

# Influence of Polymerization Conditions on the Viscosity and Yield of Poly(phenylene sulfide ether)

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**ABSTRACT:** High molecular weight poly(phenylene sulfide ether) (PPSE) was successfully synthesized by reaction of 4,4'-dihydroxy diphenyl sulfide with 4,4'-dichloro diphenyl sulfide in *N*-methyl-2-pyrrolidone (NMP). The influence of polymerization conditions on the intrinsic viscosity and yield of PPSE was investigated and the optimized reaction condition was concluded. Reactions at about 180°C for 6 h along with sodium benzoate as an additive and monomer concentration of 0.588 mol/L NMP were found to produce the highest intrinsic viscosity (0.55 dL/g). Longer reaction time and/or higher temperature reduced the intrinsic viscosity and yield of the resulting product, probably due to

side reactions, such as reductive dehalogenation and chemical degradation. X-ray diffraction indicated that the polymer possessed of orthorhombic cell and had a high crystallinity of 65.8%. The high molecular weight PPSE is a crystalline polymer with  $T_m$  of 252°C and  $T_{mc}$  of 224°C. The polymer shows good chemical resistance, but is soluble in organic amide, halo-hydrocarbon and oxohydrocarbon solvent at a temperature over 150°C. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 61–65, 2008

**Key words:** poly(phenylene sulfide ether); thermoplastics; synthesis; thermal transitions; step-growth polymerization

## INTRODUCTION

Poly(aryl sulfide)s (PAS) and poly(aryl ether)s (PAE) are both high performance engineering thermoplastics with wide applications in electronic/electric, aircraft, and aerospace industries.<sup>1–5</sup> PAS consists of *p*-aromatic units alternating with sulfide linkages and PAE is the ether containing analogs to PAS. Owing to the structural similarity of PAE and PAS and the similarity of O and S in chemical properties, the thermal properties of new polymers deriving from combination of PAS and PAE may be similar to those of PAE or PAS. As one of these polymers, poly(oxy-1,4-phenylenethio-1,4-phenylene) poly(phenylene sulfide ether) (PPSE) is also considered as a substitute for PAS or PAE. From 1970s, the synthesis of PPSE has been briefly reported by electrophilic and nucleophilic substitution step polymerization.

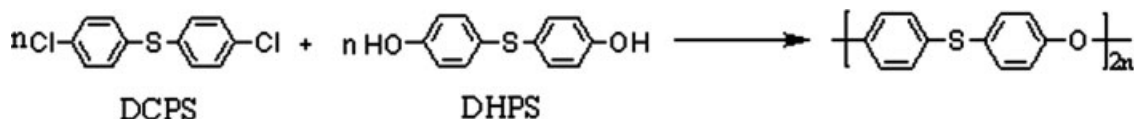
In electrophilic substitution polymerization, PPSE is prepared by several methods, such as iron-catalyzed polymerization of bis(4-chlorothiophenyl) ether with diphenyl ether,<sup>6</sup> polymerization of 4-phenoxybenzenesulfonyl chloride in the presence of SnCl<sub>4</sub>,<sup>7</sup> oxidative polymerization of diphenyl ether with S<sub>2</sub>Cl<sub>2</sub>,<sup>8</sup> thermal polymerization of bis[4-(4-bromophenoxy)phenyl] disulfides,<sup>9</sup> ring-opening poly-

merization of cyclic oligo(oxy-1,4-phenylenethio-1,4-phenylene),<sup>10</sup> dealkylation of poly(methyl-*p*-phenoxy-phenylsulfonium perchlorate),<sup>11</sup> poly(methyl-*p*-phenoxyphenylsulfonium antimony hexachloride)<sup>12</sup> and poly(octadecylsulfonio-1,4-phenyleneoxy-1,4-phenylene triflate).<sup>13</sup> PPSE is represented as a crystalline polymer with a glass transition temperature ( $T_g$ ) at 83–88°C and melting point ( $T_m$ ) at 140–240°C. Because these electrophilic reactions are usually accompanied by many side reactions, the formed products often contain diphenylene disulfide bonds or branching structure.

In nucleophilic substitution polymerization, PPSE is prepared mainly from 4,4'-dihalodiphenyl ether with sodium sulfide<sup>14,15</sup> or alkali metal salts of 4-halophenyl-4-mercaptophenyl ethers in aprotic polar solvent.<sup>16</sup> The reported PPSE is a crystalline polymer with a  $T_g$  and  $T_m$  around 47–85°C and 155–205°C, respectively. We have prepared PPSE<sup>17</sup> with a  $T_g$  around 85°C and  $T_m$  228°C, utilizing 4,4'-dihydroxy diphenyl sulfide (DHPS) and 4,4'-dichloro diphenyl sulfide (DCPS) as raw materials. Because the  $T_m$  of poly(phenylene sulfide) (PPS) and poly(phenylene ether) is 286°C and 298°C,<sup>18</sup> respectively, it seems that the thermal properties of this polymer can be further improved by increasing molecular weight.

To prepare high molecular weight PPSE, the effects of solvent, monomer ratio, monomer concentration, reaction temperature and time, as well as additives on the polymerization are investigated in this article, and the crystalline structure, solubility

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Scheme 1. The reaction equation for Poly(phenylene sulfide ether) synthesis.

behaviors and thermal properties of the product are also presented.

## EXPERIMENTAL

### Materials

Commercially available DHPS and DCPS were provided by Shoufu Chemical Co., China and recrystallized from water and ethanol, respectively, before use. Other reagents were obtained from Chengdu Chemical Inc., China. Sodium acetate and lithium acetate were dehydrated in a vacuum oven at 70°C for 24 h. *N*-methyl-2-pyrrolidone (NMP) and hexamethylphosphoramide (HMPA) were purified by vacuum distillation before use.

### Polymerization

Polymerizations were carried out in a 1 L stainless steel (316 L) autoclave equipped with a reflux condenser, mechanical stirrer, and temperature and pressure indicators. A typical synthesis procedure is illustrated as follows. The autoclave was purged with pure nitrogen prior to the addition of the monomers. To the autoclave were added 10.90 g (0.050 mol) of DHPS, 13.00 g (0.051 mol) of DCPS, 4.80 g (0.120 mol) of sodium hydroxide, 105 mL of NMP, 0.050 mol of additive, 1 mL hydrazine hydrate and 75 mL toluene. The entire operation was conducted under a constant purge of nitrogen. After the system was refluxed and dehydrated, the reaction mixture was stirred at 200°C for 6 h. The reaction mixture was then cooled to room temperature and poured into 1000 mL distilled water to give the precipitate. The precipitate was filtered, washed well with hot water and acetone, each for five times, dried in a vacuum oven at 70°C for 24 h, and then redissolved in NMP, precipitated into water, and dried again under the same conditions. The product was further purified by extraction with acetone for 24 h and dried at 70°C in a vacuum oven.

### Characterization of PPSE

FT-IR spectroscopy was used to investigate the chain structure of PPSE. The infrared spectra of polymer were recorded on SpeltrnmOne (B) Spectrometer (Perkin-Elmer Co.) using a potassium bromide disk.

### Intrinsic viscosity measurement

Measurements were conducted by using an Ubbelohde viscometer in HMPA solvent with a polymer concentration of 0.1 g PPSE/100 mL at 80°C ± 1°C. The intrinsic viscosities were calculated by the following formulae:

$$\eta_{sp} = \frac{t}{t_0} - 1 \quad \text{and} \quad \eta_r = \frac{t}{t_0}$$

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

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

### Crystalline structure

Wide-angle X-ray scattering (WAXS) patterns of powder samples were obtained on a Dandong DX-1000 X-ray diffractometer operated at 40 kV and 25 mA. Measurements were made with Ni-filtered Cu K $\alpha$  radiation and an intensity of 1-s counts taken every 0.01° over the angular range of 4–70° was recorded.

### Thermal analysis

Differential scanning calorimetry (DSC) was carried out by a NETZSCH DSC 200 PC thermal analyzer at a heating rate of 5°C/min under nitrogen.

## RESULTS AND DISCUSSION

The general synthesis of PPSE is shown in Scheme 1.

### Effect of Solvent on polymerization

As a sulfur containing arylene ether polymer, PPSE may be synthesized in the solvent for PAS or PAE. It is well known that organic amide solvent such as NMP is an ideal reaction medium in the synthesis of poly(arylene sulfide),<sup>19</sup> and diphenylsulfone is also a good reaction medium in the synthesis of poly(arylene ether ketone).<sup>20</sup> Based on the facts, the effects of NMP and diphenylsulfone on PPSE synthesis were investigated under atmosphere pressure. The operation was performed according to the following reaction conditions: DHPS/DCPS molar ratio 0.050 : 0.051,

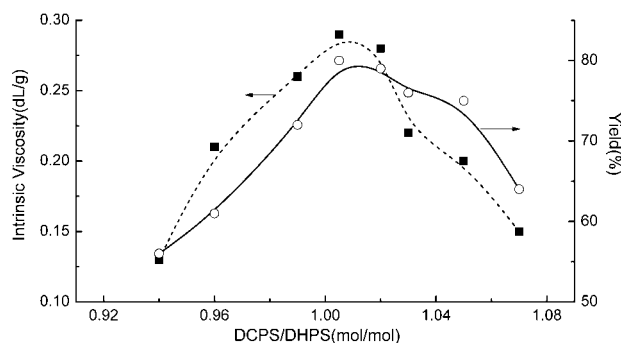
**TABLE I**  
Effect of Various Additives on Intrinsic Viscosity and Yield of PPSE

Additives	Yield (%)	$\eta$ (dL/g)
Sodium benzoate	76	0.22
Sodium formate	51	0.15
Dehydrated sodium acetate	57	0.17
Sodium phosphate	64	0.15
Dehydrated lithium acetate	66	0.14
None	45	0.13

monomer concentration 0.48 mol/L, sodium benzoate/DHPS molar ratio 1 : 1 and a reaction time of 6 h. The reaction temperature was maintained at 210°C and 270–290°C for NMP and diphenylsulfone, respectively. The results showed that diphenylsulfone was not suitable for the synthesis of PPSE because the formed product was neither soluble in HMPA nor meltable at elevated temperatures. On the contrary, NMP was effective for preparing PPSE. This may be due to its strong solvation with cations ( $\text{Na}^+$ ) in the reaction, and the naked growing phenate anion was very reactive. But the intrinsic viscosity of PPSE from NMP was insufficient high (only 0.12 dL/g), which was attributed to stoichiometrical unbalance of monomer ratio caused by sublimation of DCPS, especially under a constant purge of nitrogen in atmosphere pressure. The postulation was evidenced by the parallel synthesis reaction of PPSE in an autoclave, in which the intrinsic viscosity of PPSE was 0.22 dL/g. Consequently, it is necessary to conduct the polymerization in an autoclave to obtain high molecular weight PPSE.

#### Effect of additives on polymerization

It was reported that the incorporation of lithium acetate, sodium acetate, and sodium phosphate into the polymerization system favored the synthesis of high molecular weight PPS or poly(phenylene sulfide sulfone) (PPSS).<sup>21–23</sup> The other work<sup>24</sup> showed that alkali metal carboxylates had no effect on the molecular weight of poly(phenylene sulfide ketone), another analog of PAS. To increase the molecular weight of PPSE, the additives used in synthesis of PPS or PPSS were investigated in this work under a fixed reaction conditions (DHPS/DCPS molar ratio 0.050 : 0.051, monomer concentration 0.48 mol/L NMP, additive/DHPS molar ratio 1 : 1, reaction temperature 200°C and reaction time 6 h) and the results were listed in Table I. The highest intrinsic viscosity and yield of PPSE were obtained for sodium benzoate additive, which was ascribed to the high activity of polymer chain growing.



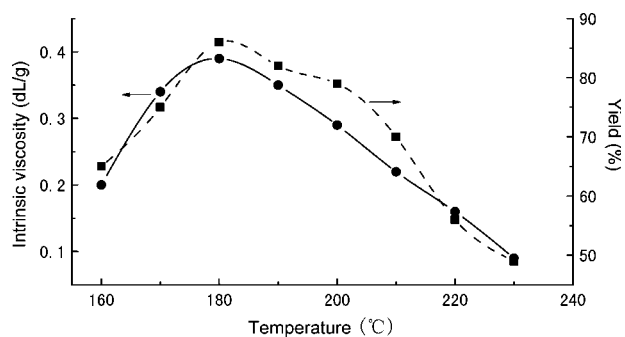
**Figure 1** Effect of monomer feed ratio on intrinsic viscosity and yield. The operation was performed under a given conditions: monomer concentration 0.48 mol/L NMP, DHPS/sodium benzoate molar ratio 1 : 1, reaction temperature 200°C and reaction time 6 h.

#### Effect of monomer feed ratio on polymerization

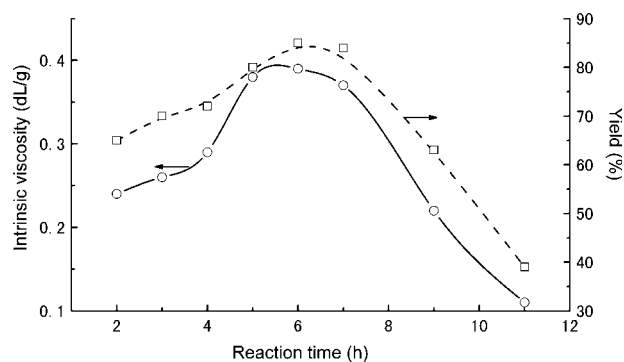
The effect of monomer feed ratio on the viscosity and yield of PPSE was investigated by varying monomer ratio (DCPS to DHPS) from 0.94 to 1.07. As shown in Figure 1, a reasonably symmetrical curve for polycondensation reaction was obtained in which the highest intrinsic viscosity appeared at DCPS/DHPS molar ratio of 1.005:1. Furthermore, the intrinsic viscosity and yield increased dramatically as the equimolar raw materials were approached.

#### Effect of reaction temperature and time on polymerization

In the fixed monomer ratio (DCPS/DHPS = 1.005 : 1), the effects of reaction temperature on the viscosity and yield of PPSE were studied from 160–230°C. The results are illustrated in Figure 2. A maximum intrinsic viscosity (0.39 dL/g) and yield (86%) of PPSE were obtained when the polymerization proceeded at 180°C. The lower intrinsic viscosities of PPSE at lower temperatures were possibly attributed to the kinetic reason. On the other hand, the dramatic decrease of intrinsic viscosity above 200°C



**Figure 2** Effect of reaction temperature on intrinsic viscosity and yield. The operation was performed under a given conditions: DCPS/DHPS molar ratio 1.005:1, monomer concentration 0.48 mol/L NMP, DHPS/sodium benzoate molar ratio 1 : 1 and reaction time 6 h.



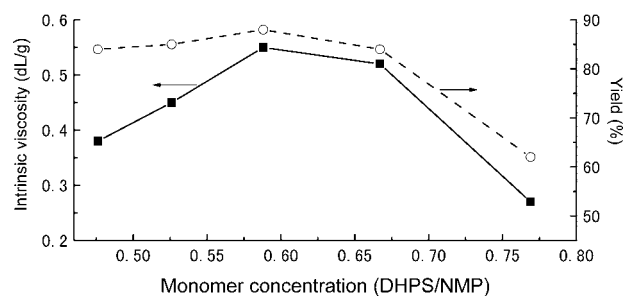
**Figure 3** Effect of reaction time on intrinsic viscosity and yield. The operation was performed under a given conditions: DCPS/DHPS molar ratio 1.005 : 1, monomer concentration 0.48 mol/L NMP, DHPS/sodium benzoate molar ratio 1 : 1 and reaction temperature 180°C.

might be caused by side reactions. Reductive dehalogenation, observed in the synthesis of poly(ether ketone)s,<sup>25</sup> might result in the formation of unreactive diphenylsulfide end-groups and stopped the polymer chain propagation in our polymerization. In addition, degradation of the activated sulfide phenylene ether chains in the presence of trace amount of water was another disadvantageous factor affecting intrinsic viscosity.

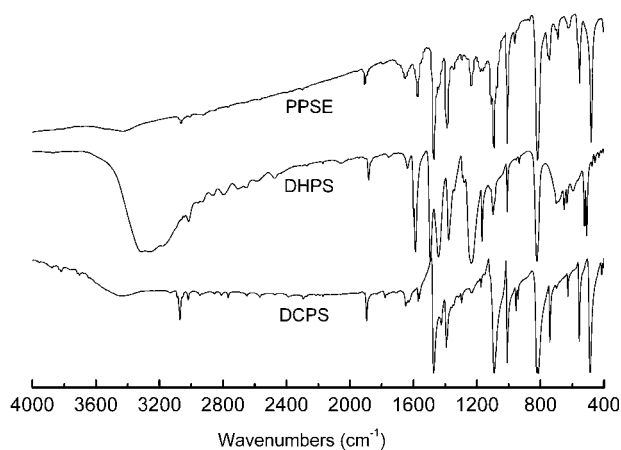
The effects of reaction time on polymerization were also examined in the range of 2–11 h at 180°C. The higher intrinsic viscosity and yield of PPSE, as shown in Figure 3, were obtained in 5–7 h. However, longer reaction times, such as above 9 h, resulted in lower intrinsic viscosity due to reductive dehalogenation and degradation as discussed before.

#### Effect of monomer concentration (DHPS/NMP) on polymerization

It is well known that monomer concentration has obvious effect on polymerization. High dilution monomers often produce oligomers, especially cyclic



**Figure 4** Effect of monomer concentration on intrinsic viscosity and yield. The operation was performed under a given conditions: DCPS/DHPS molar ratio 1.005 : 1, DHPS/sodium benzoate molar ratio 1 : 1, reaction temperature 180°C and reaction time 6 h.



**Figure 5** FT-IR spectra of PPSE and the two starting materials.

oligomers. Too high monomer concentration tends to cause agitation and heat exchanging troubles. The effects of monomer concentration on the viscosity and yield of PPSE synthesis (Fig. 4) indicate that the highest intrinsic viscosity (0.55 dL/g) and yield (86%) were appeared at monomer concentration (DHPS/NMP) of 0.588 mol/L.

Therefore, the optimized reaction condition for PPSE synthesis is as follows: monomer ratio (DHPS/DCPS) of 1/1.005, monomer concentration of 0.588 mol/L NMP, reaction temperature of 180°C and reaction time of 6 h.

#### Characterization and physical properties

The absorption bands in infrared spectra of resulting PPSE (Fig. 5) are consistent with those of reported PPSE,<sup>17</sup> suggesting that the formed PPSE has the proposed structure as Scheme 1.

The resulting PPSE and commercially available PPS show the similar X-ray diffraction patterns attributed to orthorhombic unit cells, indicating the equivalence of sulfur and oxygen in crystal structures. Although the molecular weight of PPSE increased, the lattice parameters are in agreement with those of reported PPSE with moderate molecular weight.<sup>17</sup> The degree of crystallinity was evaluated to be 65.8%, which is consistent with that of PPSE (65.1%).<sup>26</sup>

High molecular weight PPSE displays attractive solubility in some solvents. Our experiments indicated that PPSE was soluble in organic amide, halo-hydrocarbon and oxohydrocarbon solvent above 150°C although it had good chemical resistance too. Compared with PPS, the linkage of C—O—C in PPSE alters the bond length and bond angle of C—S—C in PPS, and thus destructs the polymer symmetry and improves the solubility.

DSC analysis revealed that the obtained PPSE was a semicrystalline polymer with  $T_m$  of 252.3°C and  $T_{mc}$  of 223.7°C ( $T_{mc}$  represents the crystallization temperature from melt), which were higher than those of our previous report.<sup>17</sup> The increase in  $T_m$  and  $T_{mc}$  can be attributed to the higher molecular weight of PPSE.

### CONCLUSIONS

High molecular weight PPSE with intrinsic viscosity of 0.55 dL/g has been successfully prepared from DHPS and DCPS by optimization reaction parameters. The optimized polymerization conditions for PPSE synthesis were concluded as follows: NMP as solvent; sodium benzoate as polymerization assistant; monomer ratio of DHPS/DCPS: 1/1.005; polymerization temperature: 180°C; polymerization time: 6 h and monomer concentration: 0.588 mol/L NMP. High molecular weight PPSE has higher melting point (252.3°C) than moderate molecular weight PPSE, although their structures are same. PPSE is soluble in some organic amide, halo-hydrocarbon, and oxo-hydrocarbon solvent above 150°C.

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