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Influence of polymerization conditions on the molecular structure stability and physical behavior of poly(phenylene sulfide sulfone) homopolymers

Y. Liu[a], A. Bhatnagar[a], Q. Ji[a], J.S. Riffle[a], J.E. McGrath[a,*], J.F. Geibel[b], T. Kashiwagi[c]

[a]*Department of Chemistry and NSF Science and Technology Center: High Performance Polymeric Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0344, USA*
[b]*Phillips Petroleum Company, Bartlesville, OK, USA*
[c]*NIST Building and Fire Research Laboratory, Bldg. 224, Room B258, Gaithersburg, MD 20899, USA*

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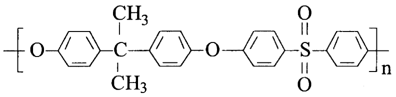
Abstract

The influence of polymerization conditions on the nucleophilic substitution step polymerization of high molecular weight poly(phenylene sulfide sulfone) (PPSS) has been studied and optimized with respect to molecular weight for the system 4,4′-dichlorodiphenylsulfone, sodium sulfide, NMP/water/sodium acetate. Reactions at about 200°C for 3 h were observed to produce the highest molecular weight. Longer reaction times and/or higher temperature degrade the molecular weight, probably because of base-catalyzed reactions on the activated backbone. These polymeric materials are amorphous with T_g values up to 222°C. However, the systems show some ordering in the presence of organic liquids, and this allows for an unexpectedly high degree of solvent resistance for molded films. The materials also show a high refractive index of 1.69 and cone calorimetry showed the PPSS system to have very good fire resistance. © 2000 Elsevier Science Ltd. All rights reserved.

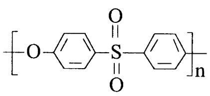
Keywords: Poly(phenylene sulfide sulfone); Synthesis; Transitions

1. Introduction

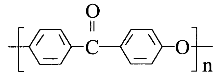
Thermoplastic materials are well known to display several inherently attractive characteristics such as rapid processibility. A number of new or improved engineering thermoplastics have been developed, including commercially available poly(arylene ether)s, such as Udel, Victrex, PEK, PEEK, etc. (shown below), which are known for their excellent mechanical and thermal properties.



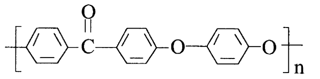
Udel



Victrex



PEK



PEEK

However, the sulfur containing analogs to the poly(arylene ether)s, the most important of which is poly(phenylene sulfide) (PPS), have not been as thoroughly investigated [1–3]. PPS is an important semicrystalline polymer with T_g around 85°C and a T_m of about 285°C, and is considered to have excellent fire and chemical resistance. A related sulfide sulfone, poly(phenylene sulfide sulfone) (PPSS), has also been briefly investigated. In fact, references to it are mostly limited to either the patent or commercial trade literature. PPSS has been described as an amorphous polymer with a T_g around 217°C [4], which can be prepared by nucleophilic aromatic substitution step polymerization, utilizing sodium sulfide as the nucleophile and 4,4′-dichlorodiphenyl sulfone as the activated aromatic halide. Although there have been several patents that discuss the effect of reaction conditions on molecular weight [4,5], a detailed study has not been reported. This paper examines the complex effects of reaction temperature and time, as well as the use of various additives described in the patent literature such as water and acetate salts on the polymerization. The relationship of molecular weight to thermal and mechanical behavior was also studied. Degradation and fire resistance as judged by thermogravimetric analysis (TGA), photoelectron

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[*] Corresponding author. Tel.: +1-540-231-4457; fax: +1-540-231-8517.
E-mail address: jmcgrath@vt.edu (J.E. McGrath).

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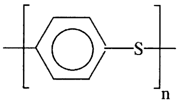
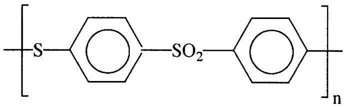
spectroscopy (XPS) and cone calorimetry were also explored.



PPS



PPSS

2. Experimental

2.1. Materials

Commercially available 4,4′-dichlorodiphenyl sulfone (DCDPS) monomer was kindly provided by Amoco Chemical Inc. and recrystallized from methanol. *N*-methyl pyrrolidinone (NMP), sodium hydrosulfide (NaSH, 70.6%), sodium hydroxide, and anhydrous sodium acetate were obtained from Aldrich Chemical Inc., and used as received. The NaSH concentration was assessed by titrating with 0.05 N HCl.

2.2. Polymerization

High molecular weight PPSS was synthesized by the aromatic nucleophilic substitution reaction of 4,4′-dichlorodiphenyl sulfone with sodium hydrosulfide at elevated reaction temperature and pressure following general procedures described in the literature [6–8]. Polymerizations were conducted in a 250 ml stainless steel pressure reactor equipped with a reflux condenser, mechanical stirrer, and temperature and pressure indicators. A typical example is described below. To the pressure reactor were added 7.0081 g (0.08830 mol) of sodium hydrosulfide, 25.6092 g (0.08918 mol) of DCDPS, 7.2435 g (0.08830 mol) of sodium acetate, 3.5318 g (00.08830 mol) of sodium hydroxide, 70 ml (0.724 moles) of NMP, and 12.9 ml (0.717 mol) of deionized water. The pressure reactor was closed, flushed with argon gas and over a 30-min period was heated to 200°C for 3 h. After the reactor was cooled and opened, the solid product was dissolved in 200 ml of NMP at 150°C, cooled and precipitated into an 75:25 (by volume) water/methanol mixture using a Waring blender. The fibrous polymer was filtered, washed well with hot water, dried in a vacuum oven at 170°C for 20 h, redissolved in NMP (20% solids), precipitated into methanol, and again dried under the same conditions.

2.3. Characterization

2.3.1. Intrinsic viscosity

Measurements were conducted at 25°C in NMP solvent, using a Cannon − Ubbelodhe viscometer, and the resulting values were obtained by calculating specific viscosity $\eta_{sp} = \eta/\eta_0 - 1$ and viscosity $\eta_{red} = \ln(\eta/\eta_0)$ at four concentrations and extrapolating (η_{sp}/c) and (η_{red}/c) to zero concentration.

2.3.2. Gel permeation chromatography (GPC)

The molecular weights of the polymers were measured by GPC using Waters GPC/ALC 150°C chromatograph equipped with a differential refractive index detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. Waters μ Styragel HT3 + HT4 columns were used. The mobile phase was NMP, containing 0.02 M P_2O_5. The flow rate was 1.0 ml/min, the injection volume was 200 μl, the experimental temperature was 60°C and the polymer concentration was approximately 4 mg/ml. TriSEC GPC Software V2.70e (Viscotek) was used to acquire and analyze the data. Absolute number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were calculated by universal calibration generated with a series of narrow molecular weight distribution polystyrene standards (Polymer Laboratories) [9].

2.3.3. Differential scanning calorimetry (DSC)

DSC measurements were conducted on a Perkin–Elmer DSC 7 instrument. Scans were run in nitrogen at a heating rate of 10°C/min. T_g values are determined as the midpoint of the change in endothermic baseline from the second heat after a quench cool from the first run.

2.3.4. Thermogravimetric analysis (TGA)

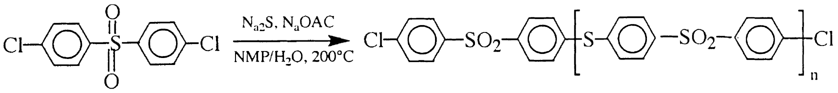
Dynamic TGA was performed on a Perkin Elmer TGA 7 thermogravimetric analyzer. Thin film or powder samples of ~10 mg were placed in a platinum pan connected to an electric microbalance. The samples were heated at a rate of 10°C/min. in air or nitrogen. Weight loss of the samples was measured as a function of temperature.

2.3.5. Dynamic mechanical analysis (DMA)

A Perkin–Elmer DMA apparatus was employed in the extension mode, at a frequency of 1 Hz and a heating rate of 5°C/min. The samples were analyzed from the compression molded pressed films which had dimensions of approximately $0.6 \times 5 \times 6\ \text{mm}^2$.

2.3.6. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed on a Perkin–Elmer PHI 5400 spectrometer employing a MgKα (1253.6 eV) achromatic X-ray source operated at 14 keV with a total power of 300 W. Typical operation pressure was $<1 \times 10^{-7}$ Torr and the surface area analyzed was about $1 \times 3\ \text{mm}^2$. The



Scheme 1.

spectrometer was calibrated to the $4f_{7/2}$ photopeak of gold at 83.8 eV and the $2p_{3/2}$ photopeak of copper at 932.4 eV, and all binding energies were referenced to the main carbon photopeak at 285.0 eV.

2.3.7. Stress–strain behavior

Stress–strain behavior was analyzed at room temperature using an Instron 1123 instrument equipped with a strain gauge extensiometer (Instron 2630-013). Dog-bone shape samples (ASTM D-638 #5) were cut out of a compression molded film of ~0.5 mm thickness. The samples were tested at an average cross head speed of 1.0 mm/min (ASTM D-638). Generally, eight samples were tested and the results were averaged.

2.3.8. Cone calorimetry

Polymer samples with dimensions of 10 cm × 10 cm × 3 mm were compression molded 50°C above their T_g and measured at the Fire Research Laboratory of the National Institute of Standards and Technology (NIST) [10,11], where they were evaluated in air using cone calorimetry at a constant heat flux of 70 kW/m^2. The instrument was run in the standard mode of ASTM E 1354 [10,17].

2.3.9. Refractive index measurements

The refractive indices of well-dried solution cast films were measured using a Metricon Model 2010 Prism Coupler which employed a low power (0.5 mW nominal) He–Ne (632.8 nm) laser.

4. Results and discussion

4.1. Effect of reaction temperature and time on molecular weight

The general synthesis of poly(phenylene sulfide sulfone)s (PPSS), is shown in Scheme 1 (synthesis of poly(phenylene sulfide sulfone). The procedure was developed on the basis of references in the patent literature [4,5,7,8] and was conducted in a pressure reactor at 100–150 psi, which was necessary to contain the solvent and reactants. The formation of PPSS proceeds via a nucleophilic aromatic substitution step polymerization. Thus, 4,4′-dichloridiphenyl sulfone (DCDPS) was reacted with sodium hydrosulfide, either sodium hydroxide or sodium carbonate and sodium acetate in NMP containing deionized water. A 1 mol% excess of the DCDPS was utilized to ensure that the endgroups of the polymer chain would be mostly derived from the relatively stable chlorophenyl groups. As noted earlier [6], high molecular weight PPSS could also be prepared from DCDPS by reacting it with performed sodium sulfide nonahydrate and sodium acetate in NMP. The synthetic variables under consideration included reaction temperature and time, and the NMP/water ratio. GPC employed on online viscosity detector and universal calibration, which allowed measurement of intrinsic viscosity and absolute molecular weight. Intrinsic viscosity measurements were also performed in NMP at 30°C.

Reaction temperatures were varied from 165 to 245°C in the presence of water at concentrations of 9 mol H_2O/1 mol NaSH. The other reaction conditions were held constant including a NaSH/DCDPS molar ratio of 1:1.01, a NaSH/NMP molar ratio of 1:8, a NaSH/NaOH/NaAc molar ratio of 1:1:1, and a reaction time of 3 h. Table 1 and Fig. 1 show that the reaction temperature had a significant effect on the molecular weight. A maximum in $\bar{M}_n$ of around 39,000 g/mol was obtained at 185–200°C. Conversely, a lower molecular weight product ($M_n = 25,100$) was obtained at 165°C, possibly due to kinetic effects (e.g. lower extent of reaction). The dramatic decrease in achievable molecular weight above 230°C was attributed to side reactions, especially the base initiated degradation of the activated sulfide arylene sulfone chains.

Table 1
Effect of reaction temperatures on molecular weights of PPSS for a 3-h reaction. (Reaction conditions: NMP/H_2O = 0.85/1, NaSH/DCDPS = 1/1.01, time: 3 h)

Run#	Reaction temp. (°C)	$\langle M_n \rangle$ by GPC (g/mol)	M_w/M_n by GPC	$[\eta]^a$ (dl/g)
1	165	25,000	2.0	0.36
2	175	38,000	1.8	0.59
3	185	38,600	1.7	0.59
4	200	39,000	1.9	0.61
5	215	30,200	1.8	0.44
6	230	15,400	1.7	0.35
7	245	7200	1.9	0.15

[a] In NMP solution at 30°C.

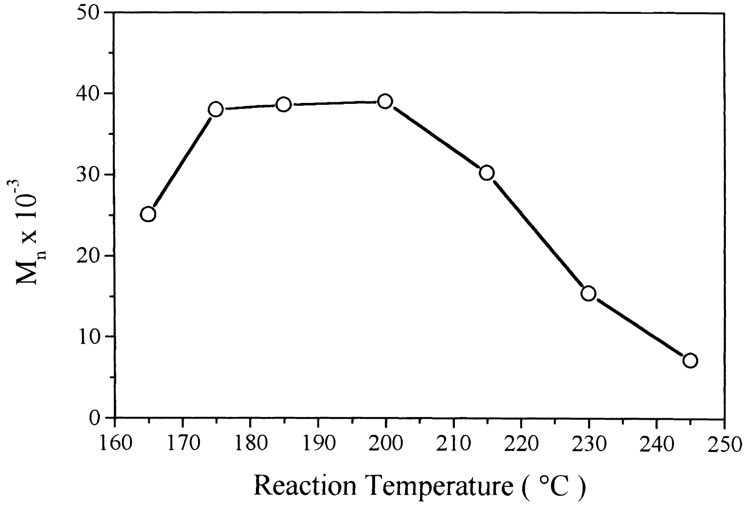
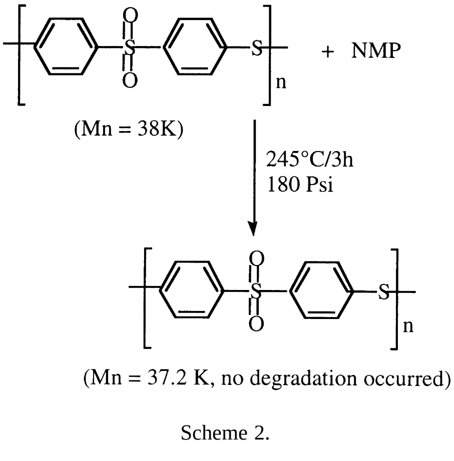


Fig. 1. Effect of reaction temperature on the M_n of PPSS for a 3-h reaction.

TGA showed that PPSS is quite thermally stable up to 480°C in either air or nitrogen atmospheres. When PPSS was dissolved in pure NMP and heated to 245°C/180 psi for 3 h, the molecular weight ($M_n = 38,000$) did not change and no obvious degradation was observed (Scheme 2 (PPSS is stable in neutral NMP solution for 3 h at 245°C)). However, degradation did occur when the PPSS in NMP solution was heated to 245°C/180 psi in the presence of water and weakly basic sodium acetate. After 3 h, $\bar{M}_n$ decreased from 38,000 to 10,800. Carbon NMR was utilized to analyze the endgroup structures of the PPSS before and after decomposition, in order to understand the degradation mechanism better. The polymeric solution in DMSO-d_6 was observed to crystallize out of the solution at room temperature, and this required the ^{13}C NMR analyses to be performed at 140°C in order to maintain the polymer in solution. Fig. 2 shows that once the PPSS degraded, the signals corresponding to the mercaptide and phenolic endgroups increased significantly. This suggests that degradation was due to chemical attack at the sulfur–carbon bonds in the polymer chain by nucleophiles, such as hydroxide or acetate anions. This likely reflects the weaker bond strength of a sulfide–carbon covalent bond, relative to sulfone–carbon and aromatic carbon–carbon bonds.



Scheme 2.

The effect of reaction time on molecular weight was also examined by varying it from 20 min to 10 h, at a constant NaSH/DCDPS molar ratio of 1:1.01, a NaSH/NaOH/NaAc molar ratio of 1:1:1, a NaSH/NMP molar ratio of 1:8, a NaSH/H_2O molar ratio of 1:9, and a reaction temperature of 200°C. The results indicate that the polymerization proceeded very rapidly and was essentially complete after 1.5 h at 200°C, for the stoichiometry; utilized Table 2 and Fig. 3. However, longer reaction times, such as 8 or 10 h, resulted in lower molecular weight materials, due to chemical degradation at the longer reaction time at 200°C in the presence of water, sodium hydroxide, and sodium acetate, as discussed earlier.

4.2. Effect of the molar ratios of H_2O/NaSH or H_2O/NMP on molecular weight

The patent literature [5,8] suggests that the molar ratios of H_2O-to-NaSH and NMP-to-H_2O, are critical for achieving optimum molecular weight. For example, the maximum molecular weight was achieved at molar ratios of 9.4:1 and 0.85:1 for H_2O-to-NaSH and NMP-to-H_2O, respectively. Unfortunately, the authors did not address the effect of water concentration on molecular weight. In this study, the molar ratios of total water volume to sodium hydrosulfide were varied from 1.3:1 to 20:1 (e.g. the water is derived from NaSH·$x$$H_2O$, no additional water was added). At the same time, the corresponding NMP/H_2O ratios were varied from 6.2:1 to 0.4:1, since a fixed amount of NMP was utilized. The other reaction conditions were held constant, including a NaSH/DCDPS molar ratio of 1:1.01, a NaSH/NaOH/NaAc molar ratio of 1:1:1, a NaSH/NMP molar ratio of 1:8 and reaction temperature of 200°C, for 3 h.

As shown in Table 3, higher molecular weight PPSS was obtained using H_2O-to-NaSH ratios from 6.0:1 to 15:1. The

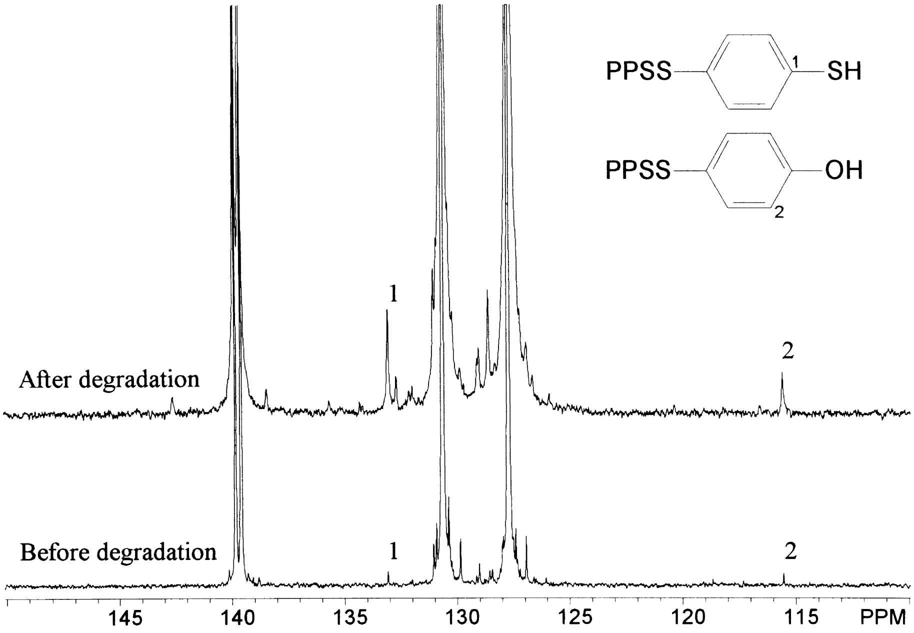


Fig. 2. ^{13}C NMR spectra of PPSS before and after degradation at 245°C.

appearance of a maximum molecular weight is suggested to be a function of the increased solubility of the nucleophile and the growing polymer chains in the reaction medium. In fact, premature precipitation of polymer chains has been cited as one of the principal reasons why low molecular weight was observed in some PPSS and similar PPS copolymers [12].

4.3. Solubility and refractive index

High molecular weight PPSS displays intriguing solubility characteristics in various solvents (Table 4). Interestingly, it is resistant to many of the solvents that ordinarily dissolve the analogous oxygen containing poly(arylene ether sulfone)s.

Furthermore, while the homopolymer was initially soluble in several polar solvents, an interesting phenomenon was noted. After the materials were dissolved and allowed to stand for a few hours, precipitation occurred. This phenomenon could be very important and may be related to the relatively low susceptibility of molded PPSS films to environmental stress-cracking and crazing (ESC). Observations on cracking and crazing were made under constant stress in a test jig, and, surprisingly, the amorphous sulfide–sulfones showed a remarkable degree of resistance to these important organic liquids. It is speculated that this may be a result of crystallization on the surface. By comparison, polyarylene ether sulfones show low resistance to acetone, MEK and toluene. These observations are supported by numerous reports that solutions of PPSS in NMP formed of spherulite-shaped PPSS–NMP solvates which results in instability of the polymer solution [13]. The PPSS–NMP solvates were found to have crystalline structures, X-ray diffraction patterns, and a melting point of approximately

Table 2
Effect of reaction time at 200°C on molecular weight of PPSS (Reaction conditions: NMP/H_2O = 0.85/1, NaSH/DCDPS = 1/1.01, reaction temp.: 200°C, time: 3 h)

Run#	Reaction temp. (h)	$\langle M_n \rangle$ by GPC (g/mol)	M_w/M_n by GPC	$[\eta]^a$ (dl/g)
1	0.33	21,100	1.7	0.30
2	0.67	28,200	1.8	0.43
3	1.0	34,000	1.8	0.49
4	1.5	40,200	1.9	0.58
5	2.0	43,100	1.9	0.59
6	3.0	42,800	1.9	0.59
7	4.0	38,300	1.9	0.50
8	6.0	30,100	1.9	0.45
9	8.0	20,200	1.8	0.29
10	10.0	12,800	2.0	0.24

[a] In NMP solution at 30°C.

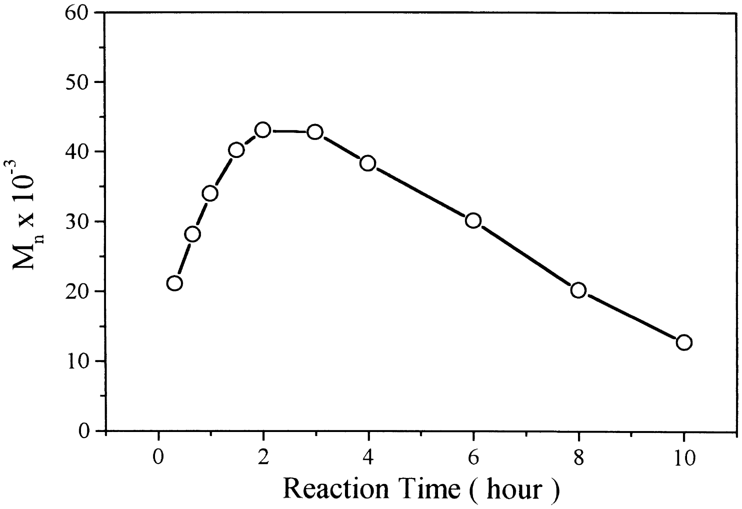


Fig. 3. Effect of reaction time at 200°C on the M_n of PPSS.

Table 3
The effect of water concentration during the polymerization of molecular weight. (Reaction conditions: NaSH/DCDPS = 1/1.01, reaction temp.: 200°C, time: 3 h)

Run#	Molar ratio H_2O/NaSH	Molar ratio NMP/H_2O	$\langle M_n \rangle$ by GPC (g/mol)	M_w/M_n by GPC	$[\eta]^a$ (dl/g)
1	1.3/1	6.2/1	12,200	1.8	0.21
2	3.0/1	2.7/1	28,100	1.9	0.44
3	6.0/1	1.3/1	30,200	1.8	0.43
4	9.4/1	0.85/1	38,500	2.0	0.59
5	12.0/1	0.67/1	35,800	1.9	0.52
6	15.0/1	0.53/1	34,800	1.9	0.49
7	20.0/1	0.40/1	19,200	1.9	0.31

[a] In NMP solution at 30°C.

200°C [13]. Elemental analysis revealed that the crystals contained 3.75% nitrogen, which was likely, derived from the NMP. Extracting the NMP from the crystal solvates with benzene at room temperature produced a sample which was almost completely amorphous [13].

Metricon measurements show that PPSS cast films exhibit a very high refractive index value of around 1.70, and this is being further investigated.

Table 4
Solubility behavior of poly(phenylene sulphide sulfone) (39 K $\bar{M}_n$)

Solvent	RT	Hot (reflux)
Chloroform	No	No
THF	No	No
Chlorobenzene	No	No
1,2-Dichlorobenzene	No	No
DMSO	Yes[a]	–
DMAc	Yes[a]	–
DMF	Yes[a]	–
NMP	Yes[a]	–

[a] Soluble initially, precipitated out of solution upon standing.

4.4. Influence of molecular weight on thermal and mechanical behavior

The glass transition temperature (T_g) of the PPSS polymers was measured by DSC at a heating rate of 10°C/min under an atmosphere of nitrogen (Table 5). DSC analyses showed glass transition temperature (T_g) of up to 222°C (2nd heat) and no crystalline melting transition.

Dynamic TGA in nitrogen or air indicate that the PPSS samples are quite thermally stable as judged by 5% weight loss temperatures (Fig. 4 and Table 5). Char yield values at 700°C ranged from 7.8 to 12.0% in air, and from 35.6 to 37.4% in nitrogen, respectively.

TGA measurements showed that the materials also displayed a two-step degradation behavior in air, as illustrated in Fig. 5. XPS analysis of the PPSS, as shown in Fig. 5, indicated that the sulfur peak at 168.0 eV (as a result of the sulfone moiety in the polymer backbone) disappeared after reaching a temperature of 580°C in air. On the contrary, the other sulfur peak at 163.9 eV, the sulfide moiety, remained. Thus, SO_2 “extrusion” appears to be an explanation of this behavior. Table 6 summarizes the XPS

Table 5
Influence of molecular weight on the thermal properties of PPSS

		TGA, °C[a] (5% weight loss)		TGA, %[a] Char yield at 700°C	
M_n (g/mol)	T_g[b] (°C)	N_2	Air	N_2	Air
15,000	207	482	477	35.6	7.8
20,000	217	485	487	36.0	9.2
25,000	218	485	485	35.8	10.7
30,000	220	489	490	35.9	12.0
39,000	220	487	490	37.4	12.0
43,000	222	486	489	37.1	11.5

[a] Heating rate of 10°C/min.

[b] Second heat, heating rate of 10°C/min under N_2.

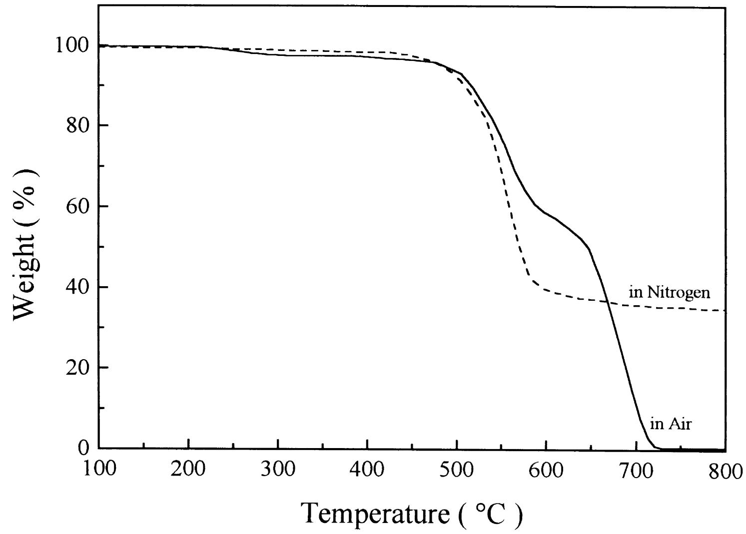


Fig. 4. TGA weight loss behavior of PPSS ($M_n = 43,000$) at a heating rate of 10°C/min.

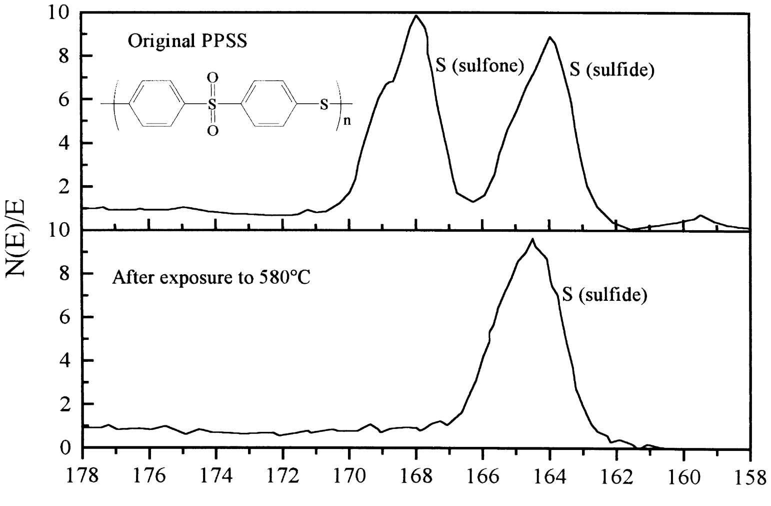


Fig. 5. XPS analysis of sulfur for PPSS showing the sulfone moiety is lost above 580°C.

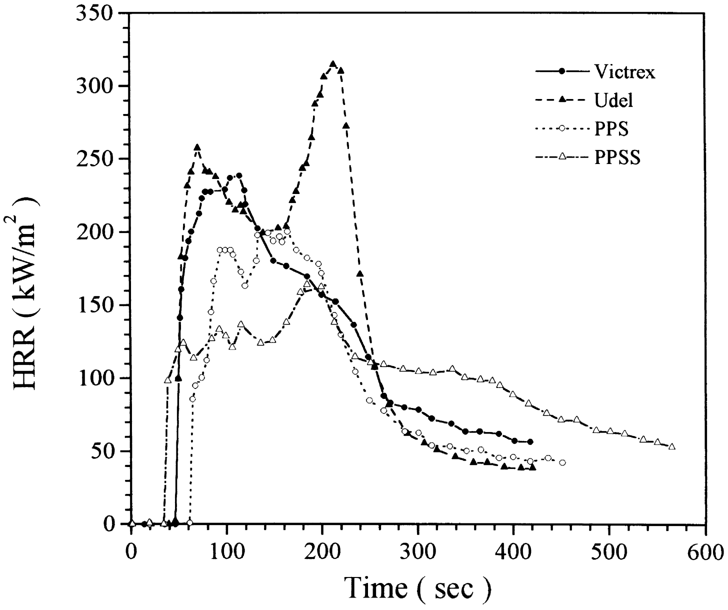


Fig. 6. Cone calorimetry results (70 kW/m^2).

Table 6
Comparison of XPS surface (Angle of 45°, depth of 50 Å) atomic concentrations of C, S, O for the PPSS before and after exposure to 580°C in air atmosphere

Element	Carbon C (%)	Sulfur (S) (%)	Oxygen (O) (%)
Theoretical value	75.0	12.5	12.5
PPSS before exposure to 500°C	72.9	12.3	14.9
PPSS after exposure to 580°C	83.3	5.5	11.1

surface atomic concentrations of carbon, sulfur, and oxygen before and after exposure to 580°C in air atmosphere. These results indicate that both sulfur and oxygen concentrations decreased after the polymer was exposed to 580°C, suggesting that the sulfide moiety in the polymer backbone may form a protective layer, such as a crosslinked sulfide char, [14] on the polymer surface to protect the material from further degradation. This would, of course, partially account for the two-step degradation phenomenon.

The DMA of the compression-molded PPSS films was also investigated. These materials displayed a high modulus approaching the glass transition temperature and exhibited a secondary relaxation at -100°C, which is indicative of molecular motion well below T_g. This is consistent with ductile behavior [15]. Mechanical tests were performed to measure the tensile properties of PPSS of varying molecular weights ($M_n = 20,000$–$43,000$ g/mol) at room temperature using an Instron equipped with a strain gauge extensiometer. The compression molded samples were tested at an average cross head speed of 1.0 mm/min. Table 7 reports tensile strength and elongation measurements that are similar to the poly(arylene ether sulfone)s. Tensile yield behavior was observed during room temperature testing of the compression molded specimen.

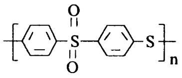
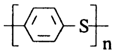
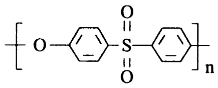
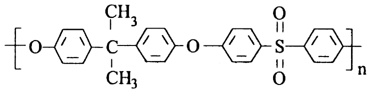
Table 7
Effect of molecular weight on room temperature stress–strain behavior of compression molded PPSS (ASTM D638 (1.0 mm/min), average value of eight samples)

M_n (g/mol)	Tensile strength (MPa)	Elongation at break (%)
20,000	74.5 ± 71	12.5 ± 3.1
25,000	88.5 ± 0.5	17.4 ± 3.1
30,000	92.8 ± 0.7	22.2 ± 3.1
39,000	92.9 ± 0.6	22.0 ± 3.7
43,000	93.9 ± 0.7	22.3 ± 4.1
Udel	70.0 ± 6.9	>40
Victrex[a]	86	17

[a] Encyclopedia of polymer science and engineering 2nd edition; Tamada HT et al, Polym J 1993;25(4):339.

The flammability behavior of PPSS was examined by cone calorimetry at the NIST Fire Laboratories, using the commercial Udel and Victrex polyarylene ether sulfones and poly(phenylene sulfide) (PPS) as controls. A fairly intense energy of 70 kW/M^2 was employed. Cone calorimetry is an important and emerging methodology for determining the heat release rate and the amount of heat released by a polymer due to combustion under a specific applied heat flux [17]. As summarized in Fig. 6 and Table 8, the Udel control had the highest heat release rate of the samples

Table 8
Comparison of peak heat release rate (HRR) of various engineering thermoplastics

Polymer	Repeat unit	Peak heat release rate[a] (kW/m^2)
PPSS		165
PPS		198
Victrex		235
Udel		310

[a] Samples tested using cone calorimetry at a flux of 70 kW/m^2.

analyzed, which may be due to its partially aliphatic bisphenol-A based structure. In addition, the poly(phenylene sulfide sulfone) displayed an equivalent or lower heat release rate to the Udel, Victrex, and PPS, which are also excellent, and all indicate good fire resistance.

The average heat release rate over a specific period of time, allows one to generate a combustion time cycle. Therefore, to better analyze how a material behaves in an actual fire, it is useful to determine the average heat release rate. Previous research [16], suggested a 3-min period for determining the average heat release rate [16] of a material. Using these 3-min conditions, the change in heat release rate of the PPSS, in comparison to the three commercial materials, PPS, Udel, and Victrex, was quite significant. Thus, the PPSS showed both a lower peak heat release rate, and an improved average heat release rate.

5. Conclusions

High molecular weight poly(phenylene sulfide sulfone) (PPSS) was successfully synthesized using the following optimum conditions: a reaction temperature of 175–200°C, a reaction time of 3–5 h, and a water-to-NaSH molar ratio of 9.4:1 to 15:1. These materials could be compression molded to produce tough, relatively solvent resistant films that showed good thermal stability in air and degraded at high temperatures via a two-step mechanism. Cone calorimetry results suggest that PPSS has good fire resistance that is comparable to, or better than, related PPS and poly(arylene ether sulfone)s. These materials also exhibited a very high refractive index of about 1.69 [18].

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