1812 *Chem. Mater.* **2005,** *17,* 1812−1817

Hyperbranched Poly(phenylene sulfide) and Poly(phenylene sulfone)

Alfredo Mellace, James E. Hanson,* and Julianne Griepenburg

Department of Chemistry and Biochemistry, Seton Hall University, 400 South Orange Avenue,
South Orange, New Jersey 07079-2694

Received September 17, 2004. Revised Manuscript Received January 20, 2005

Hyperbranched poly(phenylene sulfide) was prepared from 3,4-dichlorobenzenethiol. This monomer was treated with potassium carbonate in an amide solvent, either *N*,*N*-dimethylformamide (DMF) or *N*-methylpyrrolidone (NMP). Polymerization for 24 h at 100 °C in DMF gave a polymer with a M_w of 17 kD and a polydispersity of 2.0. Polymerization for 8.5 h at 150 °C in NMP gave a polymer with a M_w of 16 kD and a polydispersity of 1.5. Addition of 1,3,5-trichlorobenzene as a multifunctional core to the polymerizations gave reduced M_w and lower polydispersity. Addition of 1 core for every 50 monomers gave a polymer with a M_w of 8.4 kD and a polydispersity of 1.2 in DMF and a polymer with a M_w of 13 kD and a polydispersity of 1.3 in NMP. The polymers were primarily characterized by size-exclusion chromatography with light-scattering detection (which provided the molecular weights and distributions) and by thermal methods. Differential scanning calorimetry (DSC) revealed that the hyperbranched PPS was amorphous with a T_g between 60 and 90 °C and no apparent crystallinity. The polymers prepared in DMF had higher T_gs than those prepared in NMP. Thermogravimetric analysis revealed that the hyperbranched PPS was very thermally stable, with decomposition temperatures between 400 and 450 °C in both air and N_2 atmospheres. In air, complete decomposition occurred by about 625 °C, while approximately 25% of the mass remained at 700 °C under N_2. The hyperbranched PPS could be oxidized to hyperbranched poly(phenylene sulfone). This material was completely insoluble, but could be analyzed by thermal methods. By DSC, the T_g of the sulfone was approximately 155 °C, while by TGA the decomposition temperature was 325−375 °C in both air and N_2. In air, decomposition was complete by 575 °C, while in N_2 about 30% of the mass remained at 700 °C. These simple, one-pot approaches to hyperbranched poly(phenylene sulfide) and hyperbranched poly(phenylene sulfone) from commercially available monomers provide an entry to many further studies and applications for these new materials.

Introduction

Hyperbranched and dendritic polymers are classes of materials that have generated intense interest over the past decade.[1] New synthetic methodologies have allowed the preparation of highly branched molecules under controlled conditions, and new analytical techniques have allowed the characterization of these materials.[2] Numerous unexpected and novel properties have been noted for hyperbranched and dendritic macromolecules,[3] and new applications are now appearing at a rapid pace.[4] Sulfide and sulfone polymers (such as poly(phenylene sulfide) (PPS) and the polyethersulfones) are well-known and useful engineering thermoplastics,[5] but only a few studies on hyperbranched or dendritic variants of these polymers have been published.[6] We report the preparation and characterization of hyperbranched poly(phenylene sulfide) using 3,4-dichlorobenzenethiol as the AB_2 monomer, and the subsequent oxidation of these polymers to the corresponding poly(phenylene sulfone) polymers.[7]

Results

Hyperbranched Poly(phenylene sulfide). Polymerization of commercially available 3,4-dichlorobenzenethiol was accomplished using anhydrous potassium carbonate as a base in the amide solvents *N*,*N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) to give hyperbranched poly(phenylene sulfide)[8] (Scheme 1). Higher temperatures generally led to more rapid polymerization, with the best results

---

* To whom correspondence should be addressed. E-mail: hansonja@shu.edu.

(1) (a) Jikei, M.; Kakimoto, M.-A. *Prog. Polym. Sci.* **2001**, *26*, 1233−1285. (b) Tomalia, D. A.; Frechet, J. M. J. *J. Polym. Sci. A* **2002**, *40*, 2719−2728. (c) Sheiko, S. S.; Moller, M. *Topics Curr. Chem.* **2001**, *212*, 137−175. (d) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453−471. (e) Hult, A.; Johansson, M.; Malmstrom, E. *Adv. Polym. Sci.* **1999**, *143*, 1−34.

(2) (a) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183−275. (b) Ishizu, K.; Tsubaki, K.; Mori, A.; Uchida, S. *Prog. Polym. Sci.* **2002**, *28*, 27−54. (c) Voit, B. *J. Polym. Sci. A* **2000**, *38*, 2505−2525. (d) Schluter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864−883. (e) Hawker, C. J. *Adv. Polym. Sci.* **1999**, *147*, 113−160. (f) Roovers, J.; Comanita, B. *Adv. Polym. Sci.* **1999**, *142*, 179−228. (g) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402−413.

(3) (a) Wang, H.; Simon, G. P. *Adv. Polym. Mater.* **2003**, 275−309. (b) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendrimers and Dendrons*; Wiley-VCH Verlag: Weinheim, Germany, 2001. (c) Peerlings, H. W. I.; Meijer, E. W. *Chem. Eur. J.* **1997**, *3*, 1563−1570. (d) Jang, J. G.; Bae, Y. C. *Polymer* **1999**, *40*, 6761−6768.

(4) (a) Pirrung, F. O. H.; Loen, E. M.; Noordam, A. *Macromol. Symp.* **2002**, *187*, 683−693. (b) Striba, S.-E.; Frey, H.; Haag, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1329−1334. (c) Mezzenga. R.; Boogh, L.; Manson, J.-A. E. *Compos. Sci. Technol.* **2001**, *61*, 787−795. (d) Haag, R. *Chem. Eur. J.* **2001**, *7*, 327−335. (e) Uhrich, K. *Trends Polym. Sci.* **1997**, *5*, 388−393. (f) Hobson, L. J.; Harrison, R. M. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 683−392.

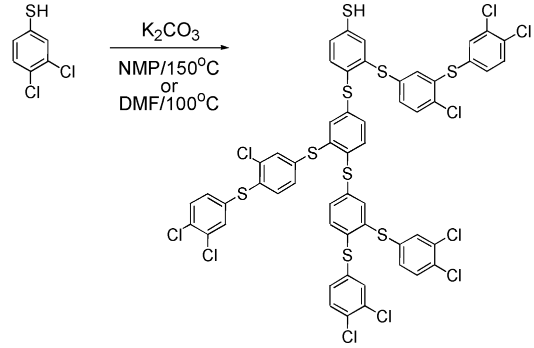
(5) (a) Edmonds, J. T.; Hill, H. W. U.S. Patent 3354129, 1967. (b) Tsuchida, E.; Shouji, E.: Yamamoto, K. *Macromolecules* **1993**, *26*, 7144−7148. (c) Robello, D. R.; Ullman, A. Urankar, E. J. *Macromolecules* **1993**, *26*, 6718−6721. (d) Colquhoun, H. M. *Polymer* **1997**, *38*, 991−994. (e) Colquhoun, H. M.; Aldred, P. L.; Kohnke, F. H.; Herbertson, P. L.; Baxter, I.; Williams, D. J. *Macromolecules* **2002**, *35*, 1685−1690.

(6) (a) Jikei, M.; Hu, Z.; Kakimoto, M.; Imai, Y. *Macromolecules* **1996**, *29*, 1062−1064. (b) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356−357.

(7) Mellace, A.; Hanson, J. E. *Polym. Prepr.* **2003**, *44* (2), 845−846.

10.1021/cm048376p CCC: $30.25

Scheme 1. Polymerization of 3,4-Dichlorobenzenethiol to Prepare a Hyperbranched Polymer[a]

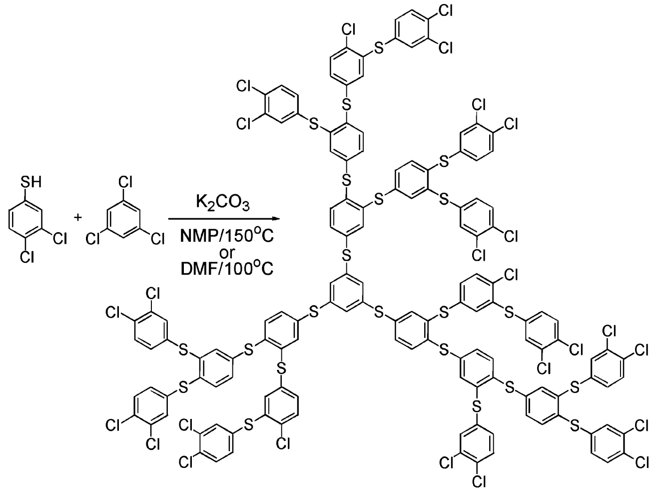


[a] A small oligomer is shown (DP = 9, MW = 1319) with examples of dendritic, terminal, and two types of linear units (1,3 and 1,4).

found at 100 °C in DMF and 150 °C in NMP. Polymerization was limited by the solubility of the resulting hyperbranched PPS (precipitation was observed at long polymerization times) and also by some degradation of the polymer as observed during preliminary runs (M_w decreased with increasing polymerization time), so polymerization was stopped after 24 h in DMF at 100 °C and after 8.5 h in NMP at 150 °C. The crude polymers were isolated by precipitation into aqueous acid (6 M HCl) to quench any remaining thiolate anions. The resulting precipitates were filtered, thoroughly dried under vacuum, and dissolved in a minimal amount of THF at room temperature. The THF solutions were then precipitated into hexanes to remove low molecular weight constituents and residual amide solvent. The resulting powdery polymers were isolated by filtration and again dried thoroughly under vacuum prior to analysis.

Polymerization of AB_2 monomers in the presence of a multifunctional core is known to reduce the polydispersity of the resulting hyperbranched polymers while also reducing the molecular weight.[9] 1,3,5-Trichlorobenzene was used as a trifunctional core for preparation of hyperbranched PPS under these conditions. (Scheme 2) Polymerizations employing this core were accomplished in both DMF and NMP. A ratio of 1 core molecule per 50 monomers (1:50) was used for both solvents. The reactions with the 1,3,5-trichlorobenzene core were conducted using procedures identical to those described above for the polymers without core for the respective solvents, including time and temperature of reaction, method of isolation, and purification conditions.

Scheme 2. Polymerization of 3,4-Dichlorobenzenethiol with 1,3,5-Trichlorobenzene as a Multifunctional Core[a]



[a] A hypothetical polymer molecule with a DP of 23 (including the core) and MW of 3316.5 is shown.

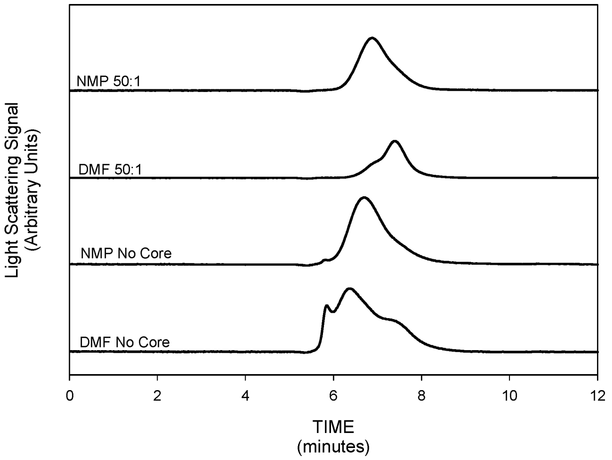


Figure 1. Size-exclusion chromatograms for hyperbranched PPS polymers (THF eluent).

Table 1. SEC-LS Data for Hyperbranched PPS[a]

sample (solvent, core:monomer)	M_w (kD)	M_w/M_n	DP[b]
DMF no core	17	2.0	59
DMF 1:50	8.4	1.2	49
NMP no core	16	1.5	73
NMP 1:50	13	1.3	71

[a] THF eluent, M_w from light scattering. [b] Based on M_n.

The polymers were characterized by size-exclusion chromatography with light-scattering detection (SEC-LS), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic light scattering (DLS, also known as quasi-elastic light scattering or QELS), ^1H NMR, IR, and elemental analysis. SEC-LS chromatograms are shown in Figure 1, and the SEC-LS data are summarized in Table 1. Without core, the polymer prepared in DMF had a higher M_w and higher polydispersity than the polymer prepared in NMP. The addition of the 1,3,5-trichlorobenzene core produced the results predicted by theory and typically observed by others:[1,9] adding core lowered both the M_w and the polydispersity. Polymerization in NMP at higher temperature and shorter time gave cleaner molecular weight distributions, as can be seen in Figure 1 and Table 1. With no core, the NMP polymerization gave a significantly lower polydispersity (1.5 vs 2.0 in DMF) with only a slight diminution of M_w (16 vs 17 kD in DMF). Addition of core

---

(8) (a) Bradshaw, J. S.; South, J. A.; Hales, R. H. *J. Org. Chem.* **1972**, *37*, 2381−2383. (b) Cogolli, P.; Maiolo, F.; Testaferri, L.; Tingoli, M.; Tiecco, M. *J. Org. Chem.* **1979**, *44*, 2642−2646. (c) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* **1983**, 751−755. (d) Pastor, S. D.; Hessell, E. T. *J. Org. Chem.* **1985**, *50*, 4812−4815. (e) Shaw, J. E. *J. Org. Chem.* **1991**, *56*, 3728−3729. (f) Caruso, A. J.; Colley, A. M.; Bryant, G. L. *J. Org. Chem.* **1991**, *56*, 862−865. (g) Palomo, C.; Oiarbide, M.; Lopez, R.; Gomez-Bengoa, E. *Tetrahedron Lett.* **2000**, *41*, 1283−1286.

(9) (a) Mock, A.; Burgath, A.; Hanselmann, R.; Frey, H. *Macromolecules* **2001**, *34*, 7692−7698. (b) Parker, D.; Feast, W. J. *Macromolecules* **2001**, *34*, 5792−5798. (c) Radke, W.; Litvinenko, G.; Muller, A. H. E. *Macromolecules* **1998**, *31*, 239−248. (d) Ishida, Y.; Sun, A. C. F.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *22*, 2832−2838. (e) Hobson, L. J.; Feast, W. J. *Polymer* **1999**, *40*, 1278−1297.

Table 2. Glass Transition Values for Hyperbranched PPS[a]

sample	T_g (°C)
DMF no core	90 ± 2
DMF 50:1	76 ± 2
NMP no core	60 ± 2
NMP 50:1	60 ± 2

[a] Samples annealed at 200 °C prior to analysis, heating rate 10 °C/min. T_g determined by midpoint.

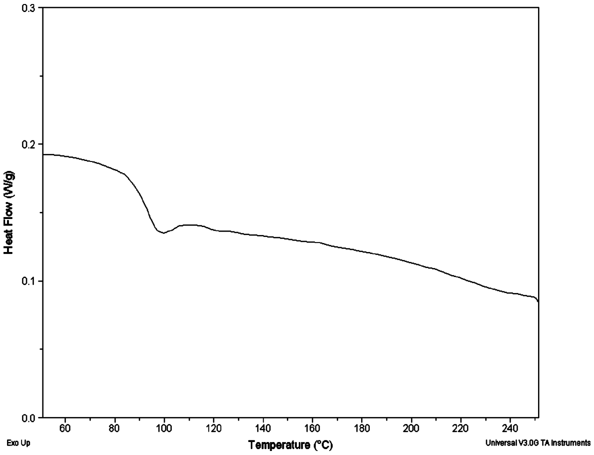


Figure 2. DSC of hyperbranched PPS (DMF, no core) showing T_g of 90 °C (scan rate 10 °C/min).

to the NMP polymerization produced less of a decrease for both the M_w and the polydispersity of the resulting polymer. Differences between the DMF and NMP polymerizations were observed in the other analyses as well (vide infra).

PPS is notable for its thermal properties. Linear PPS is a semicrystalline polymer with a T_g of ~85 °C, a T_m of ~285 °C, a T_c of ~225 °C, and excellent thermal stability (T_d > 400 °C).[10] DSC analysis of the hyperbranched PPS samples revealed both similarities and differences as compared to linear PPS. The hyperbranched PPS samples were found to be amorphous polymers with a T_g between 60 and 90 °C (Table 2) and a complete lack of crystallinity: no T_m was observed up to 375 °C. Crystallinity could not be induced by annealing: if the polymer samples were heated to 300 °C, then slowly cooled back to room temperature, no crystallization was observed (crystallization usually occurs at ~225 °C in linear PPS). When the annealed samples were reheated to 375 °C, no T_m was observed, although the T_g was observed to be more well-defined. The T_g values are similar to those of linear PPS, and considerably lower than those observed by Jikei.[6a] T_g was a function of the polymerization conditions: the polymers prepared in DMF had higher observed T_g values. A representative DSC curve showing the T_g of the polymer prepared in DMF with no core is shown in Figure 2.

Table 3. Thermogravimetric Analysis of Hyperbranched PPS[a]

sample (atmosphere)	T_d (°C)	T_{max} (°C)	T_d' (°C)	T_{max}' (°C)	residue (%)
DMF no core (N_2)	405 ± 5	457 ± 1			26 ± 1
DMF 50:1 (N_2)	415 ± 5	461 ± 1			21 ± 1
NMP no core (N_2)	442 ± 5	472 ± 1			21 ± 1
NMP 50:1 (N_2)	445 ± 5	475 ± 1			23 ± 1
DMF no core (air)	400 ± 5	449 ± 1	550 ± 5	568 ± 1	4 ± 1
DMF 50:1 (air)	412 ± 5	451 ± 1	547 ± 5	562 ± 1	1 ± 1
NMP no core (air)	418 ± 5	452 ± 1	550 ± 5	559 ± 1	2 ± 1
NMP 50:1 (air)	420 ± 5	458 ± 1	550 ± 5	565 ± 1	0.5 ± 0.5

[a] Scan rate 10 °C/min.

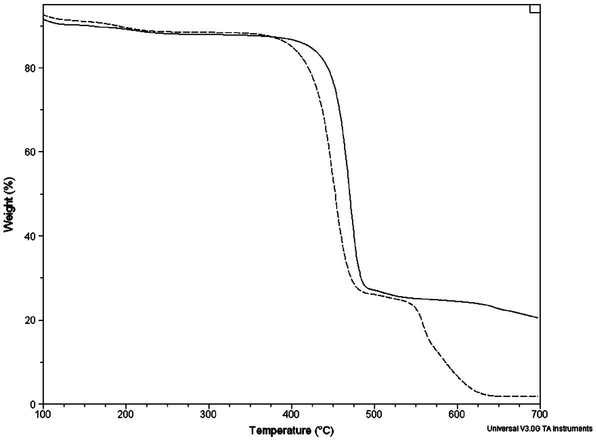


Figure 3. Thermogravimetric analysis of hyperbranched PPS under N_2 atmosphere (solid line) and under air atmosphere (dashed line) (scan rate 10 °C/min). The representative sample shown here was prepared in NMP with no core.

Thermogravimetric analysis revealed that the hyperbranched PPS samples were quite thermally stable, although not as stable as linear PPS.[10] Under an N_2 atmosphere, linear PPS was determined to have an onset temperature for decomposition (T_d) of ~480 °C, a maximum decomposition (T_{max}) of 520 °C, and more than 50% of the polymer remains as a residue at 700 °C. Under an air atmosphere, linear PPS was found to have two decomposition events: a first T_d of ~480 °C with a T_{max} of ~510 °C, and a second T_d' of ~565 °C with a T_{max}' of ~575 °C. The 700 °C residue is <5%. The hyperbranched PPS samples are not as robust, but are still quite stable. The polymers prepared in the different solvents under different time and temperature conditions gave somewhat different analyses, with the polymers prepared in NMP slightly more stable. Table 3 lists the values for all samples under both N_2 and air atmospheres, and Figure 3 shows typical TGA curves for hyperbranched PPS (NMP, no core).

Dynamic light scattering (DLS, also known as quasi-elastic light scattering or QELS) allows the measurement of diffusion coefficients for macromolecules and other particles in solution, and hence the establishment of hydrodynamic radii (R_h) through the Stokes relation.[11] DLS analysis is difficult to perform on linear PPS, since linear PPS is insoluble under normal conditions. (PPS will dissolve in some solvents above 220 °C: 2-chloronaphthalene, for example.) The solubility of the hyperbranched PPS polymers allows the determination of hydrodynamic radii by DLS. Regularization analysis (by intensity) of DLS data from the hyperbranched PPS in THF revealed diffusion coefficients between 2.2×10^{-6} cm^{2}sec^{-1} and 3.8×10^{-6} cm^{2}sec^{-1} with

---

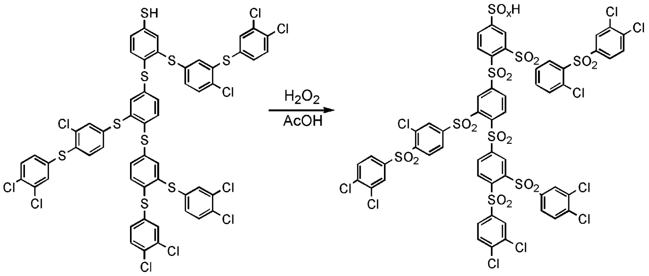
(10) (a) The values measured on our system under identical scan conditions for a commercial sample of linear PPS were as follows: T_g 82 °C, T_m 277 °C, T_c 220 °C, T_d 484 °C, 700 °C residue 50%. (b) Hohne, G.; Hemminger, W.; Flammersheim, H. J. *Differential Scanning Calorimetry: An Introduction for Practitioners*; Springer-Verlag: Berlin/Heidelberg, 1996. (c) Peters, O. A.; Still, R. H. *Polym. Degr. Stab.* **1993**, *42*, 41–48. (d) Seo, K. H.; Park, L. S.; Baek, J. B.; Brostow, W. *Polymer* **1993**, *34*, 2524–2527. (e) Dag, M.; Budgell, D. R. *Thermochim. Acta* **1992**, *203*, 465. (f) Port, A. B.; Still, R. H. *Polym. Degr. Stab.* **1979**, *1*, 193–204. (g) Hawkins, R. T. *Macromolecules* **1976**, *9*, 189.

Table 4. DLS Radii of Hyperbranched PPS

sample	D^a cm^2 sec^{-1}	R_h[b] nm	MW (DLS)[c] kD	M_w (SEC-LS) kD
DMF no core	$2.2 \pm 0.2 \times 10^{-6}$	2.1 ± 0.2	18	17
DMF 50:1	$3.8 \pm 0.4 \times 10^{-6}$	1.1 ± 0.1	4.0	8.4
NMP no core	$2.5 \pm 0.2 \times 10^{-6}$	1.7 ± 0.2	11	16
NMP 50:1	$3.0 \pm 0.3 \times 10^{-6}$	1.4 ± 0.1	6.9	13

[a] Diffusion coefficients from regularization analysis based on scattering intensity. [b] R_h calculated from the measured D using the Stokes–Einstein relation. [c] MW calculated R_h using the formula MW = $(1.549R_h)^{2.426}$ for spherical particles.

Scheme 3. Oxidation of Hyperbranched Poly(phenylene sulfide) to Hyperbranched Poly(phenylene sulfone)[a]



[a] This scheme shows complete oxidation of the hyperbranched PPS oligomer from Scheme 1. The resulting hyperbranched $PPSO_2$ oligomer has a DP of 9 and a MW of 1607.

corresponding hydrodynamic radii (R_h) between 1.1 and 2.1 nm for the different polymer samples. Molecular weights were calculated from R_h using a standard treatment for spherical particles. Such standard formulas devised for linear, random coil polymers or for polypeptides generally underestimate the molecular weights of branched and hyperbranched polymers (which tend to have more compact structures),[12] and this is seen here for all samples except the sample prepared in DMF with no core. As is apparent from the SEC-LS data in Figure 1, however, this DMF sample contains a significant high-MW fraction which could skew the intensity-based analysis toward higher apparent MW. DLS diffusion coefficients and hydrodynamic radii are provided in Table 4.

Hyperbranched Poly(phenylene sulfone). Oxidation of the hyperbranched poly(phenylene sulfide) to hyperbranched poly(phenylene sulfone) was readily accomplished with hydrogen peroxide in acetic acid (Scheme 3).[13] The resulting sulfone polymers proved to be insoluble in all common solvents including THF, DMF, DMSO, and NMP; they were characterized by thermal analysis and elemental analysis. Elemental analysis suggests that the oxidation to the sulfone is effectively quantitative (Table 5). It is difficult to determine O directly, but determination of C, H, S, and Cl accounted for 81.06% of the mass, leaving 18.94% unaccounted for and assigned to O. The expected percentage of O for a hyperbranched poly(phenylene sulfone) is 18.26%,whereas incomplete oxidation to the sulfoxide polymer would give 10.09% O. The results of elemental analysis are therefore consistent with complete oxidation to the polymeric sulfone.

Table 5. Elemental Analysis of Hyperbranched Poly(phenylene sulfones)

	C (%)	H (%)	Cl (%)	S (%)	O (%)
calculated	41.14	1.74	20.55	18.31	18.26
found[a]	41.05	2.03	20.31	17.67	18.94[b]

[a] Average of all samples. [b] Determined by difference.

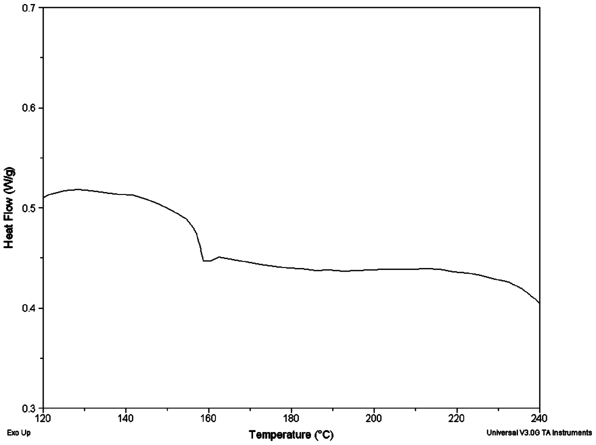


Figure 4. DSC of hyperbranched poly(phenylene sulfone) showing T_g of 157 °C (scan rate 10 °C/min).

DSC analysis of the sulfone polymers revealed a T_g of ~155 °C, with no detectable T_m. Linear aromatic polysulfones (typically sulfone–ether or sulfone–sulfide polymers) have T_g values above 200 °C.[5,14] TGA analysis revealed that the decomposition of the sulfone polymers begins at a lower temperature and is less abrupt than decomposition of the sulfide polymers. DSC and TGA curves of representative hyperbranched poly(phenylene sulfone) polymers are shown in Figures 4 and 5, and the TGA data are summarized in Table 6.

Discussion

Hyperbranched poly(phenylene sulfide) has been prepared using simple nucleophilic aromatic substitution reactions similar to those used to prepare commercial linear PPS, with 3,4-dichlorobenzenethiol as the branching AB_2 monomer. Nucleophilic aromatic substitution by thiolate anions is a well-studied reaction; these reactions generally require relatively high temperatures (100–150 °C) and proceed most readily in amide solvents such as DMF and NMP.[8] These conditions were effective at forming hyperbranched PPS, with the best results (high MW, low polydispersity) at 150 °C for approximately 8 h in NMP. If no core-forming molecules are added, and if the polymerization reaction is not stopped, polymerization proceeds until the hyperbranched

---

(11) (a) *Light Scattering: Principles and Development;* Brown, W., Ed.; Clarendon Press: Oxford, 1996. (b) Yusa, S.; Kamachi, M. Morishima, Y. *Macromolecules* **2000**, *33*, 1224–1231. (c) Bryant, G.; Thomas, J. C. *Langmuir* **1995**, *11*, 2480–2485. (d) *Polymer Characterization*; Schroder, E.; Muller, G.; Arndt, K.-F.; Hanser Publishers: Munich, 1988. (e) Ramanathan, M.; McDonnell, M. E. *Macromolecules* **1984**, *17*, 2093–2095.

(12) (a) Kee, R. A.; Gauthier, M. *Macromolecules* **2002**, *35*, 6526–6532. (b) Trollsas, M.; Atthof, B.; Wursch, A.; Hedrick, J. L.; Pople, J. A.; Gast, A. P. *Macromolecules* **2000**, *33*, 6423–6438. (c) Vlassopoulos, D.; Fytas, G.; Loppinet, B.; Isel, F.; Lutz, P. Benoit, H. *Macromolecules* **2000**, *33*, 5960–5969. (d) Schappacher, M.; Deffieux, A.; Putaux, J.-L.; Viville, P.; Lazzaroni, R. *Macromolecules* **2003**, *36*, 5776–5783.

(13) (a) Oae, S. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977. (b) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations I*; Academic Press: New York, 1983.

(14) (a) *Polymer Handbook, 4th ed.*; Brandrup, J., Immergut, E. H., Grulke, E. A., Bloch, D., Eds.; John Wiley & Sons: New York, 1999. (b) Liu, Y.; Bhatnagar, A.; Ji, Q.; Riffle, J. S.; McGrath, J. E.; Geibel, J. F.; Kashiwagi, T. *Polymer* **2000**, *41*, 5137–5146.

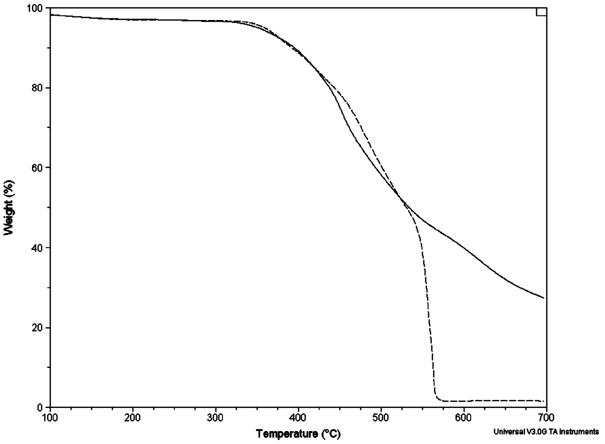


Figure 5. Thermogravimetric analysis of hyperbranched poly(phenylene sulfone) under N_2 atmosphere (solid line) and under air atmosphere (dashed line) (scan rate 10 °C/min).

Table 6. TGA Data for Hyperbranched Poly(phenylene Sulfones)

sample (atmosphere)	T_d (°C)	T_{max} (°C)	residue
DMF no core (N_2)	350 ± 5	463 ± 1	31 ± 1%
DMF 50:1 (N_2)	345 ± 5	470 ± 1	29 ± 1%
NMP no core (N_2)	375 ± 5	453 ± 1	28 ± 1%
NMP 50:1 (N_2)	370 ± 5	455 ± 1	29 ± 1%
DMF no core (air)	325 ± 5	544 ± 1	8 ± 1%
DMF 50:1 (air)	350 ± 5	557 ± 1	2 ± 1%
NMP no core (air)	365 ± 5	561 ± 1	2 ± 1%
NMP 50:1 (air)	360 ± 5	556 ± 1	1 ± 1%

polymers are insoluble. If polymerization is stopped before precipitation occurs, hyperbranched PPS with M_w of ~17 kD and M_w/M_n less than 2 can be readily isolated. As expected for hyperbranched polymers, addition of a core-forming B_3 molecule (1,3,5-trichlorobenzene) results in lower M_w and lower M_w/M_n values.[9] These hyperbranched PPS materials have significantly increased solubility compared to linear PPS. The molecular weights of the polymers were measured by SEC-LS and the proposed structure was supported by elemental analysis, NMR, and IR.

Thermal analysis revealed that the hyperbranched PPS samples were entirely amorphous with no crystallinity. This lack of crystallinity is further evidence for the highly branched nature of these materials, since hyperbranching reduces crystallinity in most polymeric materials.[1−3] The polymers maintain the excellent thermal stability known for linear PPS. The measured glass transitions for these hyperbranched PPS polymers (60−90 °C) are similar to those of linear PPS,[10] but significantly lower than those observed by Jikei.[6a] Many hyperbranched polymers have increased T_g relative to linear analogues.[1−3] The observation that our hyperbranched PPS materials have lower T_g values similar to linear PPS may be a result of the large number of terminal chlorines changing the nature of the intermolecular interactions, or a result of the nonsymmetrical branching. It is known that the nature of the terminal groups has a major impact on the thermal properties of dendritic and hyperbranched polymers, and chlorination of aromatics can depress the T_g: for example, poly(3-chlorostyrene) has a lower T_g (90 °C) than polystyrene (100 °C).[14a,15] Since our hyperbranched PPS has both nonsymmetrical branching and a nonsymmetrical arrangement of the chlorines on the terminal groups, these might have a tendency to reduce T_g. The polymers prepared in DMF had higher T_g values than the polymers prepared in NMP. The SEC-LS results show that the distribution of molecular weights in the DMF polymers is less regular, and this may be the source of the observed difference in T_g.

TGA analysis of the hyperbranched PPS revealed that these polymers were very thermally stable, although not as stable as linear PPS. The hyperbranched PPS samples showed T_d between 400 and 450 °C, compared to 480 °C for linear PPS. The reduced thermal stability may be a result of the hyperbranched structure—since hyperbranched structures with large numbers of chain ends would be expected to evolve volatiles at a lower temperature. Alternatively, the reduced thermal stability may be an effect of the chlorination of the terminal and linear groups in the polymer, which could alter the thermal chemistry and lead to more rapid chain cleavage.

DLS analysis revealed that the hyperbranched PPS samples generally gave diffusion coefficients corresponding to relatively small radii for the corresponding molecular weight, implying that these polymers are quite compact in solution. This is consistent with a hyperbranched structure.[12] The polymers with the core had a greater discrepancy between the absolute M_w values from static light scattering in the SEC-LS measurements and the apparent molecular weights calculated from the hydrodynamic radii from DLS.

Oxidation of the hyperbranched PPS materials generated hyperbranched poly(phenylene sulfone). Elemental analysis suggested that simple peroxide oxidation resulted in effectively complete oxidation of sulfide to sulfone in the materials. These sulfone polymers displayed complete insolubility and somewhat reduced thermal stability as compared to the hyperbranched PPS polymers. The hyperbranched $PPSO_2$ had a T_g of ~155 °C, higher than the observed T_g for the hyperbranched PPS. The one report on linear $PPSO_2$ describes a highly crystalline material (no T_g was observed) that is quite thermally stable; some of this stability may be a result of the exceptionally high $T_m > 500$ °C.[5c] The hyperbranched $PPSO_2$ had a somewhat lower T_g compared to the common linear sulfone−ether polymers (typical $T_g > 200$ °C).

Conclusions

Hyperbranched poly(phenylene sulfide) can be readily prepared from 3,4-dichlorobenzenethiol. The resulting polymers have a reasonably high MW (~17 kD), and show the excellent thermal stability of linear PPS, but are essentially noncrystalline and significantly more soluble. Addition of a trivalent core reduced the M_w and polydispersity, but the resulting polymers had thermal properties similar to those of the polymers with no core. Oxidation of hyperbranched PPS provides insoluble hyperbranched poly(phenylene sulfone). This simple polymerization methodology opens the door to many other investigations of hyperbranched PPS,

---

(15) (a) De Girolamo Del Mauro, A.; Loffredo, F.; Venditto, V.; Longo, P. Guerra, G. *Macromolecules* **2003**, *36*, 7577−7584. (b) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J. *Macromolecules* **1993**, *26*, 1514−1519.

and there are many questions remaining to be answered about these materials, including the effect of the terminal chlorines, the effect of the asymmetric branching, and the use of these hyperbranched materials in blends with linear PPS.

Experimental Section

General. Except as noted, all materials were purchased from commercial suppliers and used without further purification. Linear poly(phenylene sulfide) resin was purchased from Monomer-Polymer and Dajac Laboratories, Feasterville, PA. Potassium carbonate was dried 24 h in an oven at 200 °C before use. Reactions were run in three-necked round-bottom flasks with condenser, efficient magnetic stirrer, and N_2 line. All reaction vessels were dried with a heat gun under vacuum and then flushed with N_2 for 15 min. Reaction temperatures were maintained by a Thermo-watch LS1000. Air and moisture were excluded from the reaction vessels by a positive pressure of dry N_2. Infrared spectra were obtained on a MIDAC Prospect-IR at 4 cm^{-1} resolution. Nuclear magnetic resonance spectra were obtained on a Varian INOVA 500 MHz NMR. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Calculated elemental analyses were based on the degree of polymerization of the given polymer sample.

Size-Exclusion Chromatography. The SEC LS/RI system was composed of a Waters 510 Pump with an inline degasser, a Rheodyne injector, and two detectors: a Waters 410 differential refractometer and a Precision Detectors 2000 light scattering unit with 15° and 90° detectors. The stationary phase was a cross-linked polystyrene column from Polymer Laboratories (5-μm particle size, 500-Å pore size) with a guard column. Chromatograms were run using inhibitor-free THF at a flow rate of 1.0 mL/min and an injection volume of 50 μL with a sample concentration of 2.0 mg/mL. Column temperature was maintained at 30 °C for all sample runs. Before injection, all samples were filtered using a 0.45-μm filter into pre-rinsed vials using inhibitor-free THF.

Quasi-Elastic Light Scattering. QELS data were obtained on a Wyatt Technology Dawn EOS equipped with a Wyatt QELS and analyzed using Wyatt QELS software. Inhibitor-free THF was used to dissolve the polymer samples for QELS studies. The polymer solutions were filtered directly into a pre-rinsed scintillation vial using a 0.45-μm filter and inhibitor-free THF. Data were acquired at 30 °C. The first 3 data points were ignored and data were truncated after channel 99 for all runs. Diffusion coefficients were obtained by regularization analysis based on intensity. Hydrodynamic radii (R_h) were calculated using the Stokes−Einstein relation and the viscosity of THF. Molecular weights were calculated from R_h using a model for spherical particles:

$$\mathrm{MW} = (1.549R_h)^{2.426}$$

Differential Scanning Calorimetry. DSC data were obtained on a TA Instruments 2920 calorimeter with a high-resolution sample chamber. Samples were placed in hermetically sealed aluminum pans and weighed on a microbalance. Best results were obtained by annealing the samples at 200 or 300 °C for 60 min prior to analysis. Analysis was performed by raising the temperature from 0 to 375 °C at a rate of 10 °C/min. Glass transition temperatures (T_g) were identified from midpoints using TA Universal Analysis software.

Thermogravimetric Analysis. TGA data were obtained on a TA Instruments HiRes TGA 2950 thermogravimetric analyzer. Samples were placed in platinum pans and heated from 30 to 700 °C at a rate of 10 °C/min. Onset temperatures (T_d) and maximum decomposition temperatures (T_{max}) were identified using TA Universal Analysis software.

Polymerizations. *General Procedure: Polymers with No Core.* 3,4-Dichlorobenzenethiol (10 g; 56 mmol) was added to 13.4 g of K_2CO_3 (96 mmol) in 80 mL of the appropriate solvent (DMF or NMP), and the reaction was heated to the desired temperature (100 °C for DMF, 150 °C for NMP) and maintained for the required time (24 h in DMF, 8.5 h in NMP). The reactions were then cooled and diluted with an equal volume of water and carefully poured into 300 mL of 6 M HCl. The resulting precipitate was vigorously stirred for 1 h and then filtered. The precipitate was dried thoroughly under vacuum and then dissolved with vigorous stirring in a minimal amount of THF. The THF solution was added dropwise to hexanes (at least 5 times the volume of the THF solution) with vigorous stirring over a period of 2 h. This precipitate was then filtered, washed with hexanes, and dried thoroughly under vacuum. The precipitated polymers obtained from DMF were finely divided white powders. The precipitated polymers obtained from NMP were pale tan powders. The final quantity of sample obtained after work up was between 7.0 and 7.5 g (87−93%). IR (KBr): 3080, 3040, 2580, 1580, 1560, 1450, 1350, 1160, 1040, 850, 800 cm^{-1}. ^{1}H NMR (THF-d_8): 7.10, 7.24, 7.34, 7.38, 7.42, 7.55, 7.62 (all broad). Elemental analysis. DMF: Calcd (DP = 59) C 50.31, H 2.12, Cl 25.17, S 22.39; found C 50.46, H 2.36, Cl 26.78, S 20.4. NMP: Calcd (DP = 73) C 50.36, H 2.12, Cl 25.11, S 22.41; found C 49.93; H 2.93; Cl 27.14; S 20.0.

Polymers with Core. 3,4-Dichlorobenzenethiol (5 g; 30 mmol) was added to 0.10 g of 1,3,5-trichlorobenzene (0.55 mmol, 50:1 monomer/core ratio) and 6.7 g of K_2CO_3 (48 mmol) in 40 mL of the appropriate solvent (DMF or NMP). The reactions were heated to the desired temperature (100 °C for DMF, 150 °C for NMP) for the optimum time (24 h in DMF, 8.5 h in NMP). The workup was the same as the general polymerization protocol above. The polymer products had the same appearance with a core as without a core (vide supra). The final quantity of polymer sample obtained was on average 3.7 g (93%) for these reactions. IR (KBr): 3080, 3040, 1580, 1560, 1450, 1350, 1160, 1040, 850, 800 cm^{-1}. ^{1}H NMR (THF-d_8): 7.10, 7.24, 7.34, 7.38, 7.42, 7.55, 7.62 (all broad). Elemental analysis. DMF: Calcd (DP = 49) C 50.3, H 2.11, Cl 25.2, S 22.4; found C 51.34, H 2.64, Cl 24.95, S 20.1. NMP: Calcd (DP = 71) C 50.4, H 2.12, Cl 25.1, S 22.4; found C 51.52, H 2.66, Cl 23.95, S 20.1.

Oxidation.[13] Approximately 200 mg of hyperbranched poly(phenylene sulfide) was added to 12 mL of 30% H_2O_2 and 20 mL of glacial acetic acid. The resulting suspension was refluxed for 4 h, cooled, and precipitated slowly by pouring into a well-stirred solution of saturated sodium bicarbonate. The resulting precipitate was then filtered, washed thoroughly with water to remove residual sodium bicarbonate, and dried. The hyperbranched poly(phenylene sulfone) polymer products obtained were finely divided white powders. The quantity obtained after reaction was approximately 150 mg in all cases (~60%). IR (KBr): 3080, 1590, 1490, 1360, 1290, 1200, 1150, 800 cm^{-1}. Elemental analysis. DMF (no core, DP = 59): Calcd C 41.13, H 1.74, Cl 20.58, S 18.30, O 18.26; found C 41.32, H 2.02, Cl 20.64, S 17.86 (residue = O = 18.16). NMP (no core, DP = 73): Calcd C 41.15, H 1.73, Cl 20.52, S 18.31, O 18.27; found C 40.79, H 2.05, Cl 19.98, S 17.47 (residue = O = 19.71).

Acknowledgment. J.E.H. thanks the Seton Hall University University Research Council for financial support.

CM048376P