^1\text{H-NMR}$ spectrum of *m*-PPSSII.

content predicts formation of a thio-ether bond. It suggests *m*-PPSSII was successfully synthesized.

3.3.3. Proton Magnetic Resonance Spectrum

Figure 10 shows the $^1\text{H-NMR}$ spectrum of *m*-PPSSII. Four groups of peaks appear in the spectrum. The ratio of corresponding integral curves is about 2:2:2:1, the calculated result should have seven groups of peaks and the ratio of corresponding integral curves is 1:1:1:1:1:1:1, but the high viscosity of the solution restrained molecular oscillation, and the chemical shift of Ha-Hb, Hc-Hd and He-Hf are so approximate that the weak split signals are shielded. Together with the results of FT-IR, these four groups of peaks are ascribed to the construction units of Ha, Hb, Hc, Hd, He, Hf and Hg. The chemical shifts are listed in Table 4.

3.3.4. X-ray Diffraction Spectra

X-ray diffraction of *m*-PPSSII samples are shown in Figure 11. As manifested in Figure 11, both annealed and unannealed samples present no sharp peak, and the maximum intensity is less than 1000 counts/s. It suggests that *m*-PPSSII is an amorphous polymer. The reason might be the asymmetry of the molecular chain and the existence of strong polarity sulfone group limit the movement of the *m*-PPSSII's molecular chains and prevent them arrange in ordered structure.

Table 4. $^1\text{H-NMR}$ chemical shifts of *m*-PPSSII

Polymer	Ha, Hb	Hc, Hd	He, Hf	Hg
$\delta(\text{ppm})$	7.75–7.85	7.85–7.95	7.95–8.07	8.15

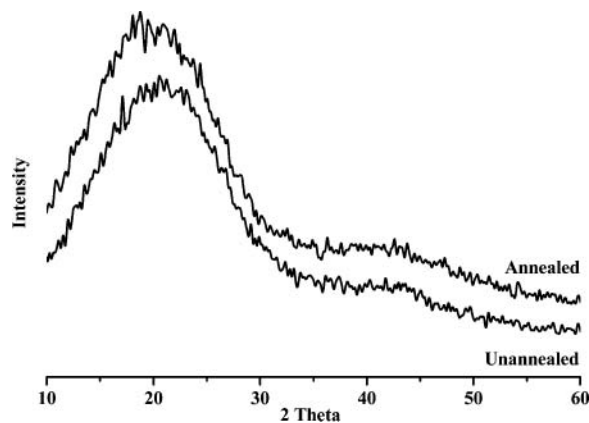


Fig. 11. XRD spectra of *m*-PPSSII.

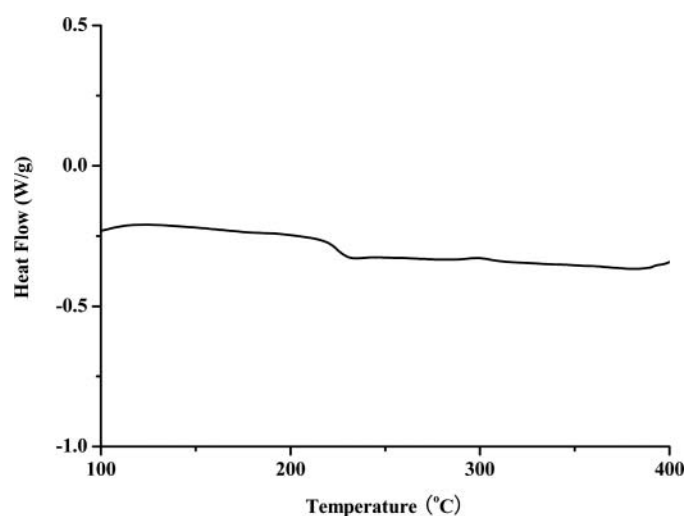


Fig. 12. DSC thermogram of *m*-PPSSII.

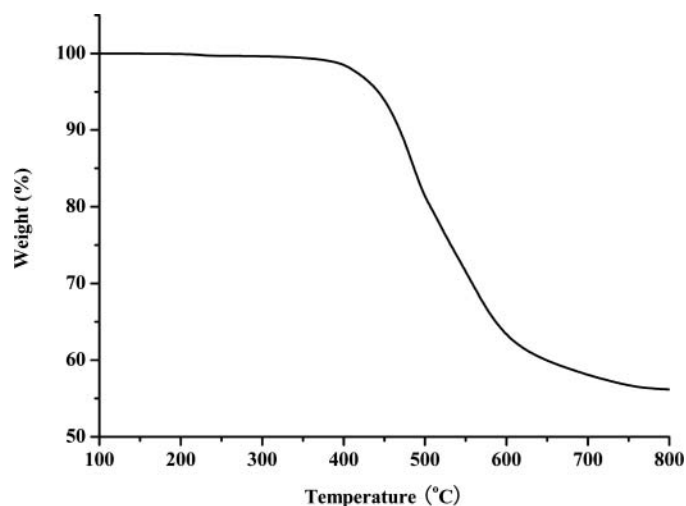


Fig. 13. TGA curve of *m*-PPSSII.

Table 5. Solubility behavior of m-PPSSII

<i>Solvent</i>	<i>Solubility</i>	<i>Solvent</i>	<i>Solubility</i>
N-Methyl-2-pyrrolidone	++	Concentrated hydrochloric acid	+-
Dimethyl sulfoxide	++	Cyclohexanone	+-
N, N-Dimethyl formamide	++	Chloroform	-
N, N-Dimethyl acetamide	++	Formic acid	-
Concentrated sulfuric acid	++	Tetrahydrofuran	-
Phenol/ Tetrachloroethane ^a	++	Cyclohexane	-

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

^a: Phenol: 1,1,2,2-Tetrachloroethane = 2: 3 (wt).

3.3.5. Intrinsic Viscosity

The intrinsic viscosity of m-PPSSII was measured in the range 0.21-0.27 dl/g. It is higher than that of oligomer (0.13 dl/g).

3.3.6. Thermal Properties

The thermal properties of m-PPSSII were examined by DSC and TG analyses. The results are displayed in Figures 12 and 13. As shown in Figure 12, the T_g value of m-PPSSII is 224°C, while oligomer has no glass transition temperature. The DSC thermogram shows no melting endothermic peak before decomposition of the polymer, it also agrees with the result of X-ray diffraction. As shown in Figure 13, the initial degradation temperature of the polymer is 441°C, which is higher than that of oligomer (396°C). It remains more than 50% char yield at 800°C. The DSC and the TGA data indicate that m-PPSSII have good thermal stability (27–28).

3.3.7. Solubility

Table 5 shows that m-PPSSII has better solubility than PPS (1). It is soluble in NMP, DMSO, DMF and concentrated sulfuric acid etc. at room temperature and shows no tendency to precipitate, so it can be processed by more methods than PPS, such as electro-spinning, solution casting, solution coating etc. Moreover, the polymer cannot dissolve in chloroform, formic acid and cyclohexane etc. Thus, m-PPSSII shows a good corrosion resistance.

4 Conclusions

In this paper, poly(meta-aryl sulfide sulfone imide imide) was successfully prepared by means of one-pot polymerization at atmospheric pressure. The intermediates which generated during the synthesis process were separated and characterized. Chemical structure of the polymer was confirmed as expected. m-PASSII is an amorphous polymer with glass transition temperature of 224°C and initial degradation temperature of 441°C. It can dissolve in strong

polar solvents and shows good corrosion resistance in weak polar solvents.

Acknowledgments

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References

1. Yang, J. PAS resin and its application. Chemical Industry Press: China, 2006.
2. Edmonds, J.T., Jr. and Hill, H.W., Jr. (1963) US Patent 3354129.
3. Campbell, R.W. (1975) US Patent 3919177.
4. Herd, M.D. and Kallenbach, L.R. (1992) US Patent 5147719.
5. Gaughan, R.G. (1987) US Patent 4716212.
6. Ishikawa, T. and Kondo, Y. (1989) US Patent 4818809.
7. Xu, S.X., Yang, J., Long, S.R., Chen, Y.R. and Li, G.X. (2005) *Polymer Bulletin*, 54(4–5), 251–261.
8. Mehdipour-Ataei, S. and Hatami, M. (2007) *Polymers for Advanced Technologies*, 18(4), 292–298.
9. Burks, H.D. and St. Clair, T.L. (1985) *Journal of Applied Polymer Science*, 30(6), 2401–2411.
10. Ding, M.X., Li, H.Y., Yang, Z.H., Li, Y.S., Zhang, J. and Wang, X.Q. (1996) *Journal of Applied Polymer Science*, 59(6), 923–930.
11. Dembek, A.A., Fagan, P.J. and Marsi, M. (1993) *Macromolecules*, 26(11), 2992–2994.
12. Tsuchida, E., Nishide, H., Yamamoto, K. and Yoshida, S. (1987) *Macromolecules*, 20(9), 2325–2316.
13. Tsuchida, E., Shouji, E. and Yamamoto, K. (1993) *Macromolecules*, 26(26), 7144–7148.
14. Chen, K., Liang, Z.A., Meng, Y.Z. and Hay, A.S. (2003) *Polymers for Advanced Technologies*, 14(10), 719–728.
15. Miyatake, K., Yamamoto, K., Yokoi, Y. and Tsuchida, E. (1998) *Macromolecules*, 31(2), 403–407.
16. Ding, Y. and Hay, A.S. (1997) *Macromolecules*, 30(6), 1849–1850.
17. Williams, F.J., III. (1978) US Patent 4092297.
18. Takekoshi, T. and Anderson, P.P. (1993) US Patent 5194566.
19. Teshirogi, T., Kato, M. and Ota, S., Sakota, K. (1990) JP Patent 2229829.
20. Chen, Q.X., Yang, J. and Long, S.R. (2007) *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, 22(2), 276–278.
21. Yang, J., Zhang, M.L., Long, S.R., Wang, X.J. and Zhang, G. (2009) CN Patent 101538366.

22. Yang, J., Chen, Q.X., Chen, Y.R. and Long, S.R. (2005) CN Patent 1730512.
23. Yang, J., Liu, C.L. and Long, S.R. (2006) CN Patent 1896120.
24. Zhang, G., Liu, J., Zhang, M.L., Liu, S.L., Long, S.R. and Yang, J. (2009) *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 46(10), 1015–1023.
25. Fahey, D.R. and Ash, C.E. (1991) *Macromolecules*, 24(15), 4242–4249.
26. Fahey, D.R., Hensley, H.D., Ash, C.E. and Senn, D.R. (1997) *Macromolecules*, 30(3), 387–393.
27. Zhou, Z.W., Wu, Q.X. (1997) *Journal of Applied Polymer Science*, 66(7), 1227–1230.
28. Wang, H.D., Yang, J., Long, S.R., Wang, X.J., Yang, Z. and Li, G.X. (2004) *Polymer Degradation and Stability*, 83(2), 229–235.