Chemical Modification of Polysulfones: A Facile Method of Preparing Azide Derivatives from Lithiated Polysulfone Intermediates[†]

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ABSTRACT: A quantitative and regiospecific method for attaching azide groups onto the aromatic rings of polysulfone and poly(aryl sulfone) is reported. Polysulfones were activated either on the ortho-sulfone sites or the ortho-ether sites by direct lithiation or bromination–lithiation. The lithiated intermediates were converted quantitatively to azides by treatment with tosyl azide. Polysulfones containing one, two, and three azide groups per repeat unit were obtained, the degree of substitution being determined by the degree of lithiation. The structures were confirmed principally by NMR spectroscopy. TGA and GPC data are also reported. Soluble aryl azide modified polysulfones were readily isolated and are especially useful for facile conversion to primary amines. This conversion as well as the 1,3-dipolar cycloadditions of these azides will be reported separately.

Introduction

Polysulfone is an engineering thermoplastic[1] widely used as a membrane material in the area of liquid and gas separations. It has been a goal of our work to tailor the membrane separation characteristics of this polymer and increase the scope of its use by introducing functional groups by chemical modification.[2] We reported previously the versatility of a direct lithiation procedure[3] and a bromination–lithiation procedure[4] as means of producing carboxyl,[5] hydroxyl,[6] and a number of other derivatives.[7] We have extended this work to include aromatic azide groups. The original aim of this work was to develop a novel alternative method to the nitration–reduction pathway to derivatize polysulfone[8–10] with primary amine groups, since aromatic azides can be reduced readily to amines. Amine groups are somewhat difficult to attach onto polymers but provide useful attachment sites along polymer chains or at chain ends because they react readily with several types of groups to form covalent bonds. There can be a tendency for chain degradation to occur with the nitration route, and the resulting nitrated polymers can be difficult to reduce. Apart from being convenient precursors for amines, poly(sulfone azides) are potentially useful for cross-linkable membranes and as intermediates for many other derivatives.

Several examples of polymeric alkyl azides produced by chemical modification of polymers have been reported.[8,11–13] Typically, azide groups are introduced onto polymers containing chloroalkyl groups by reaction with sodium azide. Azides are thermally and photochemically labile groups capable of being transformed readily into a number of other useful derivatives.[14–16] Cohen reported the preparation of several 1,3-dipolar cycloaddition products from poly(vinylbenzyl azide).[11] In nonpolymeric molecules, aryl azides can be prepared from aryl carbanions by reaction with a selection of appropriate electrophiles.[17] Generally, a larger selection of electrophiles is effective for aryl Grignard compounds than for aryllithium compounds. We report here an efficient procedure for introducing azide groups directly onto the polysulfone aromatic ring using lithiation chemistry.

Experimental Section

Materials and Methods. Udel P3500 and Radel R5000 (Amoco Performance Products, Inc.) were dried at 120 °C prior to use. Reagent-grade *p*-toluenesulfonyl chloride, sodium azide, and isopropyl alcohol were used as received for the synthesis of *p*-toluenesulfonyl azide (tosyl azide). n-Butyllithium (10 M in hexane) solution and other reagent-grade chemicals were obtained from Aldrich Chemical Co. and were used as received. Lithiation reactions were performed under an inert atmosphere of dry argon in glassware that had been dried overnight at 120 °C. For large-scale reactions, polymer solutions were prepared the previous day in dry glass jars using anhydrous reagent-grade tetrahydrofuran (THF) freshly distilled over lithium aluminum hydride and under argon. The reaction vessel was a 3-L three-neck glass flask equipped with a high-torque mechanical paddle stirrer, gas inlet, and septum. Dibrominated polysulfone starting material for azide functionalization ortho to the ether linkage was prepared according to a previously published procedure.[4] The modified polymers were dried in a vacuum oven.

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 a deuterated chloroform solvent and referenced to an internal tetramethylsilane (TMS) standard. Proton and carbon spectra were collected with a spectral width of 4000 and 20000 Hz, respectively, and a 16K data table.

Proton–carbon bond connectivities were obtained on a Varian VXR-300S spectrometer from two-dimensional spectra. Both the HETCOR and LRHETCOR experiments were acquired using an F1 spectral width of 2493 Hz and an F2 spectral width of 16502 Hz. The data acquired over an acquisition period of 9.062 s was digitized by 2048 points in F2. A total of 128 increments were acquired in F1 utilizing 32 scans for the HETCOR experiment and 238 scans for the LRHETCOR. A one-bond coupling of 140 Hz was used to acquire the HETCOR experiment, while 7.5 Hz was selected for the long-range variant. Sine-bell weighting was applied in both dimensions prior to zero-filling, 2048 × 256, and Fourier transformation.

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 as U, M, and D, respectively.

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Polymer Analyses and Measurements. Infrared (IR) spectra were measured on a Nicolet 520 FTIR spectrometer. 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, a Waters 996 UV detector, and a selection of μ-Styragel columns. Thermal decompositions of azide polymers were evaluated by thermogravimetric analysis (TGA) using a DuPont 951 thermogravimetric analyzer. Samples were placed in the sample pan without being compressed and were measured in an atmosphere of nitrogen flowing at 50 mL/min. Initially, samples were kept at room temperature for 20 min and then heated and maintained at 40 °C for 30 min to degas or remove any volatile species. Thereafter, the heating rate for the experiments was 10 °C/min except for the triazide, which was 1 °C/min. The slower heating rate was necessary to overcome measurement difficulties due to the sample's unstable behavior. Glass transition (T_g) temperatures for polysulfone azides could not be measured because thermal decomposition occurred below the T_g.

Attempted Azide Formation with Trimethylsilyl Azide. Polysulfone (4.42 g, 10 mmol (a mol is defined as a molecular weight of a polymer repeat unit)) in dry THF (88 mL) was lithiated with *n*-butyllithium (1.1 mL, 11 mmol) at −78 °C, and then trimethylsilyl azide (TMSA; 10 mL, 75 mmol) cooled at −50 °C was added quickly to the solution. Within a few minutes the color changed from brown to pale green and later became cloudy white. The mixture was stirred at −78 °C for 3.5 h, then gradually warmed to −20 °C, and stirred at that temperature for 30 min. The polymer was recovered by precipitation from ethanol, washed, and then dried (4.7 g). ^{1}H-NMR (without TMS): δ 0.36 (9H, Me_3Si). Degree of substitution (DS) = 0.67 by Me_3Si versus isopropylidene integration. Anal. Found: C, 70.07; H, 5.72; N, 0.00; S, 7.06.

Attempted Azide Formation with (Trimethylsilyl)methyl Azide. A THF solution of polysulfone (2.21 g, 5 mmol) lithiated to approximately a DS of 2.0 was prepared at −78 °C. To this was added a cooled (−78 °C) solution of (trimethylsilyl)methyl azide[18] (2.66 g, 20.6 mmol) in THF (2.5 mL). Upon addition, a thick purple gel formed which became less viscous after gradually warming the mixture to −30 °C. 1.1 g of product was recovered by precipitation from ethanol. The product was not soluble in DMSO and formed a gel in chloroform, indicating some cross-linking had occurred.

Triazene Formation with Diphenylphosphoryl Azide. Polysulfone (11.06 g, 25 mmol) in dry THF (200 mL) was lithiated with *n*-butyllithium (3.0 mL, 30 mmol) to approximately a DS of 1.2 at −78 °C, and then a solution of diphenylphosphoryl azide (27.5 g, 100 mmol) in dry THF (22 mL) cooled to −78 °C was poured quickly into the solution. The viscosity of the solution immediately increased, and the color changed from brown to a green−yellow and later became yellow as the viscosity decreased. The mixture was stirred at −78 °C for 2.0 h and recovered by precipitation from ethanol, washed, and then dried (16.35 g). IR showed no azide bands at ~2117 cm^{-1}. Anal. Calcd for $PSfN{=}NNHP({=}O)O(C_6H_5)_{2(DS=0.65)}$ $(C_{27}H_{22}O_4S)_{0.35}(C_{39}H_{32}N_3O_7PS)_{0.65}$: C, 67.33; H, 4.63; N, 4.35; S, 5.18. Found: C, 67.23; H, 4.88; N, 4.31; S, 5.85.

Tosyl Azide. This procedure is a modification of a brief account of the preparation of tosyl azide reported by Doering and DePuy.[19] If necessary, *p*-toluenesulfonyl chloride was purified[20] by precipitating acid impurities from a saturated chloroform solution with five volumes of petroleum ether. The solution was filtered, clarified with charcoal, and filtered again, and the solvent was removed to give the purified product. A solution of sodium azide (*toxic!*) (58.5 g, 0.90 mol) in distilled water (170 mL) was quickly added to a stirred suspension (partly in solution) of *p*-toluenesulfonyl chloride (143.0 g, 0.75 mol) in isopropyl alcohol (850 mL) contained in a beaker at room temperature. The mixture was stirred for 1 h, then poured into 3 L of distilled water, and stirred for 1 h more. The separated oily tosyl azide was washed three times with water, dried over anhydrous magnesium sulfate, and then dried by stirring under vacuum. It is important for its use as a reagent in the lithiation reaction that tosyl azide contains a negligible amount of water (measured by proton NMR). A total of 114 g of a colorless tosyl azide oil was obtained (yield 77%). A 95% yield could be obtained by extracting the drying agent with chloroform. *Caution!* Tosyl azide is known to be thermally unstable, and distillation should never be attempted. It has also been reported to be shock sensitive.[21] Although we have been unable to intentionally detonate small quantities of this compound, all low molecular weight azides should be treated with caution and stored under argon in vessels that do not contain ground-glass joints. The pure reagent was stored in an Erlenmeyer flask stoppered with a rubber septum. ^{1}H-NMR: δ 7.84 (d, $J \approx 8.3$, 2H, H *o*-sulfonyl), 7.41 (d, $J \approx 8.3$, 2H, H *o*-CH_3), 2.49 (s, 3H, CH_3).

Poly(sulfone (ortho-sulfone) azide), DS = 2.0. A solution of polysulfone (44.2 g, 100 mmol) in THF (800 mL) was cooled to −78 °C by immersion in a dry ice/alcohol bath. *n*-Butyllithium (21.5 mL, 215 mmol) was injected dropwise at a rate of 30 mL/h using a syringe pump. The mixture initially turned green and then later developed a brown coloration and became more viscous. It was stirred for 30 min following the *n*-butyllithium addition. A solution of tosyl azide (59.1 g, 300 mmol) in THF (60 mL) under argon was cooled to −35 °C and poured promptly into the reaction flask. The polymer precipitated immediately but within 5 min changed to a creamy yellow homogeneous suspension as it was stirred during 15 min at −78 °C. The temperature of the cold bath was then gradually warmed to −50 °C over a period of 90 min when the reaction mixture abruptly changed to a thick gel and then within a few minutes to a clear yellow liquid. The solution was stirred at −50 °C for 15 min and then mixed with 5 L of ethanol/water (2:3 ratio) in a Waring blender.

The resulting cloudy white solution was transferred to a beaker and stirred. Water (~1 L) was immediately added slowly until the yellowish poly(sulfone azide) precipitated from solution. The supernatant was decanted, and the polymer was washed three times by stirring for several hours with warm ethanol/water (4:1 ratio) to remove residual tosyl azide. After filtration, the polymer was dried in a vacuum oven at 25 °C. The pale yellow product (49.8 g, 95% yield) contained almost two azide groups ortho to sulfone per polysulfone repeat unit and was photosensitive and thermally unstable. ^{1}H-NMR: Udel polysulfone, δ 7.85 (d, 4H, H_d); 7.24 (d, 4H, H_b), 7.00 (d, 4H, H_c), 6.94 (d, 4H, H_a), 1.69 (s, 6H, $C(CH_3)_2$); PSf-(*o*-sulfone-$N_3)_{(DS=2.0)}$, 8.19 (d, $J \approx 8.8$, 2H, H_d), 7.29 (d, $J \approx 8.7$, 4H, H_b), 7.00 (d, $J \approx 8.7$, 4H, H_a), 6.78 (dd, $J \approx 8.8$, $J \approx 2.1$, 2H, H_c), 6.74 (d, $J \approx 2.1$, 2H, H_e), 1.73 (s, 6H, $C(CH_3)_2$). IR: $\nu_{N=N=N}$ 2118 cm^{-1} (strong, asym str). Anal. Calcd for PSf-$N_{3(DS=2.0)}$ $(C_{27}H_{20}N_6O_4S)$: C, 61.82; H, 3.84; N, 16.02; O, 12.20; S, 6.11. Found: C, 61.69; H, 3.78; N, 15.75; S, 6.07.

Poly(sulfone (ortho-sulfone) azide), DS = 1.0. The procedure was repeated as before, but using 11.0 mL of *n*-butyllithium (110 mmol) to lithiate polysulfone and using 29.5 g of tosyl azide (150 mmol) in 30 mL of THF. The pale yellow product was recovered as before (46.0 g, 95% yield) and contained an average of almost one azide group ortho to sulfone per polysulfone repeat unit. ^{1}H-NMR [PSf-(*o*-sulfone-$N_3)_{(DS=1.0)}$]: δ 8.20 (d, H_d (D)), 8.10 (d, H_d (M)), 7.92 (d, $H_{d'}$ (M)), 7.85 (d, H_d (U)), 7.23−7.31 (m, H_b's (U, M, D)), 6.92−7.03 (m, H_c (U) and H_a's (U, M, D)), 6.74−6.81 (m, H_c (M, D), H_e (M, D)), 1.71 (s, 6H, $C(CH_3)_2$). Anal. Calcd for PSf-$N_{3(DS=1.0)}$ $(C_{27}H_{21}N_3O_4S)$: C, 67.07; H, 4.38; N, 8.69; O, 13.24; S, 6.63. Found: C, 66.82; H, 4.37; N, 8.13; S, 6.29.

Poly(aryl sulfone (ortho-sulfone) azide), DS = 2.0. A solution of Radel R5000 poly(aryl sulfone) (4.00 g, 10.0 mmol) in THF (160 mL) was cooled to −78 °C by immersion in a dry ice/alcohol bath. It should be noted that the polymer is only completely soluble when cooled. *n*-Butyllithium (2.15 mL, 21.5 mmol) was injected dropwise using a syringe pump. The mixture initially turned pale yellow and then later darker yellow and became more viscous. It was stirred for 15 min after the *n*-butyllithium addition was completed, and then a solution of tosyl azide (5.91 g, 30.0 mmol) in THF (6 mL) cooled at −35 °C under argon was poured promptly into the reaction flask. The polymer precipitated immediately but within 5 min changed to a creamy yellow homogeneous suspension. The temperature of the cold bath was gradually warmed to −50 °C (over 60 min), at which point the mixture abruptly changed to a thick paste and then within a few minutes to a clear yellow liquid. The clear solution was stirred at −50 °C for 5 min and then mixed with 700 mL of ethanol/water (1:2 ratio) in a Waring blender. The resulting white polymer suspension was transferred to a beaker and stirred. Water (~200 mL) was immediately added slowly until the yellowish poly(aryl sulfone azide) precipitated from solution. The supernatant was decanted, and the polymer was washed three times by stirring it with warm ethanol/water (4:1 ratio). After filtration, the polymer was dried in a vacuum oven at 25 °C. The pale yellow product (4.50 g, 93% yield) contained almost two azide groups ortho to sulfone per poly(aryl sulfone) repeat unit and was photosensitive and thermally unstable. The polymer can be purified by dissolving it into cold chloroform, filtering through a glass frit, and precipitating in ethanol. ^{1}H-NMR [Radel-PSf-(*o*-sulfone-N_3)$_{(DS=2.0)}$ (cold $CDCl_3$)]: δ 8.24 (d, $J \approx 8.8$, 2H, H_d), 7.65 (d, $J \approx 8.7$, 4H, H_b), 7.19 (d, $J \approx 8.7$, 4H, H_a), 6.86 (dd, $J \approx 8.8$ and 2.2, 2H, H_c), 6.83 (d, $J \approx 2.2$, 2H, H_e). IR: ν_{N-N-N} 2116 cm^{-1} (strong, asym str). Anal. Calcd for Radel-$N_{3(DS=2.0)}$ ($C_{24}H_{14}O_4N_6S$): C, 59.75; H, 2.92; N, 17.42; S, 6.64. Found: C, 60.29; H, 2.63; N, 17.19; S, 6.22.

Poly(sulfone (ortho-ether) azide), DS = 2.0. A solution of dibrominated polysulfone[4] (60.0 g, 100 mmol) in THF (1100 mL) was cooled to −78 °C by immersion in a dry ice/alcohol bath. The polymer was lithiated with *n*-butyllithium (21.5 mL, 215 mmol) then reacted with a solution of tosyl azide (59.1 g, 300 mmol) in THF (60 mL) as before. The polymer precipitated immediately and then changed to a creamy yellow suspension as it was stirred during 15 min at −78 °C. The temperature of the cold bath was then gradually increased to −50 °C over a 90 min period. Then the suspension was stirred at −50 °C for 15 min. The creamy yellow suspension, which did not form a clear solution as before, was mixed with 6 L of ethanol/water (2:3 ratio) in a Waring blender.

The resulting yellow solution was transferred to a beaker and stirred. Water (~1 L) was immediately added slowly until the yellowish polysulfone azide precipitated from solution. The polymer was recovered as before. The pale yellow product (49.8 g, 95% yield) contained almost two azide groups ortho to ether per polysulfone repeat unit and was more photosensitive and thermally unstable than the ortho-sulfone product. ^{1}H-NMR: dibrominated Udel, δ 7.87 (d, $J \approx 8.8$, 4H, H_d), 7.52 (d, $J \approx 2.0$, 2H, H_e), 7.16 (dd, $J \approx 8.3$ and 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, $C(CH_3)_2$); PSf-(*o*-ether-N_3)$_{(DS=2.0)}$, δ 7.87 (d, 4H, H_d), 6.95−7.03 (m, remainder of protons), 1.71 (s, 6H, $C(CH_3)_2$). IR: ν_{N-N-N} 2117 cm^{-1} (strong, asym str). Anal. Calcd for PSf-$N_{3(DS=2.0)}$ ($C_{27}H_{20}N_6O_4S$): C, 61.82; H, 3.84; N, 16.02; O, 12.20; S, 6.11. Found: C, 61.14; H, 3.78; N, 16.10; S, 6.45.

Poly(sulfone (ortho-ether, ortho-sulfone) azide), DS = 2.75. A solution of dibrominated polysulfone[4] (4.5 g, 7.5 mmol) in THF (150 mL) was cooled to −78 °C. The polymer was lithiated with *n*-butyllithium (2.3 mL, 23.3 mmol). The first 15 mmol of *n*-butyllithium was added dropwise as before to prepare dilithiated polysulfone. The polymer was further lithiated by adding the remainder of the metalating agent more rapidly. The resulting trilithiated polymer precipitated from solution as a thick paste. A cooled solution (−35 °C) of tosyl azide (7.4 g, 37.5 mmol) in THF (8 mL) was added rapidly to the trilithiated polymer. A yellow−green solution formed immediately, and this mixture was stirred for 15 min at −78 °C. The temperature of the cold bath was gradually increased over a 90-min period to −50 °C, and the creamy yellow suspension which had formed was stirred at −50 °C for 15 min. The polymer was recovered by mixing the suspension with 800 mL of ethanol/water (1:1 ratio) in a Waring blender. Water was added to the resulting clear solution until a polymer precipitate formed. The product was washed and dried as before and was more photosensitive than the other polymeric azides. The pale yellow polymer contained approximately two azide groups ortho to ether and an average of 0.80 azide groups ortho to sulfone per polysulfone repeat unit. In this example, U, M, and D refer to the distribution of the ortho-sulfone azide, assuming there are two ortho-ether azide groups already present; i.e. U, M, and D represent di-, tri-, and tetraazide repeat units, respectively. ^{1}H-NMR PSf-(2 *o*-ether-N_3, *o*-sulfone-N_3)$_{(DS=3.0)}$: δ 8.20 (small d, H_d (D)), 8.11 (d, H_d (M)), 7.94 (d, $H_{d'}$ (M)), 7.87 (d, H_d (U)), 6.95−7.07 (m, $H_{a,b,c',e}$ and H_c (U)), 6.76 (bs, H_f), 6.65 (bd, H_c), 1.73 (s, 6H, $C(CH_3)_2$). Anal. Calcd for PSf-$N_{3(DS=3.0)}$ ($C_{27}H_{19}N_9O_4S$): C, 57.34; H, 3.39; N, 22.29; S, 5.67. Found: C, 57.65; H, 3.56; N, 21.03; S, 5.81.

Results and Discussion

Synthesis. Polysulfones were lithiated by two different routes. In the first method, Udel P3500 polysulfone (PSf) was reacted directly with *n*-butyllithium at reduced temperature, resulting in a THF-soluble intermediate containing up to two lithium atoms per repeat unit (degree of substitution or DS = 2) ortho to the sulfone linkage.[3,7] This chemistry, known as ortholithiation or directed metalation,[22] is highly regioselective because of the powerful directing ability of the sulfone group. The reaction is also rapid and virtually quantitative, such that the degree of lithiation on the polymer can be controlled by the molar ratio of *n*-butyllithium to polysulfone. In the second method, polysulfone was brominated to a DS of 2 on the bisphenol portion of the chain.[4] Treatment of the dibrominated polymer with *n*-butyllithium resulted in a lithium−halogen exchange reaction predominately, giving almost two lithium atoms ortho to the ether linkage and with a minor quantity of ortholithiation product.[4] We have recently found[23] that it is more difficult to obtain regioselectively functionalized polysulfones by lithiating polymers containing less than two bromine atoms per repeat unit. Bromine appears to deactivate the proximal ortho-sulfone site to ortholithiation, so that when the bromine DS = 2, only minor amounts of ortho-sulfone sites are lithiated. However, when the bromine DS < 2, there is competition for lithiation at both the halogen and ortho-sulfone sites (approximate ratio is 2:1). Lower temperatures (−70 °C) favor lithium−halogen exchange.

Organolithium compounds are well-known to react with azides to give 1,3-disubstituted triazenes.[17] These often labile triazenes are prone to fragmentation, giving azides, or can be readily hydrolyzed or reduced to amines. In our initial attempts to make polysulfone azides and triazenes, trimethylsilyl azide (TMSA) and (trimethylsilyl)methyl azide (TMSMA) were reacted with ortho-sulfone-lithiated polymers. TMSA was reactive to the lithiated polymer, but substitution of the azide group by the polymer occurred, analogously to a reaction reported by Wiberg et al.[24] Thus, lithiated polymer (DS = 1.1) with TMSA led to a polysulfone containing trimethylsilyl groups (DS = 0.67), identical to products obtained previously from lithiated polysulfone and chlorotrimethylsilane.[7] The elemental analysis of the product showed no nitrogen, indicating the absence of an azide. TMSMA has been reported previously as a useful reagent for preparing labile triazenes from aryllithium compounds which undergo hydrolysis under mild neutral conditions to arylamines.[18] The reaction of lithiated polysulfone (DS = 2) with TMSMA at −78 °C led to insoluble products or gels. A ^{1}H-NMR spectrum of the gel showed that a small amount of ortho-sulfone modification occurred and the presence of a methylsilyl or methylenesilyl functionality. Diphenylphosphoryl azide (DPPA) has been reported to react easily with aryllithium compounds to yield phosphoryltriazenes which can be reduced to arylamines.[25] The reaction of DPPA with lithiated polymers of various DS gave the expected phosphoryltriazene-substituted polysulfone according to eq 1.

However, the reaction with DPPA was somewhat prone to cross-linking, especially with polymers having

$$\mathrm{PSf{-}Li} + (\mathrm{C_6H_5O})_2\mathrm{P({=}O)N_3} \rightarrow \mathrm{PSfN{=}NNHP({=}O)(OC_6H_5)_2} \quad (1)$$

repeat units containing moderate amounts of lithium disubstitution (i.e., DS > 1.2). The reaction of DPPA with lithiated polysulfone (DS = 1.2) yielded a phosphoryltriazene derivative of DS ≈ 0.65. Derivatives obtained from lithiated polysulfones of DS ≤ 1.2 were soluble in chloroform. The polysulfone–triazene was decomposed to an amine using sodium hydroxide.[25]

Aryllithium compounds react with tosyl azide (TsN_3, *p*-toluenesulfonyl azide) to give sulfonyltriazenes, which are prone to fragment either to diazo compounds or to azides and sulfinates as shown in eq 2.

$$\mathrm{ArLi} + p\text{-}\mathrm{CH_3C_6H_4SO_2N_3} \rightarrow \mathrm{ArN{=}NNLiSO_2C_6H_4CH_3} \rightarrow \mathrm{ArN_3} + p\text{-}\mathrm{CH_3C_6H_4SO_2Li} \quad (2)$$

This reaction has been utilized to functionalize aromatic rings and heterocyclics with azide groups that are easily reducible to primary amines. Using tosyl azide sequentially as an electrophile, following ortholithiation of aromatic amides,[26,27] ethers,[27] tertiary amines,[27] and bithienyls,[28] ortho-substituted azide and amine groups were efficiently introduced.

We originally prepared tosyl azide by slowly adding an aqueous solution of sodium azide to a warm ethanol solution of *p*-toluenesulfonyl chloride following a procedure similar to Doering and DePuy.[19] Tosyl azide with about 20% impurity of ethyl tosylate was produced. In the reported procedure, we found warm ethanol was required to completely dissolve the reagent, and this led to side products. To avoid this impurity, a sodium azide solution was added rapidly in one lot to a stirred suspension of tosyl chloride in isopropyl alcohol at room temperature. Although we and others[29] have not experienced difficulty with tosyl azide, we advise caution in handling this compound because it has been reported to be shock sensitive.[21]

Azide-substituted polysulfones were prepared with TsN_3 from both ortho-sulfone-lithiated polymers and from ortho-ether-lithiated polymers. Figure 1 shows the reaction scheme for preparing the DS = 2 ortho-sulfone azide derivative from commercial Udel P3500 polysulfone. A cooled 5.5% solution of polysulfone **1** was lithiated with 2.15 equiv of *n*-butyllithium to give soluble viscous dilithiated intermediate **2**. Tosyl azide was added, presumably to give a labile intermediate sulfonyltriazene (eq 2), which fragmented to poly(sulfone azide) **3** upon aqueous workup. The pale yellow product **3** contains almost two azide groups ortho to sulfone per repeat unit. Using more concentrated solutions of **1** resulted in some insolubility of the azide product **3**. While excess tosyl azide was used to quench the lithiated polymer, a lesser amount may be required because the procedure was not optimized. Elemental analysis for nitrogen indicated the azide derivative had over 98% of the theoretical nitrogen content for repeat units of structure **3**. The polymer is soluble in $CHCl_3$, THF, and polar aprotic solvents and is photosensitive and thermally unstable. Poly(sulfone azides) with lower DS were readily prepared by using lower mole equivalents of *n*-butyllithium and gave products with the expected DS.

This reaction was equally effective on commercial Radel R5000 poly(aryl sulfone) **4a**, providing the diazide derivative **4c** from the lithiated intermediate **4b** as shown in Figure 2. The difference relative to **1** is its poor solubility in THF, thus requiring a more dilute solution for the lithiation step.

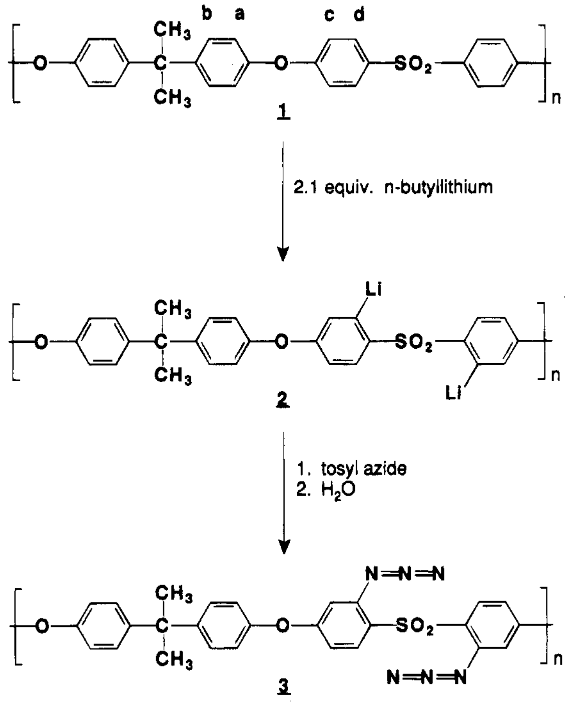

Figure 1. Reaction scheme for preparing the ortho-sulfone azide derivative **3** from commercial Udel P3500 polysulfone **1** via lithiated intermediate **2**.

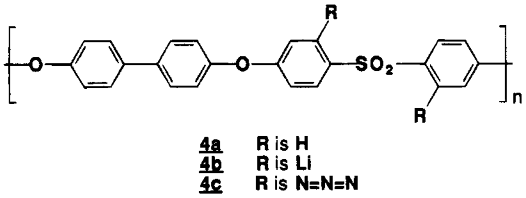

Figure 2. Structures of commercial Radel R5000 poly(aryl sulfone) **4a**, providing the diazide derivative **4c** from lithiated intermediate **4b**.

Ortho-ether poly(sulfone diazide) derivative was prepared by the route shown in Figure 3 from dibrominated polysulfone.[4] Dibrominated polysulfone **5** was lithiated with 2.15 equiv of *n*-butyllithium to give a soluble dilithiated intermediate **6** which was reacted with tosyl azide to give poly(sulfone azide) **7** upon aqueous workup. The product had a nitrogen content of 100.5% of the theoretical value for repeat units of the structure **7**. Product **7** is apparently more photosensitive than **3**. Ortho-ether azide polymers with DS < 2 were not made because when the bromine DS < 2, competition for lithiation at both the halogen and ortho-sulfone sites would lead to a polymer containing a variety of different repeat units. However, highly substituted azide polymer with DS > 2 could be made by treating **5** with 3.1 mol equiv of *n*-butyllithium. Once the bromine atoms are exchanged by lithium, the third mole of *n*-butyllithium lithiates the ortho-sulfone site to give a THF-insoluble trilithiated intermediate **8a** (Figure 4). After treatment of **8a** with tosyl azide, polymer **8b** had a high loading of azide (DS = 2.75 by NMR) on the polymer chain, slightly less than the theoretical DS of 3.0. Polymeric azide **8b** had a nitrogen content of 94.3% of the theoretical value of a triazide repeat unit, given a DS = 2.83 by elemental analysis. The polymer was

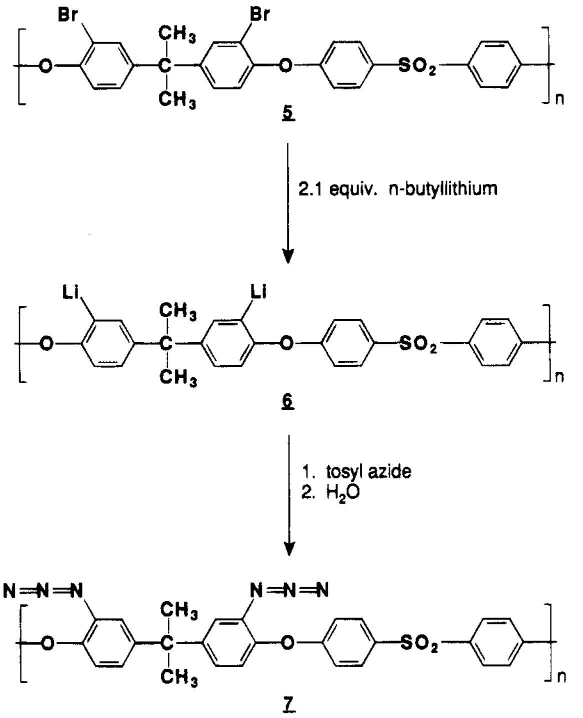

Figure 3. Reaction scheme for preparing DS = 2 ortho-ether azide derivative **7** from dibrominated polysulfone **5** via lithiated intermediate **6**.

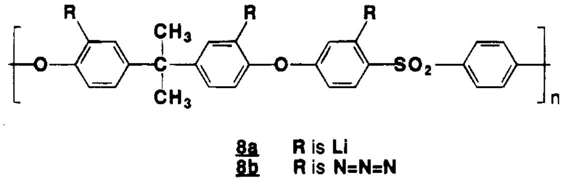

Figure 4. Structures of trilithiated intermediate **8a** and poly(sulfone triazide) **8b**.

particularly photosensitive and less thermally stable than any of the other polymeric azides. These examples demonstrate the high control of DS and regioselectivity of the ortholithiation process and the bromination–lithiation modification process in producing homopolymer type derivatives.

Structural Characterization. ^{1}H-NMR. Udel polysulfone **1** has an AA'XX' type aromatic spectrum composed of four doublets.[4,5] On the two bisphenol rings, ortho-ether protons (H_a, δ 6.94) are coupled to ortho-isopropylidene protons (H_b, δ 7.24), and on the two phenyl sulfone rings, ortho-ether protons (H_c, δ 7.00) are coupled to ortho-sulfone protons (H_d, δ 7.85). The latter protons are shifted downfield because of the deshielding effect of the sulfone group.

The diphenylphosphoryltriazene-substituted polysulfone from the reaction with DPPA gave a complicated spectrum as shown in Figure 5. Proton signals additional to the one at δ 7.85 in the deshielded ortho-sulfone region indicate substitution of functionality at that site. In addition, a large multiplet in the phenyl region is consistent with the presence of the diphenylphosphoryl residue.

By contrast, the spectrum of poly(sulfone diazide) **3** is simple and unambiguous (Figure 6a), resembling a homopolymer. The bisphenol protons H_a and H_b are little changed from the unmodified polymer. Protons H_c give a doublet of doublets, being both ortho-coupled ($J \approx 8.8$) to the deshielded H_d protons (2H) and meta-coupled ($J \approx 2.1$) to the H_e protons (2H). The H_d signal

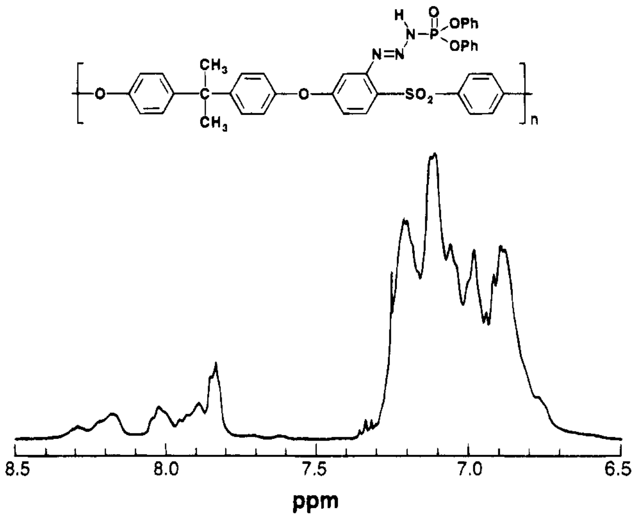

Figure 5. ^{1}H-NMR spectrum of diphenylphosphoryltriazene-substituted polysulfone from the reaction with DPPA.

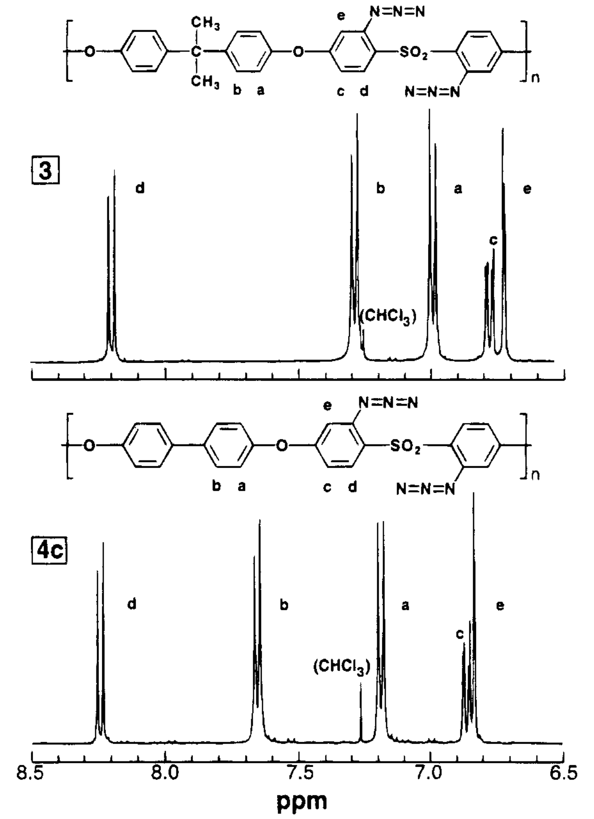

Figure 6. Comparative ^{1}H-NMR spectra (aromatic region) of ortho-sulfone azide derivatives of polysulfone **3** and of poly(aryl sulfone) **4c**.

from unmodified polymer is completely absent. The poly(aryl sulfone diazide) (**4c**) spectrum (Figure 6b) is very similar to that of **3**, indicating that virtually every repeat unit consists of the structure shown. Spectra of poly(sulfone azides) with DS < 2 are more complicated because of the presence of unsubstituted, monosubstituted, and disubstituted repeat units. The ratio among these three types of units for a given DS was previously determined for carboxyl-substituted polysulfones.[5] These three types of units are distinguished by the deshielded H_d protons in the poly(sulfone azide) DS = 1 derivative. Unsubstituted and disubstituted repeat units each have 4H and 2H doublets at δ 7.85 and 8.20, respectively. The monosubstituted units have two doublets: a 1H doublet at δ 8.10 arising from the ortho-sulfone proton

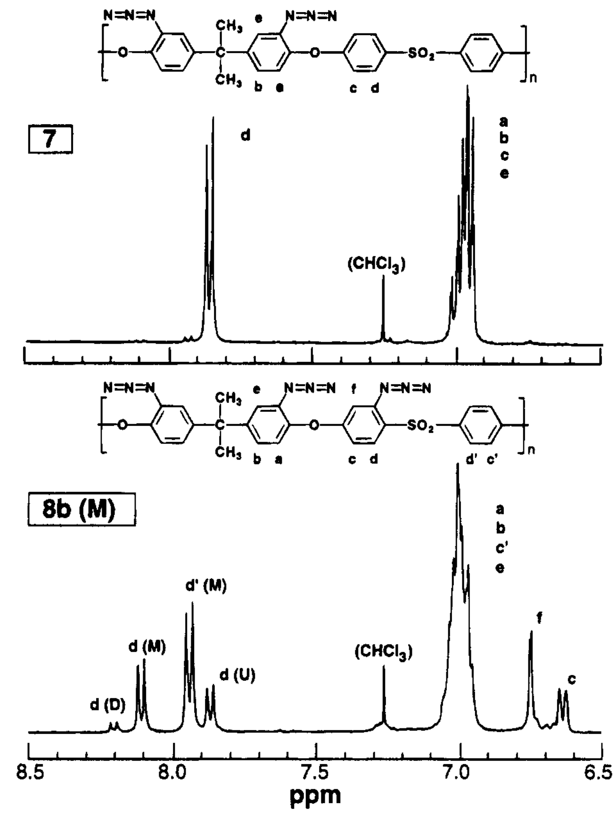

Figure 7. Comparative ^{1}H-NMR spectra (aromatic region) of ortho-ether poly(sulfone azide) **7** and of poly(sulfone triazide) **8b**.

on the phenyl azide and a 2H doublet at δ 7.92 from the ortho-sulfone protons on the phenyl without the azide.

The ortho-ether poly(sulfone azide) **7** was obtained from dibrominated polymer **5**. The spectrum of **5** has been described elsewhere.[4] The spectrum of **7** (Figure 7a) is distinctly different from that of **3**, having a 4H doublet arising from ortho-sulfone protons and a broad multiplet encompassing all the other proton signals. Only a trace amount of ortho-sulfone azide is apparent from the minor doublet at δ 7.92. A characteristic δ 7.52 H_e doublet of the brominated starting material **5** is entirely absent and the equivalent H_e in **7** is shifted upfield, presumably due to the shielding effect of the azide group.

The spectrum of triazide **8b** (DS = 2.75 by NMR) has four ortho-sulfone doublet signals (Figure 7b). A 4H doublet for H_d at δ 7.87, which is much reduced from that in spectrum **7**, corresponds to repeat units **7**. A 2H doublet at δ 7.94 and a 1H doublet at δ 8.11 correspond to repeat unit **8b** where the protons are in two different environments. A small 2H doublet at δ 8.20 is assigned to ortho-sulfone protons of a tetrasubstituted azide repeat unit. Two other signals of note are a meta-coupled doublet at δ 6.76 and a broadened doublet at δ 6.65.

^{13}C-NMR. We previously reported ^{13}C-NMR data for unmodified[4] as well as symmetrically substituted derivatives in both the bisphenol[4] and the aryl sulfone[5] portions of polysulfone. There are few data for aryl azides in the literature. The substituent effects in phenyl azide compared to benzene are +11.96 (C-1), −9.09 (C-2), +1.66 (C-3), and −3.26 (C-4), calculated from chemical shift values of phenyl azide reported by Denisov et al.[30] Shifts of −9.39 ppm (C-2), +1.35 ppm (C-3), and −3.56 (C-4) were derived from the values reported by Coulson.[31] The azide group is similar to a halogen in regard to its moderate inductive electron-withdrawing effect counteracted by a stronger mesomeric electron-donating effect and group polarizability.[15] Figures 8 and 9 show the respective ^{13}C-NMR spectra (aromatic region) of poly(sulfone azides) **3** and **7** along with the assigned chemical shifts.

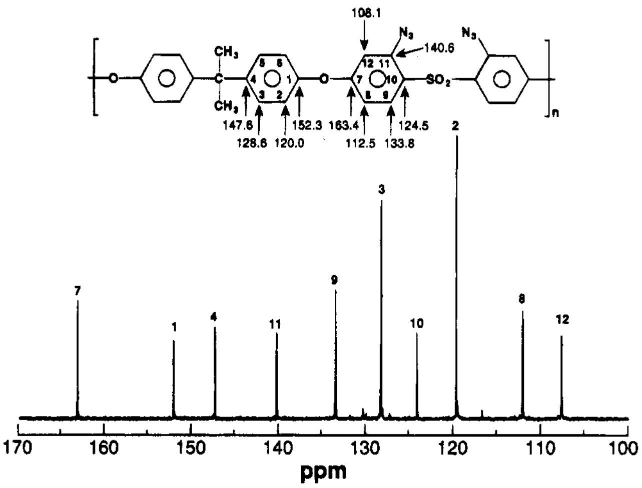

Figure 8. ^{13}C-NMR (aromatic region) and chemical shift assignments of poly(sulfone(ortho-sulfone)azide) derivative **3**.

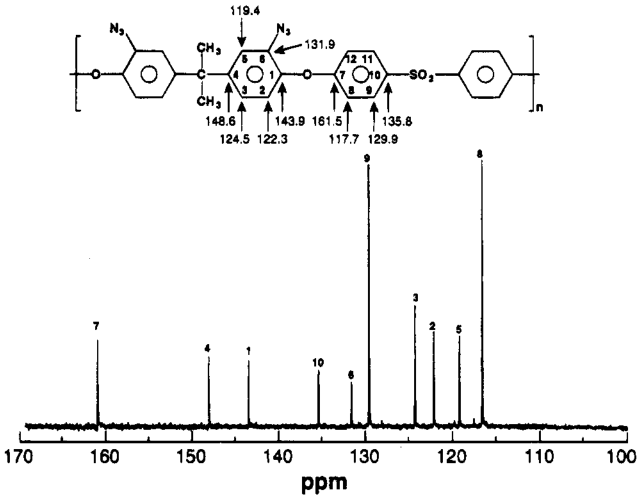

Figure 9. ^{13}C-NMR (aromatic region) and chemical shift assignments of poly(sulfone(ortho-ether)azide) derivative **7**.

The combination of one-bond (HETCOR) and three-bond long-range 2D heteronuclear correlation (LRHETCOR) techniques allowed full unambiguous assignment of ^{1}H- and ^{13}C-NMR spectra. The assignments obtained for azides **3** and **7** compare well with those shifts predicted using SIS data.[30,31] For azide **7**, the methyl resonance shows long-range correlations to two quaternary carbons, one being the methyl-bearing carbon and the other identified to be C-4. C-4 shows the expected correlation to H-2 which exhibits the three-bond coupling to C-6. C-2 was identified by the absence of any 7.5-Hz long-range couplings and the doublet structure within the proton spectrum. H-5 exhibits a long-range coupling to C-3. C-1 shows three-bond couplings, as expected, to both H-5 and H-3. The single quaternary carbon at low field, 161.5 ppm, exhibits the characteristic shift for a carbon adjacent to the oxygen in a polysulfone. Using this as a starting point and utilizing 7.5-Hz long-range correlations and direct one-bond correlations, the remainder of the second aromatic ring

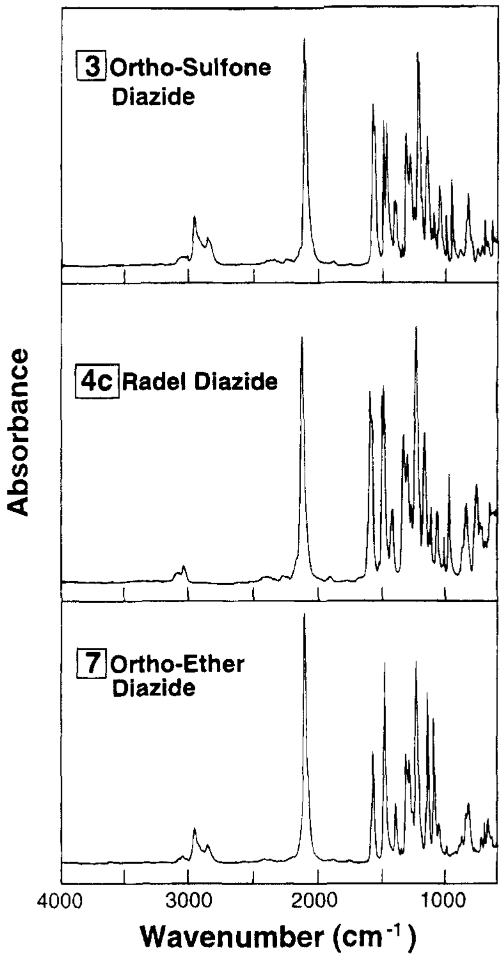

Figure 10. FTIR spectra of three diazide derivatives **3**, **4c**, and **7**.

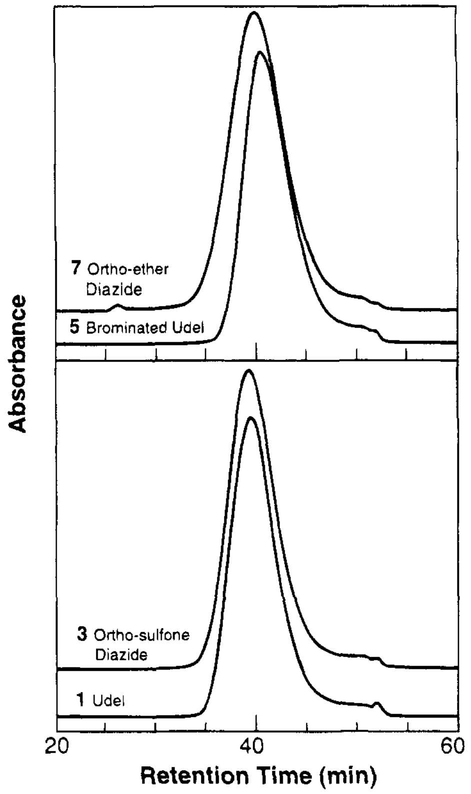

Figure 11. GPC profiles of Udel **1** and dibrominated Udel **5** compared with diazides **3** and **7**.

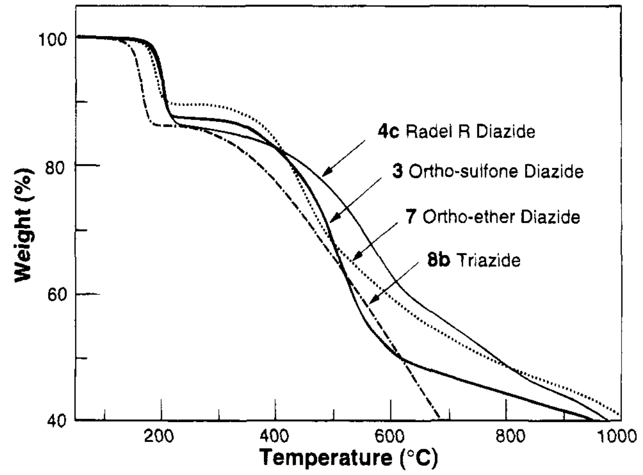

Figure 12. TGA curves of diazides **3**, **4c**, and **7** and triazide **8b**.

may be readily assigned. Using similar techniques for azide **3**, assignments were also made unambiguously.

Infrared. The FTIR spectra of diazide polymers **3**, **4c**, and **7** are shown in Figure 10. Azides give characteristic strong IR absorptions arising from asymmetric $-N{=}N{=}N$ stretching. The azide band was the strongest absorption at 2118, 2117, and 2116 cm^{-1}, respectively.

Gel Permeation Chromatography. The effect of ortho-sulfone and ortho-ether modification chemistry on molecular weight distribution was determined by GPC. Figure 11 shows the GPC profiles of starting materials Udel **1** and dibrominated Udel **5** compared with those of diazides **3** and **7**. Ortho-sulfone diazide **3** had a virtually identical profile to that of the starting material, showing that no changes in molecular weight distribution had occurred. In the case of the ortho-ether diazide **7**, there was a slight broadening of the peak, with the polydispersity increasing from 3.5 to 5.0. A minor amount of higher molecular weight polymer was evident from the slight tail before the main sample eluted. The slight change in molecular weight distribution had no apparent effect on the solubility. Radel R **4a** and diazide **4c** were not measured because of insolubility in THF. However, a soluble amine derived from the reduced azide had a molecular weight profile similar to that of Udel.[23]

Thermogravimetric Analysis. Organic azides are well-known to be thermally unstable. The initial thermal degradation product is generally a reactive intermediate nitrene arising from the loss of N_2. The diazide polymers exhibited similar profiles for two-stage decomposition as shown in Figure 12. Both initial extrapolated onsets for ortho-sulfone diazides **3** and **4c** occurred at 184 °C. Theoretical weight losses of 10.7% and 11.6% are expected for the loss of two molecules of nitrogen from diazides of structure **3** or **7** and **4c**, respectively. The experimental weight losses for ortho-sulfone azides **3** and **4c** were 12.4% and 13.9%, respectively, higher than the expected $-2N_2$ loss, suggesting additional degradation pathways. This anomalous higher weight loss was also observed for ortho-sulfone azide with DS = 1. For ortho-ether diazide **7**, initial extrapolated onset occurred at 176 °C with a weight loss of 10.5%, close to the theoretical value for the expected degradation. Triazide polymer **8b** was experimentally difficult to measure because of the tendency to lose material from the pan during explosive decomposition. A lower heating rate of 1 °C/min avoided this problem.

The initial extrapolated onset occurred at 148 °C with a weight loss of 13.8%. A polymer composed completely of repeat units **8b** would give an expected weight loss of 14.8% for $3N_2$. Experimentally, **8b** had a DS = 2.75 by ^{1}H-NMR and a DS = 2.83 by elemental analysis. Assuming the loss only of N_2 from each azide group, the DS of **8b** from the TGA decomposition is 2.80.

Conclusions

Modified polysulfones and poly(aryl sulfones) containing azide groups were prepared by a two-stage process of lithiation followed by quenching with tosyl azide. Although several other electrophilic azide or amine reagents were tested, only tosyl azide was found be highly effective in converting the lithiated polysulfone intermediates to azide derivatives without cross-linking. Polymers modified by direct lithiation led to highly regioselective azide substitution ortho to sulfone. By this route, homopolymer type products could be prepared containing two azide groups per repeat unit. Because of the near-quantitative nature of the direct lithiation chemistry, lower amounts of azide substitution were obtained simply by controlling the molar equivalent of the lithiating agent added to the polymer. Lithiation of dibrominated polysulfone resulted predominantely in a lithium–halogen exchange reaction leading to polymer with two azide groups in the bisphenol ring ortho to the ether linkage. This reaction was regioselective to this site, with only a minor amount of the competing ortho-sulfone product evident. Polysulfone containing close to three azide groups per repeat unit was obtained using 3 mol equiv of lithiating agent with the dibrominated polymer. The chemical structures of the polymeric azides were supported by ^{1}H- and ^{13}C-NMR measurements as well as IR and elemental analyses. Molecular weight distribution, measured by GPC, was unchanged from the starting material for the ortho-sulfone diazide and slightly broadened for the ortho-ether diazide. Thermal degradation of the polymeric diazides occurs in the range of 176–184 °C. Loss of N_2 from the azide groups leading to polymeric nitrenes is apparently the exclusive degradation pathway for the ortho-ether diazide and triazide polymers. This also appears to be the principal pathway for the ortho-sulfone diazide, but a slight additional nitrogen loss suggests a secondary degradation pathway. We are currently investigating the potential of reactive poly(sulfone nitrene) intermediates as a material for cross-linkable membranes. The efficient reduction of azides to polysulfone amines as well as the 1,3-dipolar cycloaddition reactions of the azides will be reported in separate publications.

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