

Chemical Modification of Polysulfones II: An Efficient Method for Introducing Primary Amine Groups onto the Aromatic Chain[†]

Michael D. Guiver,* Gilles P. Robertson, and Stephen Foley

Institute for Environmental Research and Technology, National Research Council, Ottawa, Ontario, K1A 0R6, Canada

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ABSTRACT: Three modification approaches to aminated polysulfones were investigated: replacement of aromatic bromine with nucleophilic NH_2 ; amination by electrophilic NH_2 ; and amination of lithiated polysulfones via azides and other electrophilic NH_2 synthons. The former two approaches resulted in low levels of amination, or in polymer degradation. For the latter approach using lithiated polysulfones, we report an efficient alternative to the nitration-reduction methodology for introducing amine groups onto polysulfones and poly(aryl sulfones). Polysulfones activated either on the ortho sulfone sites or on the ortho ether sites by direct lithiation or bromination-lithiation, were converted to azides by treatment with tosyl azide, and then reduced to amine derivatives with sodium borohydride. This could be accomplished either by a two-step procedure whereby the azide was isolated, or by a "one-pot" modification. Near-quantitative conversions and high levels of functionalization were achieved for the overall process. Polymers having an amine degree of substitution (DS) of 1.0, 2.0, and 2.75 are reported. Structures were confirmed by NMR and IR spectroscopy. GPC, TGA, and T_g data are also reported. A nonquantitative reaction of diphenylphosphoryl azide as well as 4-acetamidobenzenesulfonyl azide with lithiated polysulfones also gave aminated derivatives.

Introduction

Amine groups are useful as attachment sites along polymer chains or at chain ends because they are reactive and readily form covalent bonds with many types of groups. Amination of aromatic polymer chains is frequently achieved by a process of nitration followed by reduction. Until the present time, aminated polysulfones have been prepared only by this procedure, or by polymerization of amine-containing monomers. However, chain degradation may occur during nitration and moreover, aromatic nitro groups can be unusually difficult to reduce.

The introduction of amine and other functional groups onto aromatic polysulfones has been a topic of research in our laboratories¹ and in those of others. There is recent interest in aminated aromatic polysulfones and poly(ether sulfones) for use as components to toughen brittle epoxy networks and thermosetting resins. There is also potential utility as high-performance composites whereby the amine groups or their derivatives are used to achieve cross-linking or chain extension. In addition, polysulfones are among the most versatile and widely used membrane materials, and functionalized membranes have the potential to open up new avenues, for example in reactive or affinity membranes.

Daly et al.² reported the amination of commercial polysulfone by nitration using an ammonium nitrate/trifluoroacetic anhydride mixture to avoid extensive degradation by more aggressive reagents. However, even under mild nitration conditions some degradation was observed. Although the nitrated polymer was resistant to reduction by several standard methods, aminated products were obtained using stannous chloride and acid. Naik et al.³ and Conningham et al.⁴ reported the nitration-reduction procedure for aminating poly(ether ether sulfones) and poly(ether sulfones).

Pak et al.⁵ and Bottino et al.⁶ reported the preparation of aminated aromatic polysulfone copolymers from nitro and amine-containing monomers respectively. Aminomethylated polysulfones have also been reported by Daly et al.² and by Kahana et al.⁷

We report here a new and efficient alternative methodology for introducing amine groups onto commercially available Udel P3500 polysulfone and Radel R5000 poly(aryl sulfone). The process provides aminated polysulfones having a high degree of functionality as well as site specificity to either the sulfone aromatic ring or the bisphenol ring, depending on the path chosen. Since aromatic polysulfones are widely used as membrane materials in liquid and gas separations, an objective of our work is to tailor membrane separation characteristics and increase the scope of their use by introducing functional groups by chemical modification.⁸

Three synthetic approaches to aminated polysulfones were investigated, which can be categorized broadly as follows: (1) replacement of bromine on dibrominated polysulfone with nucleophilic NH_2 synthons; (2) direct amination of aromatic rings by electrophilic NH_2 synthons; and (3) amination of lithiated polymers via azides and other electrophilic NH_2 synthons.

Experimental Section

Materials. Polymeric starting materials Udel P3500 (**1A**) and Radel R5000 (**1B**) were obtained from Amoco Performance Products, Inc. Dibrominated polysulfone⁹ **5**, poly(sulfone azides)¹ and poly(aryl sulfone azides)¹ were prepared by previously reported procedures. All reagent grade chemicals were obtained from Aldrich Chemical Co. and were used as received, except THF which was distilled from LiAlH_4 .

Nuclear Magnetic Resonance (NMR) Spectroscopy. Proton and carbon spectra were obtained on a Bruker AM-400 spectrometer operating at a proton frequency of 400.13 MHz and a carbon frequency of 100.61 MHz. Spectra were acquired at room temperature using deuterated dimethyl sulfoxide (DMSO) or chloroform solvent and referenced to an internal tetramethylsilane (TMS) standard. Proton and carbon spectra were collected with a spectral width of 4000 and

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Table 1. Amination with Sodium Amide

NaNH ₂	T, °C	t, h	DS
8 equiv NaNH ₂ /15 mL of NH ₃	-78	2	0.33
10 equiv NaNH ₂ /12 mL of NH ₃	-78 to -33	2	0.31
12 equiv NaNH ₂ /15 mL of NH ₃	-33	6	XL ^a
10 equiv NaNH ₂ /no NH ₃	+40	3	0

^a XL denotes that the sample was insoluble and cross-linked.

20 000 Hz respectively, and a 16K data table. Proton-carbon one-bond and three-bond connectivities were obtained from two-dimensional spectra by HETCOR and LRHETCOR experiments respectively under similar operating conditions to those reported before.¹ Chemical shifts are expressed in parts per million (ppm) and the spectral resonances are designated broadened (b), singlet (s), doublet (d), and multiplet (m). Coupling constants (*J*) are in Hertz. Unmodified, monosubstituted and disubstituted repeat units are designated U, M, and D respectively.

Polymer Analyses and Measurements. Infrared (IR) spectra were measured on a Nicolet 520 FTIR spectrophotometer. Polymer samples were mounted by evaporating a THF solution on a NaCl window. Gel permeation chromatography (GPC) measurements were made on THF polymer solutions using a Waters 510 pump, Waters 996 UV detector, and a selection of μ -Styragel columns. Thermal decomposition of polymers were evaluated by thermogravimetric analysis (TGA) using a DuPont 951 thermogravimetric analyzer and were measured in an atmosphere of nitrogen flowing at 50 mL/min. Samples were kept at room temperature for 20 min, maintained at 40 °C for 30 min to degas or remove any volatile species, and then heated at a rate of 10 °C per minute. Glass transition (*T_g*) temperatures were measured using a DuPont 910 differential scanning calorimeter (DSC) calibrated from indium (156.6 °C) and tin (231.9 °C). Samples were heated from room temperature to 250 °C at 10 °C/min in an atmosphere of nitrogen flowing at 50 mL/min and then quenched in liquid nitrogen. For the second run, in which the *T_g* was measured, the sample was heated to 350 °C.

Partial Amination of Brominated Polysulfone with Sodium Amide/Ammonia. A solution of dibrominated polysulfone⁹ **5** (4.42 g, 7.4 mmol) in THF (40 mL) was added at a rate of 1 mL/min to a stirred solution of NaNH₂ (8 equiv, 2.30 g, 59.0 mmol) in liquid ammonia (15 mL) and THF (40 mL) at -78 °C and under argon. At the start of the addition, a green solution formed which changed to brown after 30 min. The solution was stirred at -78 °C for 2 h and then quickly precipitated into ethanol. The polymer was washed with ethanol and water and then dried. A polymer containing amine groups with a degree of substitution (DS) = 0.33 was obtained. ¹H-NMR starting material **5** (CDCl₃): δ 7.87 (d, *J* \approx 8.8, 4H, H_d), 7.52 (d, *J* \approx 2.0, 2H, H_e), 7.16 (dd, *J* \approx 8.3, *J* \approx 2.0, 2H, H_b), 6.97 (d, *J* \approx 8.3, 2H, H_a), 6.96 (d, *J* \approx 8.8, 4H, H_c), 1.69 (s, 6H, C(CH₃)₂). ¹H-NMR product (CDCl₃): δ 7.68 (d, 4H, H_d), 7.57 (small d, H_e) 7.24 (dd, H_b) 7.04 (d, H_a) 7.10 (dd, H_c) 3.31 (s, NH₂). The spectra were complicated by signals of unreacted starting polymer. IR: ν -N-H 3475 cm⁻¹, asymmetric stretch, weak, ν -N-H 3390 cm⁻¹, symmetric stretch weak.

A summary of experiments in Table 1 showed that DS did not increase when the temperature was raised to -33 °C (the bp of NH₃) and also produced insoluble cross-linked polymer.

Attempted Amination of Brominated Polysulfone with Sodium Amide/Ethylenediamine. A solution of dibrominated polysulfone⁹ **5** (2.21 g, 3.7 mmol) in THF (20 mL) was added at a rate of 1.7 mL/min to a stirred solution of NaNH₂ (4 equiv, 0.58 g, 15.0 mmol) and CuCl (10 mg) in ethylenediamine (5 mL) and THF (15 mL) at 0 °C and under argon. A jade green mixture formed which was stirred for a total of 45 min. Stirring was continued for 30 min at room temperature, and then the polymer was recovered and washed as before. ¹H-NMR showed that no reaction had occurred. The experiment was repeated, but for 2 h at room temperature, and gave no product. A similar experiment, but at reflux temperature and using 10 equiv of NaNH₂, also gave a negative result.

Table 2. Attempted Amination with Hydroxylamine-O-sulfonic Acid (HOSA)

solvent	reagent	T, °C	t, h
DMF	4 equiv of HOSA/2 equiv of FeSO ₄	100	8
DMF	1 equiv of HOSA/1 equiv of FeSO ₄	25	1
chlorobenzene	6 equiv of HOSA/3 equiv of AlCl ₃	100	4
nitrobenzene	5 equiv of HOSA/3 equiv of AlCl ₃	125	4

Table 3. Degradative Amination with TMS Azide/Triflic Acid

solvent	reagent	temp, °C	t	amination
CHCl ₃	6 equiv of triflic acid/ 2 equiv of TMS azide	reflux	6 h	yes
CH ₂ Cl ₂	5 equiv of triflic acid/ 2 equiv of TMS azide	25	2 h	no
CH ₂ Cl ₂	6 equiv of triflic acid/ 7 equiv of TMS azide	25	3 days	yes
CHCl ₃	4 equiv of triflic acid/ 4 equiv of TMS azide	50	6 h	yes
CH ₂ Cl ₂	2 equiv of triflic acid/ 4 equiv of TMS azide	reflux	6 h	no

Attempted Phthalimide of Brominated Polysulfone. Potassium phthalimide (3.0 g, 16.0 mmol) was added to a solution of dibrominated polysulfone⁹ **5** (2.21 g, 3.7 mmol) in DMF (30 mL) and the mixture was stirred at 125 °C under argon for 8 h. The recovered polymer was unreacted. In a similar experiment, CuBr (1.06 g, 7.3 mmol) was added, but no phthalimide occurred.

Attempted Amination of Polysulfone with Hydroxylamine-O-sulfonic Acid (HOSA). To a solution of HOSA (2.30 g, 20.0 mmol) and iron(II) sulfate heptahydrate (2.78 g, 10 mmol) in 25 mL of DMF at 0 °C and under argon was added a solution of polysulfone **1A** (2.21 g, 5.0 mmol) in DMF (25 mL). The mixture was heated at 100 °C for 8 h. The polymer product was recovered by precipitation in ethanol, washed several times with hot water, and dried. No aminated polymer was evident from this reaction or from other reactions summarized in Table 2.

Amination of Polysulfone with Trifluoromethanesulfonic Acid (Triflic Acid) and Trimethylsilyl azide (TMS Azide). In a typical procedure, triflic acid (6 equiv, 4.5 g, 30 mmol) was added to a solution of polysulfone **1A** (2.21 g, 5.0 mmol) in chloroform (20 mL) at 25 °C. The reddish brown solution became noticeably less viscous. TMS azide (2 equiv, 1.15 g, 10.0 mmol) was added slowly, and the mixture went through several color changes, ultimately becoming green, and then blue. In most experiments, gas evolution was observed during the addition of TMS azide. After 1 h at 25 °C, the solution was heated at 60 °C for an additional hour. The solution was then refluxed for 6 h and precipitated in ethanol. A small amount of polymer (0.2 g) was recovered after precipitating the reaction mixture from ethanol and washing the product with ethanol and then water. The product was aminated and had an apparent DS of 0.88 by comparative integration of amine vs isopropylidene. However, this was not the actual DS because GPC measurements showed that severe polymer degradation had occurred. ¹H-NMR spectrum (CDCl₃) was complicated by extensive degradation: δ 3.05 (bs, NH₂). IR: very weak absorption bands at ν -N-H 3470 cm⁻¹, asymmetric stretch, ν -N-H 3375 cm⁻¹, symmetric stretch, indicating low DS. A summary of experiments performed is shown in Table 3.

Attempted Amination of Lithiated Polysulfone with Methoxyamine. A THF solution of polysulfone **1A** (2.21 g, 5.0 mmol) lithiated to approximately DS of 2.0 was prepared at -78 °C.¹ To this was added a solution of methoxyamine (0.94 g, 20.0 mmol) in THF (1.0 mL) at -78 °C. Within a few minutes the color changed from brown to pale green and then later became clear. The mixture was stirred at -78 °C for 1.5 h and then gradually warmed to -10 °C and stirred at that temperature for 2 h. The polymer was recovered by precipitation from ethanol, washed and then dried (2.00 g). A ¹H-NMR spectrum in CDCl₃ showed unchanged starting material, resulting from deprotonation of methoxyamine by the lithiated polymer.

Partial Amination of Lithiated Polysulfone with Lithium Methoxylamide. In a typical procedure, a THF solution of polysulfone **1A** (2.21 g, 5.0 mmol) lithiated to approximately DS of 1.2 with 1.2 equiv of *n*-butyllithium was prepared at -78°C . To this was added a solution of lithium methoxylamide (40 mmol) at -78°C , previously prepared by adding methoxyamine (1.88 g, 40 mmol) slowly to methyl-lithium (34.2 mL of 1.4 M solution in diethyl ether, 48 mmol) at -78°C . The polymer precipitated immediately, but within 1 min changed to a creamy yellow solution. The mixture was stirred at -78°C for 2.5 h, then gradually warmed to -20°C , and stirred at that temperature for 1 h. The polymer was recovered by precipitation from ethanol, washed, and then dried (1.20 g). The product formed a gel in DMSO and was almost completely soluble in chloroform. A $^1\text{H-NMR}$ spectrum in CDCl_3 showed the presence of a small amount of ortho sulfone amine substituted polysulfone (DS ≈ 0.20). IR: very weak absorption bands at ν N-H 3473 cm^{-1} , asymmetric stretch, ν N-H 3375 cm^{-1} , symmetric stretch

Amination by Hydrolysis of Triazene Formed from Reaction of Lithiated Polysulfone with Diphenylphosphoryl Azide. A diphenylphosphoryl triazene (DS 0.67) substituted polysulfone (2 g), prepared previously¹ by the reaction of lithiated polymer with diphenylphosphoryl azide was hydrolyzed by stirring with 3 M NaOH at 80°C for 16 h. The aminated polymer was recovered and washed with mildly acidic water and then distilled water. The $^1\text{H-NMR}$ spectrum in $\text{DMSO-}d_6$ was closely similar to that of poly(sulfone (ortho sulfone) amine) (DS = 1.0) described forthwith, except that a trace of unhydrolyzed triazene was present.

Preparation of Poly(sulfone (ortho sulfone) amine) (DS = 2.0). **3A.** Sodium borohydride powder (18.9 g, 0.50 mol) was added quickly to a yellow solution of poly(sulfone (ortho sulfone) azide)¹ **2A** (DS = 2.0, 52.4 g, 100 mmol) in THF (950 mL) and absolute ethanol (95 mL) cooled at -60°C in a flask equipped with argon inlet and a magnetic stirrer. The cooling bath was allowed to warm up to room temperature slowly, during which time gas evolution was observed. The reaction mixture was stirred for 24 h at room temperature. Approximately half of the solvent volume was removed by distillation under reduced pressure using a warm water bath ($\sim 40^{\circ}\text{C}$) and rotary evaporator. The concentrated reaction mixture was precipitated from 3 L of ethanol-water (1:1 ratio) in a Waring blender. The polymer was filtered and washed 3 times by stirring in hot water for 2 h. The polymer was filtered, then dried in a vacuum oven at 40°C to give 44.8 g of product (95% yield). The white product **3A** contained close to two amine groups ortho to sulfone per polysulfone repeat unit. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.72 (d, $J \approx 8.8$, 2H, H_a), 7.27 (d, $J \approx 8.7$, 4H, H_b), 7.00 (d, $J \approx 8.7$, 4H, H_a), 6.26 (d, $J \approx 2.2$, 2H, H_c), 6.21 (dd, $J \approx 8.8$, $J \approx 2.2$, 2H, H_c), 6.09 (s, 4H, NH_2), 1.64 (s, 6H, $\text{CH}_3\text{-C-CH}_3$). $^{13}\text{C-NMR}$: δ 162.40 (C_7), 152.48 (C_{11}), 148.52 (C_{11}), 146.41 (C_4), 131.63 (C_9), 128.21 (C_3), 119.79 (C_2), 115.14 (C_{10}), 105.09 (C_8), 103.32 (C_{12}), 41.85 ($\text{CH}_3\text{-C-CH}_3$), 30.59 ($\text{CH}_3\text{-C-CH}_3$). IR: ν N-H 3474 cm^{-1} , asymmetric stretch, ν N-H 3377 cm^{-1} , symmetric stretch, ν N-H 1620 cm^{-1} , N-H bend, strong. Anal. Calcd. for $\text{PSf}(\text{NH}_2)_{\text{DS}=2.0}$ ($\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$): C, 68.63; H, 5.12; N, 5.93; O, 13.54; S, 6.78. Found C, 69.24; H, 5.11; N, 5.91; S, 6.60.

Preparation of Poly(sulfone (ortho sulfone) amine) (DS = 1.0). **4.** The previous procedure was repeated, but using sodium borohydride (11.3 g, 0.30 mol) and poly(sulfone (ortho sulfone) azide)¹ (DS = 1.0, 48.2 g, 100 mmol) in THF (800 mL) and absolute ethanol (80 mL). The recovered polymer **4** (43.4 g 95% yield) had a DS = 1.0. $^1\text{H-NMR}$ ($\text{DMSO-}d_6\text{-CDCl}_3$ 10:1, multiplet signals appear as broadened singlets): δ 7.84 (m, H_a (M) and H_a (U)), 7.68 (d, H_d (D)), 7.62 (d, H_d (M)), 7.23 (m, H_b (U,M,D)), 6.96 (m, H_a (U,M,D)), 6.27 (bs, H_e (M,D)), 6.21 (bs, H-c (M,D) and NH_2 (M)), 6.07 (bs, NH_2 (D)). Anal. calcd for $\text{PSf}(\text{NH}_2)_{\text{DS}=1.0}$ ($\text{C}_{27}\text{H}_{23}\text{NO}_4\text{S}$): C, 70.88; H, 5.07; N, 3.06; O, 13.99; S, 7.01. Found C, 70.98; H, 5.14; N, 2.66; S, 6.45.

Preparation of Poly(arylsulfone (ortho sulfone) amine) (DS = 2.0). **3B.** A solution of Radel R5000 poly(aryl sulfone diazide)¹ **2B** (0.75 g, 1.5 mmol) in NMP (7.5 mL) was slowly added by syringe into a one-neck round-bottom flask containing a cooled (-15°C) suspension of sodium borohydride (0.58

g, 15 mmol) in NMP. The mixture initially turned green, then gray, and then later darker red. It was stirred for 24 h after completion of addition. The polymer was recovered from the clear red solution by precipitation into ethanol 95% and further washed 3 times by stirring for a few hours in ethanol-water solutions and recovered to give 0.58 g of product (90% yield). The white polymer **3B** contained an average of 2.0 amine groups per polysulfone repeat unit. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.76 (d, $J \approx 8.4$, 2H, H_d), 7.72 (d, $J \approx 8.4$, 4H, H_b), 7.18 (d, $J \approx 8.4$, 4H, H_a), 6.35–6.26 (m, 4H, H_c and H_e), 6.11 (s, 4H, NH_2). $^{13}\text{C-NMR}$: δ 162.20 (C_7), 154.09 (C_{11}), 148.47 (C_{11}), 135.72 (C_4), 131.59 (C_9), 128.21 (C_3), 120.73 (C_2), 115.18 (C_{10}), 105.14 (C_8), 103.36 (C_{12}). IR: ν N-H 3469 cm^{-1} , asymmetric stretch, ν N-H 3375 cm^{-1} , symmetric stretch, ν N-H 1620 cm^{-1} , N-H bend, strong.

Preparation of Poly(sulfone (ortho ether) amine) (DS = 2.0). **7.** Sodium borohydride powder (18.9 g, 0.50 mol) was added quickly to a yellow solution of poly(sulfone (ortho ether) azide)¹ **6** (DS = 2.0, 52.4 g, 100 mmol) in THF (900 mL) and absolute ethanol (90 mL) cooled at -60°C . The polymer was recovered following the procedure for **3A** to give 44.8 g of product (95% yield). The white product **7** contained almost two amine groups ortho to ether per polysulfone repeat unit. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.86 (d, $J \approx 8.4$, 4H, H_a), 6.99 (d, $J \approx 8.4$, 4H, H_c), 6.78 (d, 2H, H_a), 6.72 (bs, 2H, H_c), 6.47 (bd, 2H, H_b), 4.92 (s, 4H, NH_2), 1.56 (s, 6H, $\text{CH}_3\text{-C-CH}_3$). $^{13}\text{C-NMR}$: δ 161.75 (C_7), 148.40 (C_4), 139.98 (C_6), 137.55 (C_1), 134.48 (C_{10}), 129.48 (C_9), 120.80 (C_2), 116.51 (C_3), 114.82 (C_3), 114.67 (C_5), 41.85 ($\text{CH}_3\text{-C-CH}_3$), 30.67 ($\text{CH}_3\text{-C-CH}_3$). IR: ν N-H 3470 cm^{-1} , asymmetric stretch, ν N-H 3375 cm^{-1} , symmetric stretch, ν N-H 1621 cm^{-1} , N-H bend, strong. Anal. calcd for $\text{PSf}(\text{NH}_2)_{\text{DS}=2.0}$ ($\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$): C, 68.63; H, 5.12; N, 5.93; O, 13.54; S, 6.78. Found C, 68.57; H, 5.20; N, 5.96; S, 6.71.

Preparation of Poly(sulfone (ortho ether, ortho sulfone) amine) (DS = 2.75). **8.** Sodium borohydride powder (1.1 g, 28.3 mmol) was added quickly to a yellow solution of poly(sulfone triazide)¹ (DS ≈ 2.75 , 1.0 g, 1.8 mmol) in THF (18 mL) and absolute ethanol (1.8 mL) cooled at -60°C . The polymer was recovered following the procedure for **3A** to give 0.75 g of product (90% yield). The white polymer contained an average of 2.75 amine groups per polysulfone repeat unit. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): U, M, and D refer to the distribution of the ortho sulfone amine, assuming there are two amine groups ortho ether already present, i.e. U, M, and D represent di-, tri-, and tetra-amine repeat units, respectively. δ 7.92–7.80 (m, H_a (U) and H_a (M)), 7.66 (small d, H_d (D)), 7.61 (d, H_d (M)), 7.05–6.92 (m, H_c (U) and H_c (M)), 6.85–6.65 (m, H_a (U,M,D) and H_e (U,M,D)), 6.52–6.42 (m, H_b (U,M,D)), 6.30–6.11 (m, H_c (M,D) and H_f (M,D) and ortho sulfone NH_2), 4.91 and 4.82 (ss, ortho ether NH_2 arising from amine being adjacent to an aromatic ring containing either an amine or no amine), 1.55 (s, 6H, $\text{CH}_3\text{-C-CH}_3$). IR: ν N-H 3470 cm^{-1} , asymmetric stretch, ν N-H 3375 cm^{-1} , symmetric stretch, ν N-H 1620 cm^{-1} , N-H bend, strong. Anal. calcd for $\text{PSf}(\text{NH}_2)_{\text{DS}=3.0}$ ($\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_4\text{S}$): C, 66.51; H, 5.17; N, 8.62; S, 6.58. Found C, 66.37; H, 5.04; N, 8.40; S, 6.52.

Azidation and Amination of Polysulfone 1A using 4-Acetamidobenzenesulfonyl azide (ABSA): An Alternative Azide Transfer Agent to Tosyl Azide. Polysulfone **1A** (4.42 g, 10.0 mmol) in THF (80 mL, 5.5% w/v) was dilithiated using 2.15 equiv of *n*-butyllithium (2.15 mL of 10 M, 21.5 mmol) as reported before,¹ but at -65°C . The higher temperature provided better mixing when ABSA was added. ABSA (7.2 g, 30.0 mmol) was dissolved in THF (11 mL) to form a slightly cloudy solution. This was cooled in the dry ice bath until it became more cloudy, and then poured rapidly into the reaction mixture. A yellow polymer precipitated out of solution immediately which turned to a creamy suspension within ~ 10 min. The mixture was gradually warmed to -50°C with stirring and held at that temperature for 15 min. The heterogeneous mixture (at -50°C) was poured quickly into a beaker containing a vigorously stirred (magnetic) mixture of ethanol-water (100 mL, 1:1). Initially, a nearly clear bright yellow solution resulted out of which precipitated a yellow product (poly(sulfone azide)) within a few seconds. After the solution was stirred for 10 min, the polymer was filtered and

then stirred in warm ethanol for several hours to remove any reagent trapped in the precipitate. A total of 4.0 g of yellow poly(sulfone (ortho sulfone) azide) was obtained, but with a lower than expected DS (<2.0). A 2.6 g sample of the azide was reduced with NaBH₄ to yield 2.15 g of poly(sulfone (ortho sulfone) amine) with DS = 0.88, following a similar procedure to **3A**. The DS was determined by ¹H-NMR integration.

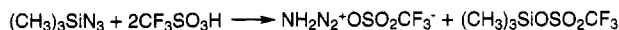
A "One-Pot" Procedure for Preparing Poly(sulfone (ortho sulfone) amine) **3A, Including an Improved Recovery Procedure for Azide **2A** and Heterogeneous Reduction with NaBH₄.** A mechanically mixed solution of polysulfone **1A** (11.06 g, 25.0 mmol) in THF (200 mL, 5.5% w/v) was dilithiated using 2.15 equiv of *n*-butyllithium (5.40 mL of 10 M, 53.7 mmol) in a 1 L flask following a similar procedure as before¹ but at -65 °C. The higher temperature provided better mixing during the tosyl azide addition. A solution of tosyl azide (14.8 g, 75.0 mmol) in THF (15 mL) at -35 °C was poured rapidly into the reaction mixture under vigorous stirring. A yellow precipitate formed immediately, changing to a slurry within ~3 min. Stirring was reduced and the mixture was gradually warmed to -50 °C and stirred at that temperature for 15 min during which time a clear solution formed. The cooled (-50 °C) solution was rapidly poured into a vigorously stirred ethanol-water mixture (250 mL, 10:1) contained in a 1 L round-bottom flask. Poly(sulfone (ortho sulfone) azide) **2A** precipitated from the resulting bright yellow solution within ~2 min. The mixture was left stirring until the temperature reached 10 °C, and then the polymer was reduced to the amine in the same flask. The polymer suspension was cooled to 0 °C and NaBH₄ (14.2 g, 75 mmol) was added gradually while monitoring gas evolution. Ten minutes following the addition of NaBH₄, the ice bath was removed and the mixture was stirred overnight. The polymer was collected on a Buchner funnel, rinsed with ethanol, and then stirred with water for 30 min. The polymer was washed by stirring twice in hot water for periods of 2 h, filtered and dried to yield 11.2 g (94%) of poly(sulfone (ortho sulfone) amine) **3A** with DS = 2.0.

Results and Discussion

Synthesis. Three main modification approaches to prepare aminated polymers were undertaken. The first of these was replacement of bromine on dibrominated polysulfone with nucleophilic NH₂ synthons. The dibrominated starting material **5** was readily prepared by a published procedure.⁹ Halogenobenzenes are known to undergo elimination-addition reactions leading to aminobenzenes in the presence of sodium or potassium amide and an amine nucleophile.^{10,11} The mechanism involves the formation of an unstable benzyne intermediate during the elimination step. When the transformation is performed in liquid ammonia, it acts as a primary amine nucleophile. Amination, described by Han et al.¹¹ using sodium amide in liquid ammonia, was attempted on dibrominated polysulfone. The maximum degree of substitution (DS, average number of functional groups per repeat unit) achieved was 0.33 (determined by NMR integration) at -78 °C and only insoluble products were obtained at -33 °C, the condensation temperature of ammonia. In retrospect, potassium amide may have been a more effective reagent because of its greater solubility in ammonia.¹⁰ A D₂O exchangeable amine signal at 3.31 in the proton spectrum and IR absorptions at 3475 and 3390 cm⁻¹ confirmed the presence of a primary amine. An unsuccessful attempt to introduce aminoalkyl groups was also made by using ethylenediamine nucleophile on the benzyne intermediate. This approach has been applied previously to the surface modification of Kevlar polyamide.¹²

Nucleophilic substitution of phthalimide, a masked nucleophilic amine, on the dibrominated polymer was

Scheme 1. Reaction Scheme for Amination of Aryl Compounds with TMS Azide/Triflic Acid



also explored. This is known as the Gabriel reaction¹³ which has wide applicability for converting alkyl halides to alkylamines after hydrazinolysis of the intermediate phthalimide. It has also been reported that a copper-catalyzed Gabriel reaction is effective for aryl halides.¹⁴ However, no Gabriel reaction between dibrominated polysulfone and potassium phthalimide in the presence of copper(I) bromide was evident.

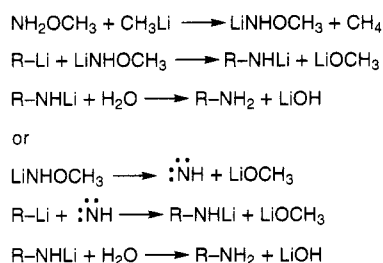
In another approach to aminated polysulfones, electrophilic amine synthons were investigated. The use of hydroxylamine-*O*-sulfonic acid (HOSA) as a versatile reagent for aminating aromatic rings has been reviewed.¹⁵ Amination of polysulfone **1A** with HOSA in DMF was attempted under conditions similar to those described by Minisci¹⁶ for aminating anisole using iron-(II) sulfate heptahydrate. The amination mechanism is described as an electrophilic amine radical in a redox system. Under these conditions, no reaction occurred with polysulfone. Reaction conditions similar to those described by Kovacic et al.¹⁷ for aminating toluene in the presence of aluminum chloride were also attempted. These more extreme conditions of higher temperature and excess reagent also failed to produce any amination reaction on polysulfone.

Olah et al.¹⁸ used the amidodiazonium ion to obtain reasonable yields of aminoarenes from aromatic hydrocarbons. In this case, the ion was obtained by protonating hydrazoic acid with a superacid, trifluoromethanesulfonic acid (triflic acid). From this, Olah and Ernst¹⁹ developed an improved reagent, trimethylsilyl azide/triflic acid, that allowed simple and nearly quantitative amination of aromatics as outlined in Scheme 1.

The trimethylsilyl azide reagent is a convenient amine synthon because it is an organic soluble source of azide, and does not form insoluble salts when the Si-N bond is cleaved. This reagent was investigated as a promising route to aminated polysulfones. In a typical procedure, trimethylsilyl azide was added slowly to a solution of triflic acid and polysulfone in chloroform. In common with the original report,¹⁹ the reaction generally started immediately as indicated by the evolution of nitrogen. A variety of different reaction conditions were tested and gave amine-substituted polysulfones with apparent DS ranging from 0 to 0.88, determined by comparative integration of the amine vs the isopropylidene signal in the proton spectrum. However, it was evident that extensive degradation at the isopropylidene site occurred as the relative signal strength to aromatics was variable, in one case 12 times lower than its correct value. The proton NMR spectrum showed an amine signal at 3.05, exchangeable with D₂O, but the aromatic region was difficult to interpret due to the complex mixture arising from chain degradation. The true DS is probably less than 0.3, based on the very weak amine absorption bands at 3470 and 3375 cm⁻¹. Severe polymer degradation was confirmed by GPC measurements. This chain degradation most likely occurs very rapidly in the presence of triflic acid as there is a noticeable decrease in polymer solution viscosity even before the addition of trimethylsilyl azide.

A third and ultimately successful modification approach was amination of lithiated polymers. Polysul-

Scheme 2. Possible Reaction Schemes for Aminating Organolithium Compounds with Methoxyamine Lithium Salt

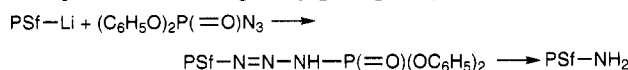


fone can be lithiated controllably, site specifically, and to a high DS either through direct lithiation²⁰ or through bromination–lithiation.⁹ Lithiated polysulfones are useful activated intermediates that undergo efficient conversion to carboxyl,²¹ hydroxyl,²² and a number of other derivatives.²³ Their utility for producing primary amines is less apparent since primary amine groups intrinsically contain acidic protons that are readily abstracted. Therefore, masked amines (electrophilic NH₂ synthons) must be used instead. A comprehensive review of many reactions for the electrophilic amination of carbanions NH₂ synthons has been published by Erdik et al.²⁴

Methoxyamine, or the lithium salt of methoxyamine, is a commonly reported amine synthon for the conversion of lithiated compounds to primary amines. This class of reagent has been used to convert lithiated aromatic sulfone to aromatic amines. Gilman et al.²⁵ reported the preparation of 1-aminothianthrene derivative by treating lithiated thianthrene with methoxyamine. It is implicitly obvious that methoxyamine is inherently inefficient for converting aryllithium compounds to arylamines because the basic aryllithium can also be protonated by the removal of the amine protons of the reagent. In general, 2 equiv organo- or aryllithium starting material are required for 1 equiv of methoxyamine, ruling out this reagent for quantitative polymer functionalization. Beak et al.²⁶ reported the use of a methoxyamine/methylithium reagent pair that led to much more efficient conversions of organolithium compounds to amines. Methylithium serves as a surrogate first equivalent by lithiating methoxyamine. Scheme 2 shows two possible reaction mechanisms that are proposed: either direct displacement by a carbanion on an anionic nitrogen, or reaction of a nitrene intermediate with a nucleophile. Quirk et al.²⁷ successfully used this reagent pair in polymeric systems for aminating the chain ends (92% conversion) of anionically polymerized polystyrene.

In our own experiments, aminating lithiated polysulfone with methoxyamine under a variety of conditions resulted in negligible amine functionalization of the polymer. Hinke and Staude²⁸ independently reported obtaining a DS of 0.12 amine functionalization from methoxyamine and lithiated polysulfone with DS of ca. 0.74. We achieved a DS of 0.20 by reaction of the lithium salt of methoxyamine (CH₃ONHLi) with lithiated polysulfone containing an average of 1.2 lithium atoms per repeat unit. This translates to a conversion rate of only 17%, similar to that obtained by Staude. Furthermore, there was an insoluble component present in the products of all the reactions, indicating some cross-linking had occurred. The evidence for amination were weak IR absorption bands at 3473 and 3375 cm⁻¹, characteristic of a primary amine group.

Scheme 3. Reaction Scheme for Aminating Polysulfone via Diphenylphosphoryl Azide (DPPA)



Another NH₂ synthon reported to yield arylamines readily from aryllithium compounds is diphenylphosphoryl azide (DPPA).²⁹ Previously we reported the preparation of a phosphoryl triazene-substituted polysulfone¹ as a possible route to aminated derivatives. Although the reaction was prone to give insoluble products from high DS lithiated polysulfones, a soluble phosphoryl triazene of DS 0.67 was obtained from a DS 1.2 lithiated polysulfone. Completely soluble products with higher DS could not be prepared.

Polysulfone phosphoryl triazene was decomposed with sodium hydroxide according to the procedure of Mori et al.,²⁹ as outlined in Scheme 3. The proton NMR spectrum was closely similar to that of poly(sulfone (ortho sulfone) amine) (DS = 1.0), described later. For the conversion from triazene to amine, only a trace of remaining triazene was evident. A DS of 0.65 was determined by comparative integration of the group of signals H_c, H_e and NH₂ vs isopropylidene. Absorption bands at 3473, 3375, and 1620 cm⁻¹ confirmed the presence of primary amine.

In nonpolymeric compounds, the value of azides as efficient precursors to primary amines is well recognized. Tosyl azide is a particularly useful reagent for converting ortho-lithiated aromatic or heteroaromatic compounds to azides, which can be transformed to amines that are poorly accessible by classical electrophilic substitution. Spagnolo et al.³⁰ reported the conversion of ortho-lithiated bithienyls to amines via azidation with tosyl azide and reduction either with hydrogen sulfide or with lithium aluminum hydride. Narasimhan et al.³¹ used Ni–Al/KOH to reduce azides derived from ortho-lithiated aromatic compounds. Reed and Sniekus³² used the ortho-lithiation methodology with tosyl azide as a convenient route to polysubstituted anthranilamides, using sodium borohydride under phase transfer conditions for the reducing agent. Interestingly, sodium borohydride reductions normally give poor yields for the conversion of azides to amines under homogeneous conditions, but work efficiently under heterogeneous phase transfer conditions.³³

In the publication preceding this,¹ we reported the near-quantitative conversion of lithiated polysulfones and lithiated poly(aryl sulfones) to azide derivatives **2** using tosyl azide as a reagent. It was apparent to us from the standpoint of practicality, simplicity, and ease of removal that the best choice of reagent for reducing the polymeric azides to amines was sodium borohydride. The initial series of reductions using sodium borohydride gave cross-linked or undesirable products. The reaction of tosyl azide with lithiated polymers gives an intermediate sulfonyl triazene which only fragments to azide during aqueous workup. The borohydride reduction of the sulfonyl triazene intermediate instead of the azide led to these side products. Reduction of poly(sulfone (ortho sulfone) diazide) **2A**, prepared from polysulfone **1A** by reaction of butyllithium followed by tosyl azide, gave complete conversion to poly(sulfone (ortho sulfone) diamine) **3A** using sodium borohydride as shown in Figure 1. Similarly, poly(aryl sulfone (ortho sulfone) diamine) **3B** was prepared in the same way from **1B**. In contrast to previously reported reductions,³³ this reduction was very efficient under homo-

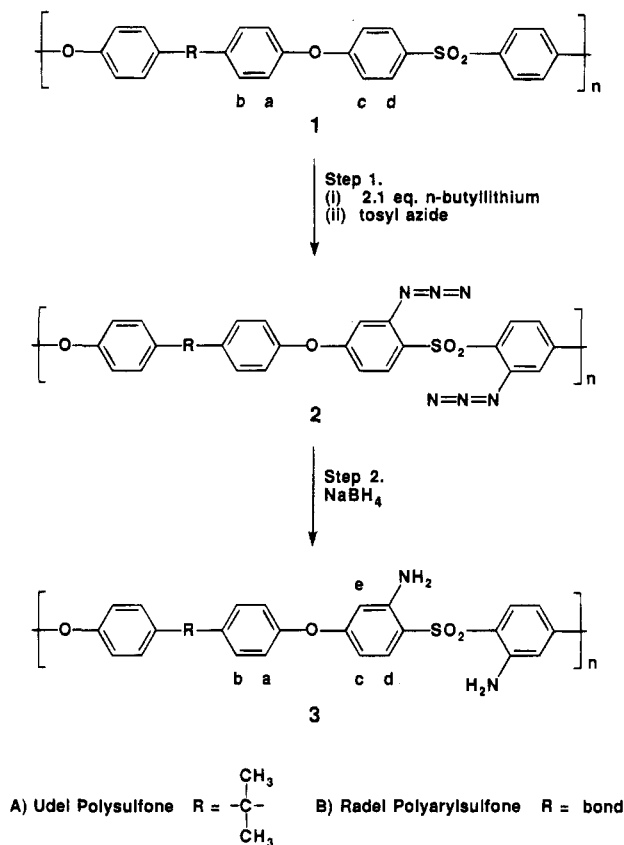


Figure 1. Reaction scheme for preparing ortho sulfone amine derivatives **3** from commercial Udel polysulfone (**1A**) and Radel poly(aryl sulfone) (**1B**) via azide intermediates **2**.

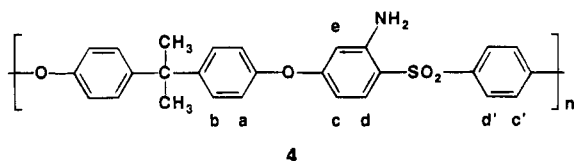


Figure 2. Poly(sulfone (ortho sulfone) amine) monosubstituted repeat unit **4**.

geneous conditions, using excess sodium borohydride in THF containing 10% ethanol. In the absence of ethanol, an insoluble polymer gel formed.

Poly(sulfone (ortho sulfone) amines) having lower DS were easily prepared by reduction of the corresponding polymeric azides, the DS ultimately being controlled during the near-quantitative lithiation step. Figure 2 shows the monosubstituted amine repeat unit **4** with the corresponding labels for proton NMR assignments.

The ortho ether-functionalized poly(sulfone diamine) **3A** was prepared by lithium-halogen exchange on dibrominated polysulfone **5**, azidation with tosyl azide, and then reduction using sodium borohydride according to Figure 3. Step 1 gives near-quantitative conversion of dibrominated polymer **5** to diazide polymer **6**. Conversion to diamine **7** in step 2 is complete, using conditions as before.

A highly substituted polymeric amine was prepared by lithiating dibrominated polymer **5** with 3.1 equiv of *n*-butyllithium and then azidation followed by reduction. The azidation step resulted in a polymer containing an average of 2.75 azide groups per repeat unit.¹ Upon reduction, aminated polymer having the same DS was obtained. The product is composed primarily of trisubstituted repeat units shown in Figure 4, as well as lesser amounts of disubstituted repeat units **7** and very minor amounts of tetrasubstituted units.

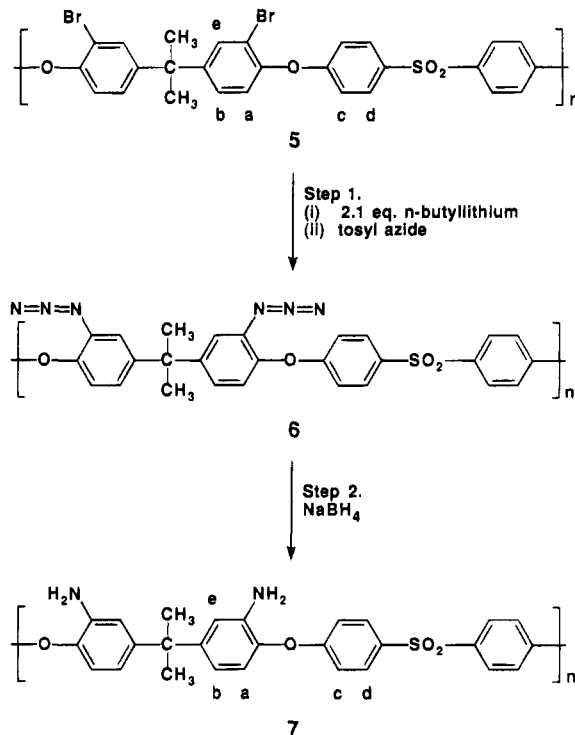


Figure 3. Reaction scheme for preparing poly(sulfone (ortho ether) diamine) **7** from dibrominated polysulfone **5** via the diazide intermediate **6**.

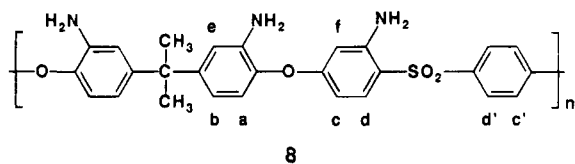


Figure 4. Poly(sulfone amine) trisubstituted repeat unit **8**.

Since the preceding publication,¹ polysulfone azides were prepared using an alternative azide transfer agent to tosyl azide. 4-Acetamidobenzenesulfonyl azide has been reported as a diazo transfer agent³⁴ that is not impact sensitive and is available commercially (Aldrich Chemical Co.). However, its role as an azide transfer reagent for preparing **2A** from lithiated polysulfone was only partly successful because of the presence of an acidic proton on the acetamido group. Poly(sulfone (ortho sulfone) azide) with a DS = 0.88 was obtained from lithiated polysulfone (DS = 2.0). It is apparent that other benzenesulfonyl azides would be capable of forming polysulfone azides, their efficiency depending on compatibility between any reagent substituent and the lithiated polysulfone.

A "one-pot" procedure for preparing **3A** from **1A** via azide **2A** was also developed. In this procedure, poly(sulfone (ortho sulfone) diazide) **2A** was prepared at a higher temperature (-65 °C) and more conveniently recovered than the previous method,¹ using a minimum quantity of solvent. It could either be isolated or directly reduced heterogeneously with NaBH_4 to poly(sulfone (ortho sulfone) diamine) **3A** in the precipitation flask, without filtration or solvent manipulation. The product (DS = 2.0) was identical spectroscopically to that prepared by the two step procedure above, except the polymer had a slight yellow coloration.

Structural Characterization by ^1H - and ^{13}C -NMR of Aminated Polysulfones Derived from Azides. The proton spectrum of **3A** (Figure 5) consists of five clear signals only, characteristic of an ortho sulfone

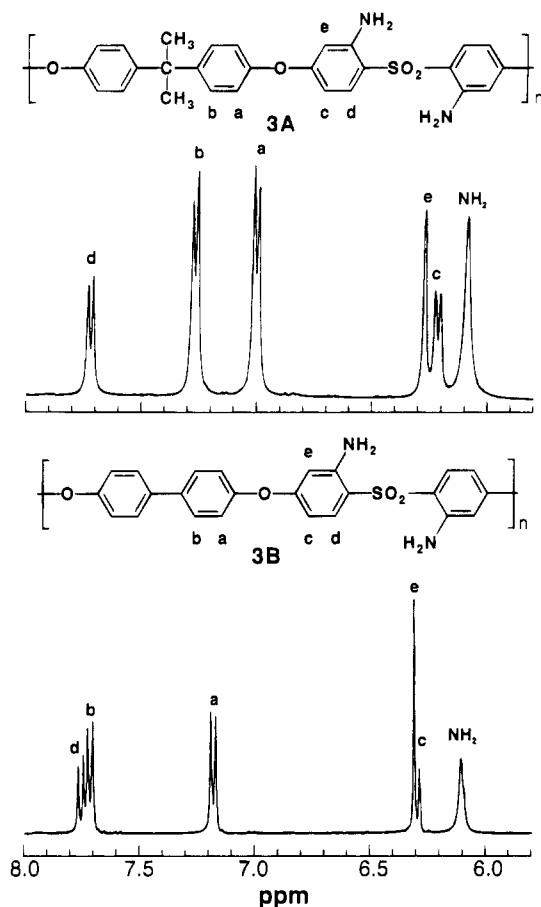


Figure 5. Comparative ^1H -NMR spectra (aromatic region) of poly(sulfone (ortho sulfone) diamine) **3A**, and of poly(aryl sulfone (ortho sulfone) diamine) **3B**.

disubstitution pattern in polysulfones. Bisphenol protons H_b (7.27) and H_a (7.00) are coupled and are largely unchanged from respective protons of both the azide precursor **2A** and **1A**. In the aminated phenyl sulfone ring, a doublet of doublets arising from H_c (6.21) is coupled both to H_d (7.72) and long range to H_e (6.26). H_e and H_c , being ortho and para to amine, have large upfield shifts from electronic substituent effects. The amine signal appears as a broadened singlet at 6.09, exchangeable with D_2O . The downfield shift arises from amine protons being in the deshielding environment of the sulfone group. By analogy to the azide precursors, aminated polysulfones with $\text{DS} < 2$ are more complicated because of the presence of unsubstituted, monosubstituted, and disubstituted repeat units. As before, these three types of units are distinguished by the deshielded H_d protons in the $\text{DS} = 1$ derivative **4**. Unsubstituted and disubstituted repeat units each have 4H and 2H doublets at 7.85 and 7.68, respectively. The monosubstituted units have two doublets: a 1H H_d doublet at 7.62 arising from the ortho sulfone proton on the phenyl amine and a 2H H_d' doublet at 7.84 from the other phenylsulfone ring.

The proton spectrum of **3B** (Figure 5) is also unambiguous, although less well defined compared to **3A**, because of signal overlap of H_e and H_c .

The carbon spectrum of **3A** (Figure 6) consists of 10 aromatic and two aliphatic signals. One-bond proton-carbon connectivities (HETCOR) are exhibited for C_2 - H_a , C_3 - H_b , C_8 - H_c , C_9 - H_d , and C_{12} - H_e . Three-bond long-range correlations (LRHETCOR) enabled the remaining carbon resonances to be assigned. In the

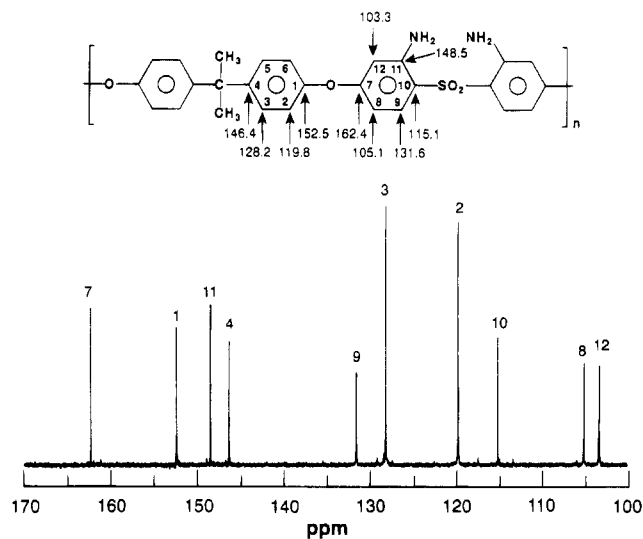


Figure 6. ^{13}C -NMR (aromatic region) and chemical shift assignments of poly(sulfone (ortho sulfone) diamine) **3A**.

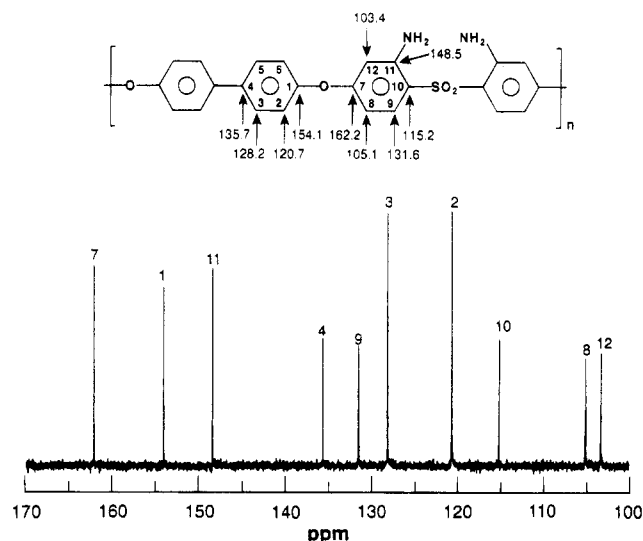


Figure 7. ^{13}C -NMR and chemical shift assignments of poly(aryl sulfone (ortho sulfone) diamine) **3B**.

bisphenol ring, C_1 and C_4 show the expected correlation to H_b and H_a respectively. In the substituted ring, C_{10} shows long-range couplings to both H_c and H_e . Although C_7 and C_{11} both exhibit correlations with H_d , their chemical shifts are sufficiently distinct to allow confident assignment based on calculated substituent shifts³⁵ applied to polysulfone chemical shifts. Thus, the chemical shifts of C_7 and C_{11} are separated by 13.9 ppm and are within less than 1 ppm of their calculated values. All experimental chemical shifts compare closely with calculated shifts except for C_{10} .

The carbon spectrum of **3B** (Figure 7) consists of 10 aromatic resonances only, confirming full disubstitution of the repeat units. Using the preceding routine, assignments for C_2 , C_3 , C_8 , C_9 , and C_{12} are determined from one-bond proton-carbon connectivities. The remaining carbons are identified by three-bond long-range correlations, except for C_7 and C_{11} which are based on calculated substituent shifts.

The proton spectrum of **7** (Figure 8) consists of five clear signals only, characteristic of ortho ether disubstitution. Doublets H_d and H_c are coupled and have similar chemical shifts to respective protons of the azide precursor. In the aminated bisphenol ring, a broadened

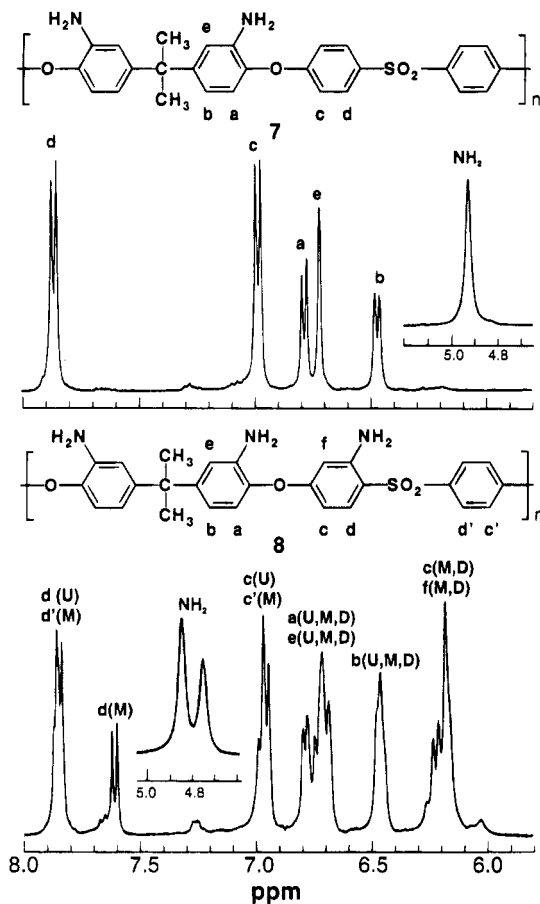


Figure 8. Comparative ^1H -NMR spectra (aromatic region) of poly(sulfone (ortho ether) diamine) **7** and of poly(sulfone triamine) **8**.

H_b doublet is coupled both to an H_a doublet and to a broadened H_e singlet. Significantly, H_b is shifted far upfield of H_a because of the electronic effects of H_b being para to amine. This is the reverse of **1A**, where H_a is upfield of H_b . The amine signal at 4.92 is more than 1 ppm upfield of the ortho sulfone analog. The more complicated spectrum of triamine **8** is also shown in Figure 8 for comparative purposes. Some assignments for the multiplets are inferred by data from ortho ether and ortho sulfone derivatives. Since the starting material azide had a DS of 2.75, there is a distribution of three types of repeat units in the amine product **8**. The predominant repeat unit contains three amine groups (designated M) as shown in Figure 4. Two other repeat units present in lesser amounts are those with two amines (designated U in this polymer, effectively structure **7**), and minor amounts with four amines (designated D). Proton-proton couplings, determined by two-dimensional COSY, enabled the correlations H_d - $\text{H}_c(\text{M,D})$, H_d - $\text{H}_c(\text{U})$, H_d - $\text{H}_c(\text{M})$, and H_a - $\text{H}_b(\text{U,M,D})$ to be made for the different repeat units.

The diazide precursor **6** was cleanly reduced to diamine **7** as shown by the carbon spectrum in Figure 9. One-bond proton-carbon connectivities are exhibited for C_2 - H_a , C_3 - H_b , C_5 - H_e , C_8 - H_c , and C_9 - H_d . Three-bond long-range correlations show C_1 is coupled to both H_b and H_e . Both C_4 and C_6 are coupled to H_a , but no C_4 correlation to methyl protons was observed to confirm C_4 . These assignments were based on close correlation to calculated substituent shifts. The remaining C_7 and C_{10} are identified by three-bond correlations to H_9 and H_8 , respectively.

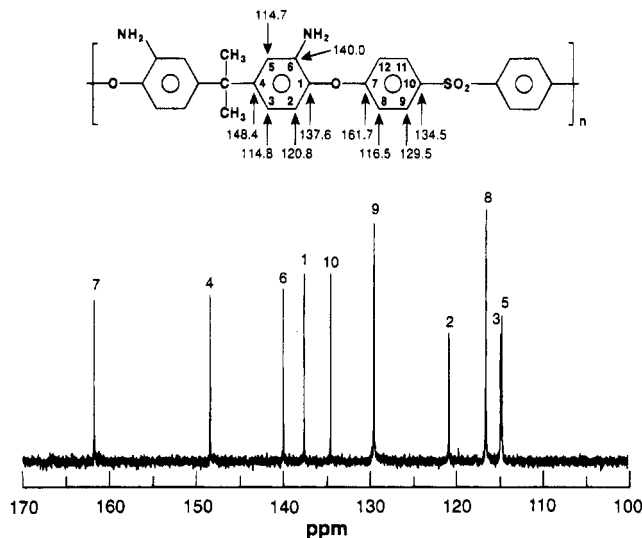


Figure 9. ^{13}C -NMR (aromatic region) and chemical shift assignments of poly(sulfone (ortho ether) diamine) **7**.

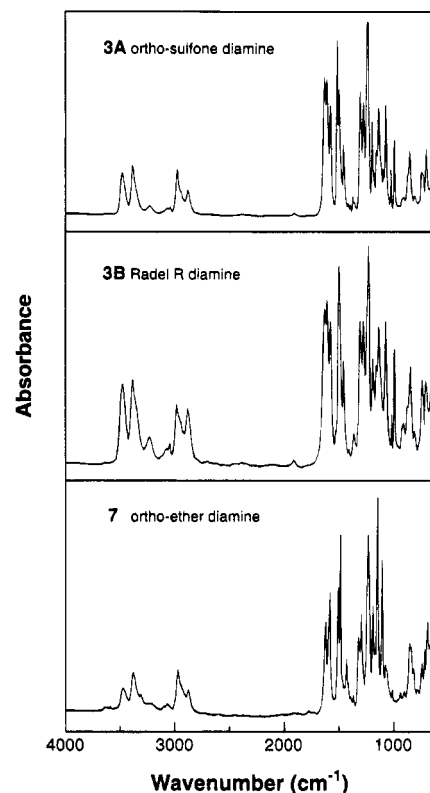


Figure 10. Comparative FTIR spectra of three polysulfone and poly(aryl sulfone amines) **3A**, **3B**, and **7**.

Infrared Spectroscopy. The complete reduction of polymeric azide precursors to primary amines was evident from the infrared spectra. Polysulfone azides have characteristically strong absorption bands in the region (2250 – 2080 cm^{-1}) arising from $-\text{N}=\text{N}^+=\text{N}^-$ asymmetric stretch, as reported previously.¹ This is the strongest absorption band in the spectrum and it occurs in a region where there are no other absorption bands for these polymers. The sodium borohydride reduced polysulfone azides show no azide absorptions and exhibit new absorptions characteristic of a primary amine. Comparative infrared spectra for three polysulfone and poly(aryl sulfone amines) **3A**, **3B** and **7** are shown in Figure 10. Asymmetric and symmetric N-H stretching absorptions of the primary amines occur at

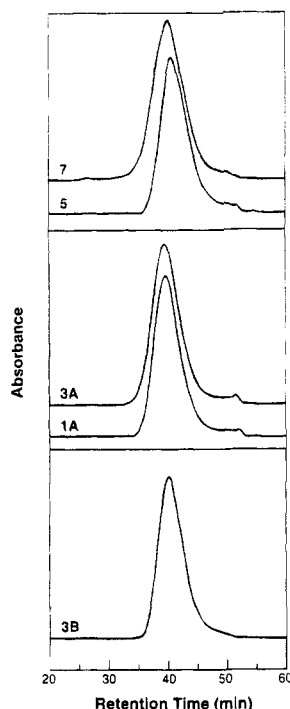


Figure 11. GPC profiles of dibrominated Udel **5** and Udel **1A** compared with diamines **7** and **3A**, and Radel **3B**.

approximately 3470 and at 3375 cm^{-1} . A medium to strong band at 1620 cm^{-1} corresponds to N–H bending vibrations.

Gel Permeation Chromatography. Figure 11 shows comparative GPC profiles of starting materials dibrominated Udel **5** vs **7**, Udel **1A** vs **3A**, and Radel diamine **3B**, to determine the effect of the modification chemistry on the molecular weight profile. Ortho ether diamine **7** has a slight broadening toward higher molecular weight, this change occurring during the azidation step.¹ Ortho sulfone diamine **3A** has a nearly identical profile to that of the starting material. Although Radel R **1B** was not measured because of insolubility in THF, the soluble diamine derivative **3B** has a molecular weight profile similar to that of Udel.

DSC and TGA Thermal Measurements. Samples were heated initially to $250\text{ }^{\circ}\text{C}$, quenched, and then heated to $350\text{ }^{\circ}\text{C}$ for the T_g measurement. T_g 's were determined from the inflection point of the endothermic transition and the average value ($<\pm 0.2\text{ }^{\circ}\text{C}$) was calculated from three measurements for each polymer. The T_g of ortho sulfone diamine **3A** is $22\text{ }^{\circ}\text{C}$ higher than unmodified polymer **1A**, whereas that of ortho ether diamine **7** is $42\text{ }^{\circ}\text{C}$ higher. This implies that the presence of amine at the ortho ether position causes significantly more chain rigidity than at the ortho sulfone position. Of the two heteroatom linkages, ether is the most flexible and is the limiting factor controlling overall flexibility. On the other hand, sulfone allows far less chain motion. The presence of amine, being a polar group, increases the polarity of the polymer and increases T_g through hydrogen-bonding interactions. Presumably, these interactions occur not only between chains but also along chains by hydrogen bonding of amine protons to the oxygen lone pair electrons of ether and of sulfone. If this is the case, hydrogen bonding with the ether linkage would increase the overall rigidity of the polymer far more than with the sulfone linkage, resulting in a larger incremental increase in T_g . The high T_g of Radel ($225.6\text{ }^{\circ}\text{C}$) was increased a

Table 4. T_g 's and Decomposition Temperatures of Aminated Polysulfones and Poly(aryl sulfones)

polymer	T_g , $^{\circ}\text{C}$	degradation onset, $^{\circ}\text{C}$	extrapolated onset, $^{\circ}\text{C}$
Udel PSf (1A)	188.1	453	518
Radel PASf (1B)	225.6	475	518
PSf-(NH ₂) ₁ (o-SO ₂) (4)	202.0	405	460
PSf-(NH ₂) ₂ (o-SO ₂) (3A)	210.5	385	430
PASf-(NH ₂) ₂ (o-SO ₂) (3B)	242.2	372	436
PSf-(NH ₂) ₂ (o-O) (7)	230.4	340	370
PSf-(NH ₂) ₃ (8)	237.1	330	367

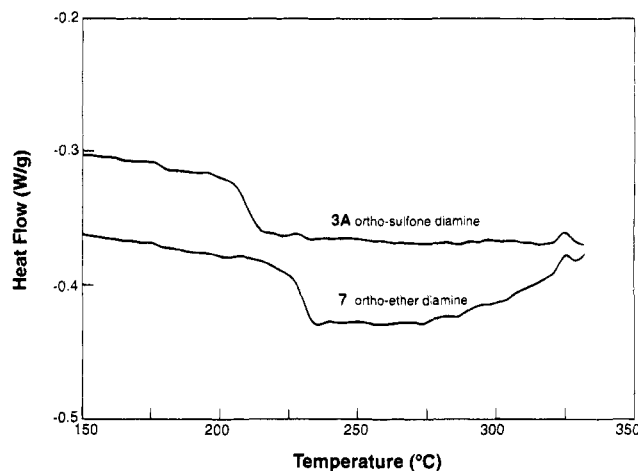


Figure 12. DSC scans for diamines **3A** and **7** showing T_g 's and showing an exothermic increase at $270\text{ }^{\circ}\text{C}$ for **7**.

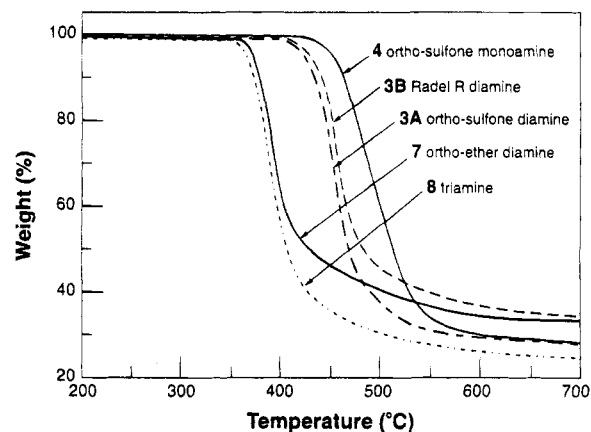


Figure 13. TGA curves of Udel monoamine **4**, diamines **3A** and **7**, triamine **8**, and Radel diamine **3B**.

further $16\text{ }^{\circ}\text{C}$ by incorporation of two ortho sulfone amine groups. All the amine derivatives have clear sharp endothermic glass transitions in the DSC and these are summarized in Table 4. Diamine **7** and triamine **8** exhibit gradual exothermic increases starting at $270\text{ }^{\circ}\text{C}$. A comparison of this gradual exothermic increase for diamine **7** is made with that of diamine **3A** in the DSC scan shown in Figure 12.

In contrast to the marked two-step degradation observed by TGA for the azide precursors,¹ the polymeric amines have simpler degradation profiles (Figure 13) more characteristic of polysulfone. However, the onsets of degradation occur at lower temperatures. Minor weight losses of less than 1% at temperatures between 150 and $175\text{ }^{\circ}\text{C}$ occurred in most of the aminated polymers. We believe these losses occur through desorption of strongly bound trace contaminants. In unrelated experiments during film preparation of diamine **7**, cross-linking occurred in this particular polymer when the film was annealed *in vacuo*

at 5 °C above T_g . Both the onsets of degradation and the extrapolated onsets for the amine derivatives are summarized in Table 4. It is noteworthy that the ortho sulfone aminated polymers have a higher thermal stability than the ortho ether series. The former structure allows resonance stabilization of the amine and sulfone group as well as hydrogen bonding of amine protons with the sulfone oxygen atoms.

Conclusions

Three modification approaches to aminated polysulfones were investigated: replacement of aromatic bromine with nucleophilic NH_2 synthons; amination by electrophilic NH_2 synthons; and amination of lithiated polysulfones via azides and other electrophilic NH_2 synthons. The two former approaches resulted either in low levels or no amination, or in polymer degradation. In the latter approach using lithiated polysulfones, the reaction with DPPA gave reasonable yields of amine groups, but was limited by a DS of 0.67. Higher DS's resulted in gel formation, indicating some cross-linking had occurred. A two-step process of azidation of lithiated polysulfones and poly(aryl sulfones) with tosyl azide, followed by sodium borohydride, gave near-quantitative conversions to aminated derivatives. In the ortho sulfone aminated polymers, DS's of 2.0 or less were readily obtained by controlling the quantity of butyllithium during the direct lithiation step. The ortho ether aminated polymers were derived from dibrominated polysulfone, and DS's of 2.0 to 2.75 were obtained also by controlling the lithiation step. The modification chemistry is both site specific and provides aminated polysulfones with controlled DS's. While the azidation-reduction reaction sequence can be accomplished as a two-step procedure with isolation of the intermediate azide, it can also be achieved conveniently by a "one-pot" process whereby the azide is reduced *in situ*.

The structures of the aminated polysulfones are well supported by detailed spectroscopic measurements. The molecular weight profiles of the products are unchanged for the ortho sulfone amines and are shifted slightly towards higher MW for the ortho ether series. All the aminated derivatives have higher T_g 's compared to those of the starting polymers, the ortho ether amine showing the largest increase.

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