

Molecular Weight Determination of Poly(phenylene sulfide ether)

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ABSTRACT: Poly(phenylene sulfide ether) and poly(phenylene sulfoxide ether sulfide ether) (PPSOESE) were successfully prepared and their structures were proved by several analytical techniques in the present work. The molecular weight (MW) of PPSOESE, a soluble polymer in common organic solvent at room temperature, was determined by gel permeation chromatography. Based on the conversion reaction of the two polymers, the MW of PPSE was calculated and correlated with its intrinsic viscosity. As a result, the Mark-Houwink equation for PPSE was concluded. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3682–3686, 2013

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INTRODUCTION

Poly(phenylene sulfide ether) (PPSE) is a versatile engineering plastic which has drawn much attentions in recent years. It was mainly synthesized by step polymerization via electrophilic and/or nucleophilic substitution.^{1–12} In electrophilic reactions, the formed PPSE often contains disulfide bonds and/or branching structure due to side reactions. In nucleophilic substitution polymerization, however, the prepared PPSE has a desirable structure even synthesized in high reaction temperatures. PPSE was often reported as a crystalline polymer with T_g and T_m around 47–85 and 155–250°C, respectively. Apart from crystalline feature, an amorphous PPSE was also presented with T_g of 94°C.¹³ To our knowledge, the diversity might be generated from its different molecular weight (MW).

Owing to the insolubility of PPSE in common solvents like tetrahydrofuran (THF) and chloroform at room temperatures, gel permeation chromatographic measurement cannot be applied to determine its MW under normal conditions. Only end group analysis was applied to estimate MW of PPSE by controlling the type of end groups.¹² Practically, MW and its distribution play a fundamental role in achieving good physical performance and processability of polymer, and therefore their determinations are always the topics in polymer science.^{14–19} For this reason, it is expected that MW of PPSE should be determined more conveniently and reasonably. From the scope of polymer reaction, the MW of PPSE could be gained by determining MW of its soluble precursor polymer which can convert to PPSE quantitatively.

As sulfoxide is a bulky group, the sulfoxide-containing polymers are proved to have improved solubility in many common sol-

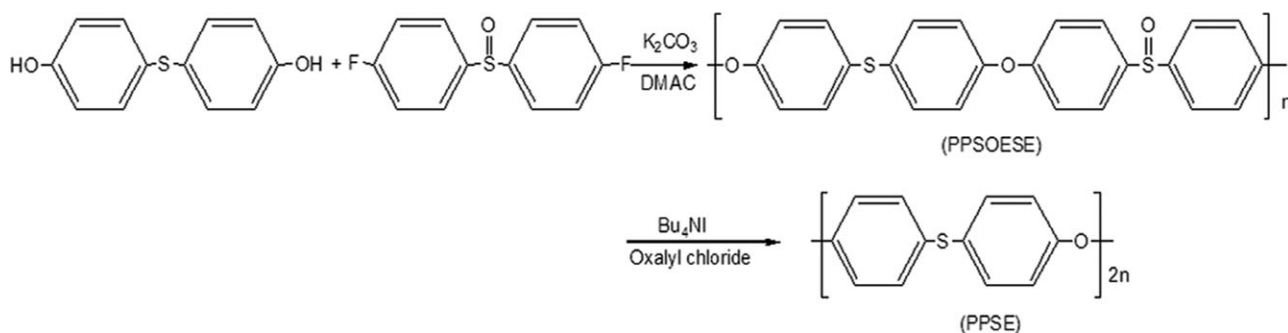
vents.^{20–22} Furthermore, sulfoxide can be converted to sulfide in appropriate reduction reaction. Consequently, MW of PPSE could be obtained by determining MW of its soluble sulfoxide-containing precursor if the conversion of sulfoxide to sulfide is quantitative and reduction reaction does not significantly affect MW. Although the reduction of sulfoxide to sulfide can proceed with various reagents,²³ oxalyl chloride was reported to be the best for the reduction of sulfoxide in which no chain extension or chain scission occurs in polymer.^{13,24}

In the present work, poly(phenylene sulfoxide ether sulfide ether) (PPSOESE), a sulfoxide-containing precursor of PPSE, was synthesized by nucleophilic substitution and its MW was determined by gel permeation chromatography (GPC). By quantitative reduction of PPSOESE with oxalyl chloride, PPSE was successfully prepared and its structure was confirmed. From the MW of PPSOESE, the MW of PPSE was calculated and correlated with its corresponding intrinsic viscosity. Accordingly, the Mark-Houwink equation for PPSE was established.

EXPERIMENTAL

Materials

Bis(4-hydroxyphenyl) sulfide (BHPS) (Zhejiang Yangfan Holding Group, China) was recrystallized from methanol before use. Other reagents were purchased from Chengdu Kelong Chemical Reagent Plant (China) and used as received unless indicated. *N,N*-Dimethylacetamide (DMAc, 99%) and *N*-methyl-2-pyrrolidone (NMP, 99%) were freshly distilled out from P₂O₅ under vacuum. Toluene was washed sequentially with concentrated H₂SO₄, aqueous solution of NaHCO₃ (5%) and deionized



Scheme 1. Synthesis of poly(phenylene sulfide ether).

water, and then dried over MgSO_4 and distilled out at reduced pressure. Anhydrous potassium carbonate was dried under vacuum at 130°C for 2 days before use.

Preparation of Bis(4-fluorophenyl)sulfoxide (BFPSO)

BFPSO was prepared by Friedel-Crafts acylation of fluorobenzene with thionyl chloride according to literature,²⁵ and the obtained product was purified twice by recrystallization in hexane. Yield 69%, purity 99.5% (GC); IR (KBr, cm^{-1}): 814 ($\omega_{\text{C-H}}$ of 1,4-substituted of phenylene), 1047 ($\nu_{\text{S=O}}$), 1221 ($\nu_{\text{C-F}}$), 1489, and 1589 ($\nu_{\text{C-C}}$, skeleton vibration of benzene nuclei); $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 7.16 (q, 4H, FAr-H, o), 7.63 (d, 4H, SOAr-H, o); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , δ): 116.65, 116.88, 127.05, 127.13, 141.11, 163.12, and 165.63¹³; Elemental analysis, calculated for $\text{C}_{12}\text{H}_8\text{SOF}_2$: C 60.49, H 3.38, S 13.46; found: C 60.53, H 3.29, S 13.49.

Preparation of PPSOESE

PPSOESE was prepared by the reaction of BFPSO with BHPS as the route illustrated in Scheme 1. A typical preparation was carried out in a 250 mL dry three-necked round bottomed flask fitted with a mechanical stirrer, Dean-Stark trap and nitrogen inlet and outlet. Into the flask, BFPSO (5.9520 g, 0.0250 mol), BHPS (5.3777 g, 0.0247 mol), anhydrous potassium carbonate (5.2536 g, 0.0381 mol), DMAc (80 mL) and toluene (40 mL) were added. Nitrogen was sparged through the reaction mixture with stirring for 20 min, and the mixture was heated to 120°C . The temperature of the reaction mixture was slowly raised over a 3 h period from 120 to 150°C with nitrogen sparging. Water generated from the formation of the phenolate was removed as an azeotrope with toluene. Then the temperature was raised to 170°C and the remaining toluene was removed from the reaction mixture by distillation. After 10 h at this temperature, the reaction mixture was cooled and precipitated into methanol for 12 h at room temperature. The solid product was washed thoroughly with methanol and hot deionized water, and then dried at 100°C in vacuum oven to a constant weight.

Preparation of PPSE

PPSE was prepared by chemical reduction of PPSOESE with oxalyl chloride in NMP solvent. The operations were carried out on a 250 mL three-necked round bottomed flask fitted with a mechanical stirrer, a dropping funnel, and nitrogen inlet and outlet. A typical reduction procedure was stated as follows. Into the flask were added 3 g PPSOESE, 8 g of tetrabutylammonium

iodide, 6 g of LiCl and 120 mL NMP. After the solids in the mixture were complete dissolved at $50\text{--}55^\circ\text{C}$ under stirring in the nitrogen stream, 1 mL oxalyl chloride was dripped into slowly. One hour later, the reaction content was cooled to room temperature and precipitated in 500 mL methanol. The precipitate was collected and washed several times with methanol and hot deionized water, respectively. The obtained crude product was purified by mixing with 5% solution of sodium thiosulfate (500 mL) for 1 h, washing several times with hot deionized water, redissolving in hot NMP, precipitating into deionized water. The product was then further purified by extraction with acetone for 24 h and vacuum dried at 120°C to a constant weight (Scheme 1).

Characterization

Elemental analysis was performed on a Euro EA 3000 Elemental Analyzer (Euro Vector S. P. A., Italy).

Gas chromatographic (GC) measurement was implemented on an Agilent 6890 with HP-5 column.

Nuclear magnetic resonance spectra were recorded on a Bruker AV II-400 MHz apparatus using CDCl_3 or DMF-d_6 as the solvents. ^1H - and ^{13}C -NMR shifts were referenced to internal

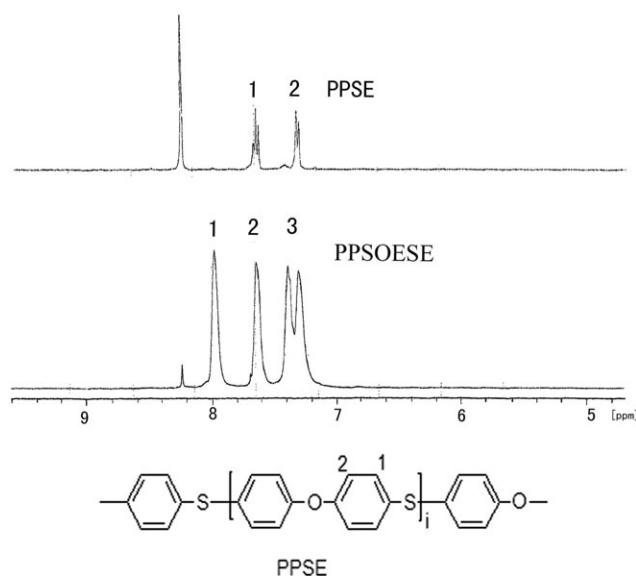


Figure 1. ^1H -NMR spectra of PPSE and PPSOESE (in DMF-d_6).

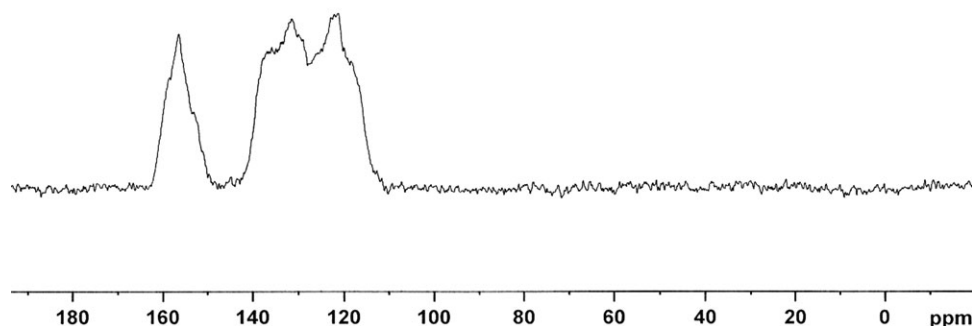


Figure 2. CP-MAS ^{13}C -NMR of PPSE.

tetramethylsilane. CP-MAS ^{13}C -NMR was recorded using Bruker AVANCE III 500 MHz apparatus.

FTIR spectra were given by Spectrum One (B) spectrometer (Perkin-Elmer) using a potassium bromide disk.

XPS analysis was carried out on a Perkin-Elmer PHI5400 spectrometer employing Mg K_{α} (1253.6 eV) achromatic X-ray source.

Intrinsic viscosities of PPSE (η) were measured at 80°C in NMP solvent using an Ubbelohde viscometer with 0.100 g of polymer dissolved in 100 mL NMP (C).

The intrinsic viscosities were calculated by the following formulae:

$$\eta_{\text{sp}} = \frac{t}{t_0} \quad \eta_r = \frac{t}{t_0}$$

$$[\eta] = \frac{[2\eta_{\text{sp}} - \ln \eta_r]^{1/2}}{C}$$

where t and t_0 represent the flow time for the solution and the solvent in a viscometer, respectively.

MW and its distribution of PPSOESE were measured by GPC on a Waters 410 chromatograph with a Super HM-H*2 column. HPLC grade THF was used as the mobile phase at a flow rate of 0.6 mL min^{-1} , and monodispersity polystyrene standards were used for the calibration of MW.

RESULTS AND DISCUSSION

According to the route indicated in Scheme 1, PPSOESE was synthesized in the yields above 90%, and PPSE in about 90% yield based on PPSOESE.

Structural Analysis of PPSE

From the structural formula, the elemental composition of PPSE was calculated as: C 71.97, H 4.03, and S 16.01. As an example, the elemental analysis result of PPSE (with intrinsic viscosity of 0.75 dL g^{-1}) is as follows: C 71.66, H 4.13, and S 16.21. The two sets of data indicate that the obtained PPSE has the predicted chemical compositions.

^1H -NMR spectrum of PPSE together with the proton assignments is shown in Figure 1. The peak intensity ratio of protons bonded to C_1 and C_2 was 1 : 0.99, suggesting that PPSE sample has linear

structures. As the precursor polymer of PPSE, ^1H -NMR spectrum of PPSOESE is also illustrated in Figure 1. It is obvious that the signal due to the protons ortho to the sulfoxide at 7.97 in PPSOESE was absent in the spectrum of PPSE. The disappearance of sulfoxide in PPSE confirms that the sulfoxide group in PPSOESE was fully reduced to the sulfide. In Figure 2, CP-MAS ^{13}C -NMR spectrum of PPSE shows four peaks representing the four types of phenylene carbons [(500 MHz, δ): 156.56, 133.56, 131.83, and 122.34]. From these observations, it can be deduced that the obtained PPSE has the desirable structure.

To confirm the fully reduction of sulfoxide to sulfide further, the XPS measurement of the two samples was performed and

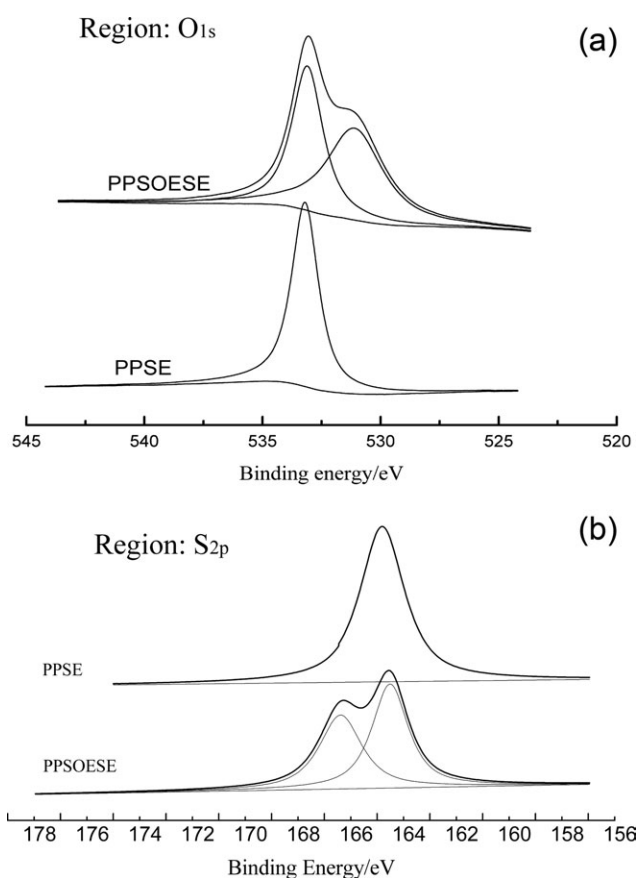


Figure 3. XPS spectra of O_{1s} and S_{2p} for PPSE and PPSOESE.

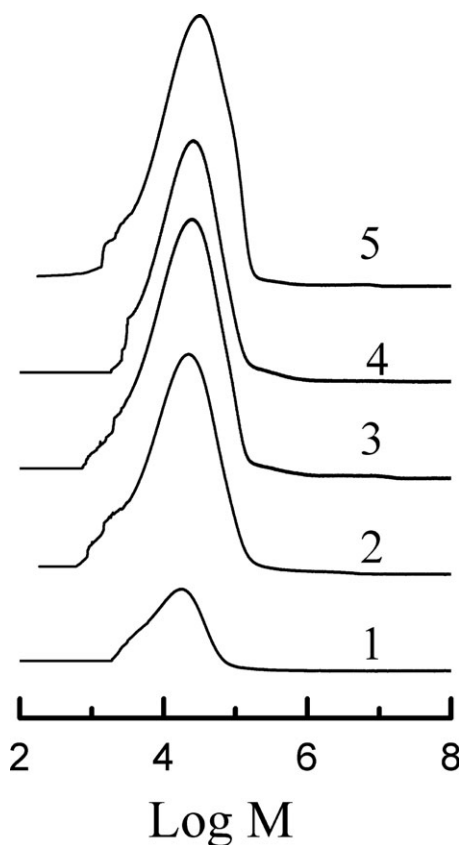


Figure 4. GPC curves of PPSOESE samples.

the results are illustrated in Figure 3. There are two kinds of sulfur (binding energies of S_{2p} at 164.23 and 166.27 eV) and oxygen atoms (binding energies of O_{1s} at 533.10 and 531.10 eV) in the structure of PPSOESE, indicating the existence of sulfoxide and sulfide moiety. In the XPS spectrum of PPSE, however, only one kind of S_{2p} and O_{1s} appears at binding energies of 164.30 and 533.10 eV, indicating only one form of S and O in the structure of PPSE. These observations imply that all sulfoxide in PPSOESE were fully reduced into the sulfide moieties.

To sum up, the above results indicate that PPSOESE has been successfully converted to PPSE and the obtained PPSE has the same structure as that synthesized by direct polycondensation. Therefore, the MW of PPSOESE could be applicable for the MW calculation of PPSE.

Table I. Molecular Weights of PPSOESE by GPC Analysis

Sample	$M_n (\times 10^4)$	$M_w (\times 10^4)$	M_w/M_n
1	1.0	2.03	2.03
2	1.25	2.48	1.98
3	1.35	2.86	2.12
4	1.56	3.06	1.96
5	1.80	3.75	2.08

Table II. Molecular Weight and Intrinsic Viscosity of the Resulting PPSE Polymers

Number	η (dL g ⁻¹) ^a	$M_n^b (\times 10^4)$
1	0.52	0.96
2	0.56	1.2
3	0.63	1.3
4	0.71	1.5
5	0.75	1.7

^aThe intrinsic viscosity was measured in NMP at 80°C.

^bCalculated from the number average MW of PPSOESE.

Determination of MW

Because PPSOESE samples are soluble in THF, their MWs were detected and the obtained GPC curves are illustrated in Figure 4. All samples displayed single peak with narrow distribution. The number average MWs of five samples were found to be located between 1.0×10^4 g mol⁻¹ and 1.8×10^4 g mol⁻¹, and polydispersity indices (M_w/M_n) were in the range of 1.96–2.12 (Table I). The MWs of PPSOESE are comparable with those of other commercial polymers by polycondensation.

Although PPSOESE samples are soluble in most organic solvents at room temperatures, their derived PPSE is insoluble in the same solvents at the same conditions. This solubility feature is consistent with the PPSE from direct polycondensation reaction.

From the reaction scheme in which 416 g of PPSOESE gives 400 g PPSE, the MW of PPSE could be calculated from the MW of PPSOESE. By introducing the conversion correlation, the following equation is given:

$$M_n(\text{PPSE}) = \frac{M_n(\text{PPSOESE})}{416} \times 400$$

The calculated MW and the obtained intrinsic viscosity of PPSE are listed in Table II. The data display that the resulting PPSE samples have also high MW.

It is convinced that the MW of polymer is relevant to its intrinsic viscosity. The famous correlation is expressed by Mark-

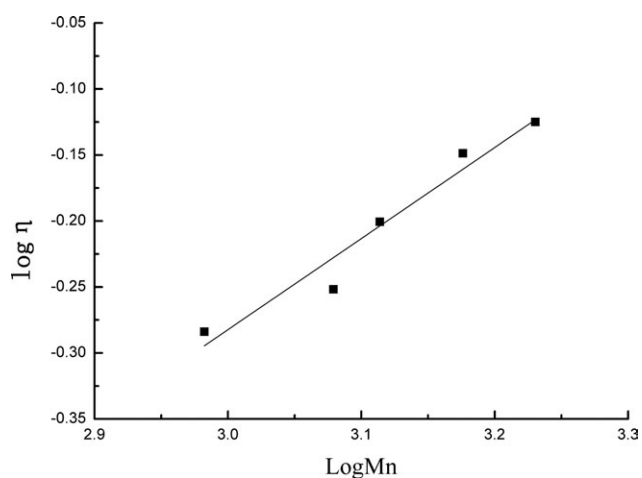


Figure 5. The plot of intrinsic viscosity versus MW for PPSE.

Houwink equation. When the pre-exponential factor and power of Mark–Houwink equation are given, the correlation between MW and intrinsic viscosity should be established. In this case, the plot of intrinsic viscosity versus MW of PPSE is illustrated in Figure 5. From Figure 5, the slope and intercept of straight line were calculated to be 0.69 and -2.35 , namely, equal to α and $\lg K$ in Mark–Houwink equation, respectively. By mathematical operation, the Mark–Houwink equation for PPSE in NMP was given as:

$$[\eta] = K \times \overline{M}_n^\alpha = 4.43 \times 10^{-3} \overline{M}_n^{0.69}$$

where $[\eta]$ is intrinsic viscosity of PPSE, K and α are pre-exponential factor and power of Mark–Houwink equation, \overline{M}_n is number average MW of PPSE.

CONCLUSION

PPSE and PPSOESE were prepared and their structures were confirmed. Based on the quantitative reduction of PPSOESE to PPSE, the MW of PPSE was reasonably obtained by determining the MW of PPSOESE. The obtained MW of PPSE was correlated with its intrinsic viscosity, and its Mark–Houwink equation was concluded. This equation is feasible for the characterization of the MW for the forthcoming PPSE studies.

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