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Reductive Dehalogenation versus Substitution in the Polyetherification of 4,4′-Dihalodiphenyl Sulfones with Bisphenolates†

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ABSTRACT: A competition between reductive dehalogenation and substitution in the polyetherification of 4,4′-dihalodiphenyl sulfones with bisphenolates is described. The polycondensations of 4,4′-dihalodiphenyl sulfones with *tert*-butylhydroquinone, 4,4′-isopropylidenediphenol (Bisphenol A), and 4,4′-oxydiphenol in the presence of excess K_2CO_3 in *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NMP) at 160 °C were investigated. The polycondensations of 4,4′-difluorodiphenyl sulfone, 4,4′-dichlorodiphenyl sulfone, and 4,4′-dibromodiphenyl sulfone with *tert*-butylhydroquinone result in high molecular weight polymers, whereas the polycondensation of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone affords a low molecular weight polymer which contains diphenyl sulfone chain ends. The polycondensations of 4,4′-diiododiphenyl sulfone with 4,4′-isopropylidenediphenol and 4,4′-oxydiphenol result in high molecular weight polymers. Only in the polyetherification of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone is reductive dehalogenation observed. The reductive elimination of iodide from the 4-iododiphenyl sulfone moiety to form a polymer containing diphenyl sulfone chain ends is proposed to occur by a single electron transfer (SET) mechanism, whereas the substitution of the halide by the phenolate occurs by a polar mechanism. The electronic and spatial properties of the 4,4′-dihalodiphenyl sulfone and bisphenolate govern the course of the reaction. These results suggest that the phenolate may act as both the nucleophile and the electron donor and can be rationalized in terms of two scenarios which describe the nature of the polar and SET pathways and their relationship to each other. One scenario views the polar and SET pathways as separate and distinct pathways with no common intermediates. The other scenario views the polar reaction as the concerted occurrence of single electron transfer and bond formation rather than a two-electron process, and consequently, the polar and SET pathways are very similar.

Introduction

Aromatic poly(ether sulfone)s and poly(ether ketone)s are frequently synthesized by an aromatic nucleophilic substitution reaction in which a bis(aryl halide), which is activated by a sulfone or carbonyl group, is condensed with a bisphenolate.[1] It is generally accepted that this aromatic nucleophilic substitution reaction proceeds via the S_NAr mechanism, which is shown in Figure 1.[2] In a previous communication on the synthesis of aromatic poly(ether ketone)s,[3] we showed that some polyetherifications of bis(aryl chloride)s activated by the carbonyl group were terminated at low molecular weights by the reductive elimination of chloride, which resulted in a polymer containing benzophenone chain ends. The occurrence of reductive elimination was found to be dependent on the structures of the aryl halide and bisphenolate, and the polymerization conditions, particularly the nature of the solvent and temperature. This paper demonstrates that bis(aryl halide)s activated by the sulfone group also undergo reductive elimination of the halide which results in low molecular weight polymers with diphenyl sulfone chain ends. As demonstrated previously in the synthesis of poly(ether ketone)s, the occurrence of reductive elimination in the synthesis of poly(ether sulfone)s is dependent on the structures of the bis(aryl halide) and bisphenolate, and the polymerization conditions. These results can be explained on the basis of a competition between polar and single electron transfer (SET) pathways.

Experimental Section

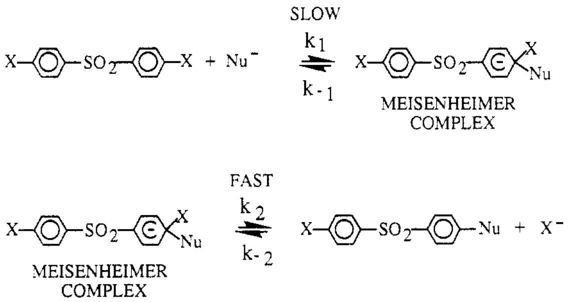

Figure 1. S_NAr mechanism of aromatic nucleophilic substitution.

Commercially available monomers which were used in the polyetherifications were purified as follows. 4,4′-Difluorodiphenyl sulfone (99%) was recrystallized from ethanol. 4,4′-Dichlorodiphenyl sulfone (98%) and 4-chlorophenyl phenyl sulfone (97+%) were treated with activated carbon in toluene and recrystallized from toluene. 4,4′-Isopropylidenediphenol (Bisphenol A, 97%) and *tert*-butylhydroquinone (97%) were recrystallized from toluene, the latter under nitrogen. All the preceding chemicals were purchased from Aldrich.

Materials used in the syntheses of 4,4′-dibromodiphenyl sulfone, 4,4′-diiododiphenyl sulfone, and 4,4′-oxydiphenol were used as received or purified as follows. 4-Bromobenzenesulfonyl chloride (98%), chlorosulfonic acid (99%), and $NaBF_4$ (97%) (all from Aldrich) were used as received. $NaNO_2$, CF_3COOH (99.8%), and concentrated HCl (37%) (all from Fisher Scientific) were used as received. Bromobenzene (Fisher Scientific) was vacuum distilled from CaH_2. Iodobenzene (Aldrich, 98%) was vacuum distilled prior to use. 4,4′-Oxydianiline (Aldrich, 97%) was recrystallized from ethanol.

N,N-Dimethylacetamide (DMAc, 99%) and *N*-methyl-2-pyrrolidone (NMP, 99%) (both from Aldrich) were vacuum distilled from P_2O_5. NMP was used within 1 week of distillation. Dimethyl sulfoxide (DMSO, Aldrich, 99+%) was vacuum distilled from CaO. Toluene was washed successively with concentrated

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† Dedicated to David A. Tirrell on the occasion of his 40th birthday.

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H_2SO_4, water, an aqueous solution of $NaHCO_3$ (5%), and water. Then it was dried over $MgSO_4$, and distilled from Na. Nitrobenzene (Aldrich, 99%) was vacuum distilled from CaH_2. K_2CO_3 (anhydrous, Fisher Scientific) was ground by mortar and pestle, and dried under vacuum at 130 °C for 2 days.

Synthesis of 4,4′-Dibromodiphenyl Sulfone. 4,4′-Dibromodiphenyl sulfone was synthesized by the Friedel–Crafts reaction of 4-bromobenzenesulfonyl chloride and bromobenzene according to a literature method[4] and recrystallized from ethanol: yield, 81.6%; mp, 171–172 °C (lit.[4] mp 171–173 °C); purity, 99.6%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.63 (d, 4H, J = 8.6 Hz, *m* to SO_2), 7.77 (d, 4H, J = 8.6 Hz, *o* to SO_2).

Synthesis of 4,4′-Diiododiphenyl Sulfone. 4,4′-Diiododiphenyl sulfone was synthesized by chlorosulfonation of iodobenzene using chloroform as solvent according to a literature procedure[5] and recrystallized from ethanol: yield, 72.3%; mp, 206–207 °C (lit.[5] mp 201–202 °C). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.61 (d, 4H, J = 8.6 Hz, *m* to SO_2), 7.87 (d, 4H, J = 8.6 Hz, *o* to SO_2).

Synthesis of 4,4′-Oxydiphenol. 4,4′-Oxydiphenol was synthesized from 4,4′-oxydianiline using a modified Sandmeyer method for the synthesis of phenols by the decomposition of aromatic diazonium tetrafluoroborate in refluxing trifluoroacetic acid containing potassium trifluoroacetate.[6] 4,4′-Oxydiphenol was recrystallized from acetone: yield, 57.1%; mp, 168 °C (lit.[7] mp 165–167 °C); purity, 99.2%. ^{1}H NMR (CD_3COCD_3, δ, ppm): 6.82 (m, 8H, aromatic protons).

Synthesis of Polyethers. Polymerizations were conducted by a conventional procedure which utilizes K_2CO_3 as the base to form the phenolate in situ.[8] All the polyetherifications were conducted with the same molar concentrations and heating schedule. A typical polymerization is as follows. A 25 mL, Pyrex, three-neck, round bottom flask equipped with a Dean-Stark trap, argon inlet–outlet, and magnetic stirrer was charged with 4,4′-dichlorodiphenyl sulfone (0.8615 g, 3.00 mmol), *tert*-butylhydroquinone (0.4987 g, 3.00 mmol), anhydrous K_2CO_3 (1.0200 g, 7.38 mmol), DMAc (6.0 mL), and toluene (3.0 mL). Argon was sparged through the reaction mixture with stirring for 20 min, and then the mixture was heated to 120 °C. The temperature of the reaction mixture was slowly raised over a 3-h period from 120 to 160 °C with argon sparging. Water generated from the formation of the phenolate was removed as an azeotrope with toluene. The reaction was maintained at 157–160 °C for 18 h under argon. Heating was accomplished with a silicone oil bath and hot plate. No special precautions were taken to exclude light from the polymerizations. The reaction mixture was allowed to cool, diluted with additional solvent, filtered to remove salts, acidified with acetic acid, and precipitated into water. The polymer was collected and dried, redissolved in DMAc, and again precipitated into water to ensure salt removal.

Model polymers with well-defined chain ends were synthesized by using an excess of the appropriate monomer. The *tert*-butylhydroquinone end-capped polymer was obtained from condensation of 4,4′-difluorodiphenyl sulfone with a 9% excess of *tert*-butylhydroquinone in DMAc. A sample was withdrawn after 6 h at 160 °C, and precipitated into water acidified with acetic acid. The diphenyl sulfone end-capped polymer was obtained by adding a solution of 4-chlorophenyl phenyl sulfone (50% excess) and toluene to the same polymerization mixture. The polymerization was continued for an additional 14 h at 160 °C. The polymer end capped with 4-chlorodiphenyl sulfone was obtained by condensation of *tert*-butylhydroquinone with a 9% excess of 4,4′-dichlorodiphenyl sulfone in DMAc.

Stability of 4,4′-Diiododiphenyl sulfone in the Absence of Bisphenolate. In order to determine the stability of 4,4′-diiododiphenyl sulfone under conditions in which the polyetherifications are conducted except for the absence of the bisphenolate, a mixture of 4,4′-diiododiphenyl sulfone (0.1716 g, 0.37 mmol), anhydrous K_2CO_3 (0.0232 g, 0.17 mmol), $KHCO_3$ (0.0731 g, 0.73 mmol), KI (0.0970 g, 0.58 mmol), DMAc (0.73 mL), and toluene (0.37 mL) was heated and sparged with argon in the same manner as described for the synthesis of the polyethers. After 18 h at 160 °C, the mixture was worked-up in the same fashion as described for the synthesis of the polyethers, except only one precipitation from DMAc into water was performed. Then the precipitate was collected by filtration and dried. 4,4′-Diiododiphenyl sulfone (0.1302 g, 75.9% based on the original amount of 4,4′-diiododiphenyl sulfone) was recovered. ^{1}H NMR analysis of the recovered product showed that no dehalogenation had occurred.

Addition of Nitrobenzene to Polyetherifications. Nitrobenzene (30 mol% based on 4,4′-dihalodiphenyl sulfone) was added to the polycondensations of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone and 4,4′-dichlorodiphenyl sulfone with *tert*-butylhydroquinone. The nitrobenzene was charged to the reaction flask with the monomers, K_2CO_3, DMAc, and toluene. These polyetherifications and the subsequent work-ups were performed in an analogous manner to the polyetherifications conducted in the absence of nitrobenzene (see Synthesis of Polyethers).

UV Irradiation of Polyetherification of 4,4′-Dibromodiphenyl Sulfone and *tert*-Butylhydroquinone. A polycondensation of 4,4′-dibromodiphenyl sulfone and *tert*-butylhydroquinone in DMAc was conducted in the same manner as described for the synthesis of the polyethers except the polyetherification was irradiated with UV light for 3 h. A 300-W UV lamp was placed outside and adjacent to the 25-mL Pyrex reaction flask, such that the light was directed at the top surface of the reaction mixture. Pyrex passes light with wavelengths greater than 290 nm. The entire setup was covered with tin foil. The reaction mixture was not irradiated for the initial 5 h. during which time the reaction mixture was slowly heated to 160 °C over a 3-h period and then held at 160 °C for 2 h. After 2 h at 160 °C, the UV lamp was turned on for 3 h and then turned off. The polyetherification was continued for an additional 13 h at 160 °C without UV irradiation. The work-up was the same as previously described for the synthesis of the polyethers.

Techniques. The purities of 4,4′-dibromodiphenyl sulfone, 4,4′-diiododiphenyl sulfone, and 4,4′-oxydiphenol were determined by high-pressure liquid chromatography (HPLC). Relative molecular weights of the polymers were determined by gel permeation chromatography (GPC). HPLC and GPC were carried out with a Perkin-Elmer Series 10LC instrument equipped with a LC-100 column oven, UV detector, and Nelson Analytical 900 series data station. HPLC measurements were performed with a PL gel column of 100-Å pore size and chloroform as solvent (1 mL/min, 40 °C). GPC measurements were performed with a set of PL gel columns of 500 and 10^4 Å pore size with chloroform as solvent (1 mL/min, 40 °C). Polystyrene standards were used for the calibration plot. The molecular weights were measured for polymers which had been precipitated from the polymerization solvent into water, and then from DMAc into water. The polymers contain a small percentage of low molecular weight cyclics, which appear at much greater elution times than the polymers in the GPC chromatographs. Only the main polymer peak, and not the cyclics, was used in the calculation of the number average molecular weight and polydispersity.

Polymer chain ends were determined by ^{1}H NMR spectroscopy. All the polymers were precipitated from chloroform into methanol, and the insoluble (higher molecular weight) fraction was collected, dried, and analyzed by ^{1}H NMR spectroscopy. The only exceptions are the polymers obtained from the polyetherifications in which nitrobenzene was added. These polymers were precipitated from DMAc into water, collected by filtration, dried, and analyzed by ^{1}H NMR spectroscopy. These polymers were not fractionated in methanol due to the low molecular weight oligomers obtained in the case of the polyetherification involving 4,4′-diiododiphenyl sulfone. ^{1}H NMR spectra of the polymers, 4,4′-dibromodiphenyl sulfone, and 4,4′-diiododiphenyl sulfone were acquired at 299.95 MHz on a Varian VXR-300 NMR spectrometer equipped with a 5-mm indirect detection probe. The spectra were obtained with a 5600-Hz spectral width, 2.926-s acquisition time, 6-μs 40° pulse, and 0-s relaxation delay. The number of transients varied with the sample. $CDCl_3$ was used as the solvent. The complete structural assignment of the ^{1}H NMR spectrum of the model polymer end-capped with *tert*-butylhydroquinone chain ends (synthesized with *tert*-butylhydroquinone in excess) required a 2-D COSY experiment to be performed. The 2-D COSY spectrum was acquired at 299.95 MHz on a Varian VXR-300 NMR spectrometer equipped with a 5-mm indirect detection probe. Phase-sensitive data were collected at ambient temperature without sample spinning using

Table I. Polyetherifications of 4,4′-Dihalodiphenyl Sulfones with Bisphenolates

	monomers			polymer				
						chain ends[c]		
polymer no.	halogen L.G.[a]	bis-(phenol)[b]	solvent	$M_n \times 10^{-3}$ (GPC)	M_w/M_n (GPC)	X	OH	H
1	F	TBH	DMAc	167.9	2.25			
2	Cl	TBH	DMAc	37.8	1.80			
3	Br	TBH	DMAc	36.8	2.15	Y	N	N
4	I	TBH	DMAc	8.9	1.70	N	N	Y
5	I	BPA	DMAc	39.8	2.50			
6	I	ODP	DMAc	58.5	1.97			
7[d]	Br	TBH	DMAc	7.2	2.23	N	Y	Y
8[e]	Cl	TBH	DMAc	5.0	1.70	Y	N	N
9[e]	I	TBH	DMAc	oligomers		N	Y	Y
10	Br	TBH	DMSO	15.0	2.04			
11	I	TBH	DMSO	5.7	1.99	N	Y	Y
12	F	TBH	NMP	77.9	2.89			
13	Cl	TBH	NMP	25.0	1.96	Y	N	N
14	Br	TBH	NMP	20.1	2.05	Y	N	N
15	I	TBH	NMP	5.8	1.95	N	Y	Y
16	Cl	BPA	NMP	50.4	2.40			
17	I	BPA	NMP	16.7	2.23	Y	Y	N

[a] L.G. = leaving group. [b] TBH = *tert*-butylhydroquinone, BPA = 4,4′-isopropylidenediphenol, ODP = 4,4′-oxydiphenol. [c] X = 4-halodiphenyl sulfone chain end, OH = bis(phenol) chain end, H = diphenyl sulfone chain end. Y = chain end present, N = chain end absent. [d] Polyetherification irradiated with UV light (see Experimental Section). [e] Nitrobenzene (30 mol % based on 4,4′-dihalodiphenyl sulfone) added to the polyetherification.

the method of States et al.[9] A total of 512 free induction decays (fid's) was acquired with a 20.5-μs 90° pulse, 0.665-s acquisition time (1024 points), 1-s relaxation delay, and 770-Hz spectral width in F_1 and F_2. Each fid was acquired with eight transients and eight dummy pulses for establishing the steady state. Data were processed on a Sun SPARCstation using VNMR software with zero filling (2× in F_2 and 4× in F_1) and shifted sinebell weighting. The ^{1}H NMR spectrum of 4,4′-oxydiphenol was acquired at 200 MHz on a Varian XL-200 spectrometer. Tetramethylsilane (TMS) was used as an internal standard, and chemical shifts (δ) are recorded in ppm from TMS.

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Results and Discussion

The molecular weights and chain ends of the polymers that were synthesized by the polyetherification of the 4,4′-dihalodiphenyl sulfones with the bisphenolates are presented in Table I. The chain ends of these polymers were determined by comparison of the ^{1}H NMR spectra of these polymers with the ^{1}H NMR spectra of the model polymers synthesized with well-defined chain ends (see Synthesis of Polyethers in Experimental Section) and the ^{1}H NMR spectra of the appropriate monomers. The chemical shifts of the model polymers and the 4,4′-dihalodiphenyl sulfone monomers are presented in Table II. Complete structural assignment of the model polymer end-capped with *tert*-butylhydroquinone chain ends required a 2-D COSY experiment to be performed. The 2-D COSY spectrum was acquired to assign the resonances from 6.90 to 6.96 ppm. The magnified 1-D ^{1}H NMR spectrum is shown in Figure 2c, and the 2-D COSY spectrum is shown in Figure 3. Key evidence for the structural assignment of the 6.90–6.96 ppm region to protons on rings 3 and 4 comes from examination of the traces at F_2 = 6.69 and 7.82 ppm in the 2-D COSY spectrum. Both proton resonances exhibit crosspeaks to proton resonances at 6.90–6.96 ppm. Examination of traces at these two F_2 positions reveals coupling to different, overlapping multiplets (proven by the different widths of the crosspeaks). The slice at F_2 = 7.82 ppm indicates coupling between resonances at 7.82 (7.80–7.85) and 6.90–6.96 ppm which arises from the A4 A4′ B4 B4′ spin system. The slice at F_2 = 6.69 ppm indicates coupling between proton resonances at 6.94 and 6.69 ppm which arises from the A3 B3 C3 spin system. Only *tert*-butylhydroquinone chain ends in which the *tert*-butyl substituent is ortho to the unreacted hydroxyl group have been observed. If *tert*-butylhydroquinone chain ends in which the *tert*-butyl substituent is meta to the hydroxyl group are present, their concentration is below the detection limit.

Table II. ^{1}H NMR Chemical Shifts of Model Polymers with Well-Defined Chain Ends, 4,4′-Dihalodiphenyl Sulfones, and Diphenyl Sulfone

protons[a]	chemical shift, δ (ppm)
A1 A1′	7.91–7.95
B1, C1 C1′	7.46–7.56
A3	6.94
B3, C3	6.64–6.70
A4 A4′	7.80–7.85
B4 B4′	6.90–6.96
B6 B6′	7.46
A8	7.11
B8, C8	6.82
A9 A9′, A10 A10′	7.85–7.90
B9 B9′, B10 B10′	6.98–7.04
A14 A14′	7.87
B14 B14′	7.61
A15 A15′	7.76
B15 B15′	7.63
A16 A16′	7.93
B16	7.55
C16 C16′	7.48

[a] See Figures 2, 7, 8, and 10 for the chemical structures which correspond to the letter–number designations.

The polycondensations of 4,4′-dihalodiphenyl sulfones with *tert*-butylhydroquinone in DMAc at 160 °C afforded poly(ether sulfone)s of high molecular weight (M_n > 35 000) when the leaving group was fluorine, chlorine, and bromine. However, when the leaving group was iodine, a low molecular weight polymer (M_n = 8900) was obtained. ^{1}H NMR analysis of the polymer formed from the condensation of 4,4′-diiododiphenyl sulfone and *tert*-butylhydroquinone established the presence of diphenyl sulfone chain ends. 4-Iododiphenyl sulfone and *tert*-butylhydroquinone chain ends were not present. The aromatic regions of the ^{1}H NMR spectra for this polymer, 4,4′-diiododiphenyl sulfone, a model polymer end-capped with diphenyl sulfone, and a model polymer end-capped with *tert*-butylhydroquinone are presented in Figure 2. 4,4′-Diiododiphenyl sulfone is a suitable model compound for the terminal group of a polymer end-capped with 4-iododiphenyl sulfone. Condensation of 4,4′-diiododiphenyl sulfone with 4,4′-isopropylidenediphenol (Bisphenol A) and 4,4′-oxydiphenol resulted in high molecular weight polymers. The polyetherifications of 4,4′-dibromodiphenyl sulfone and 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone were also conducted in DMSO. The results are similar to those obtained when DMAc was the solvent. A higher molecular weight polymer was obtained when 4,4′-dibromodiphenyl sulfone rather than 4,4′-diiododiphenyl sulfone was polycondensed with *tert*-butylhydroquinone. The use of 4,4′-diiododiphenyl sulfone resulted in a low molecular weight polymer which contained diphenyl sulfone chain ends.

The diphenyl sulfone chain end can be explained by either the thermolysis of the carbon–iodide bond[10] or a single electron transfer (SET) mechanism.[11a,b] Both these reaction mechanisms are more prominent when iodine is the leaving group. The relative rates increase in the order F < Cl < Br < I. This is opposite to the trend observed for the S_NAr mechanism in which the first step is rate limiting. In this case, the reactivity increases in the order

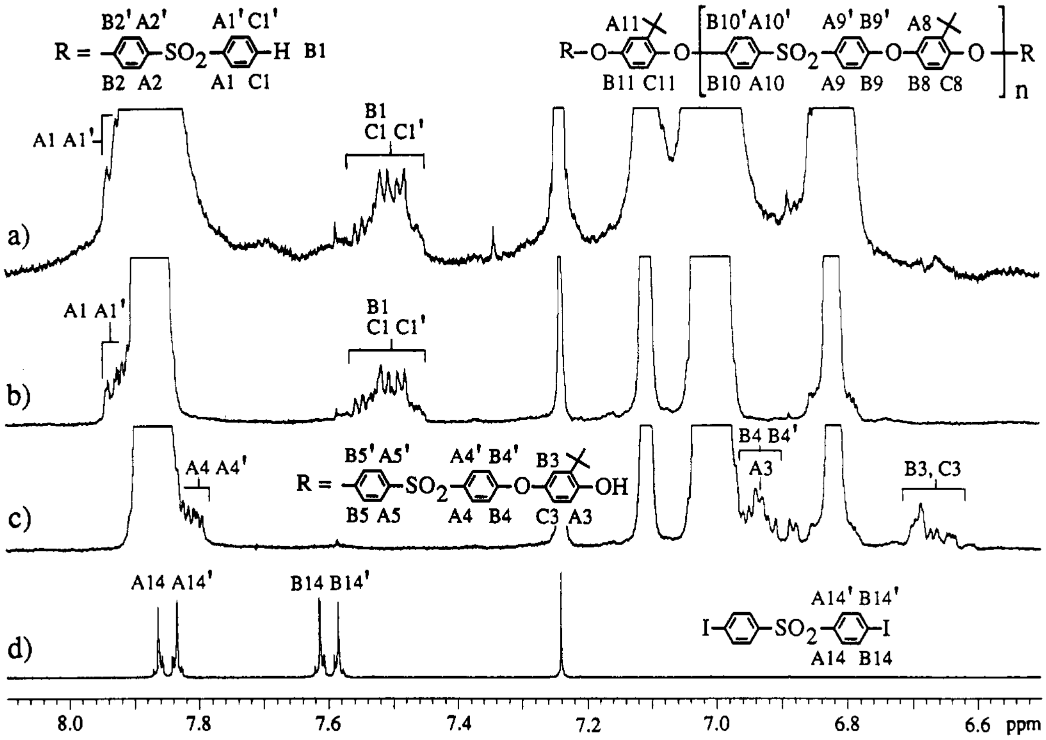

Figure 2. Comparison of the aromatic regions of the ^{1}H NMR spectra of (a) polymer from 4,4′-diiododiphenyl sulfone and *tert*-butylhydroquinone (polymer 4, see Table I), (b) model polymer end capped with diphenyl sulfone, (c) model polymer end capped with *tert*-butylhydroquinone, and (d) 4,4′-diiododiphenyl sulfone. The spectra show that polymer 4 contains diphenyl sulfone chain ends. The peaks which are off scale are due to the polymer backbone and chloroform (7.24 ppm).

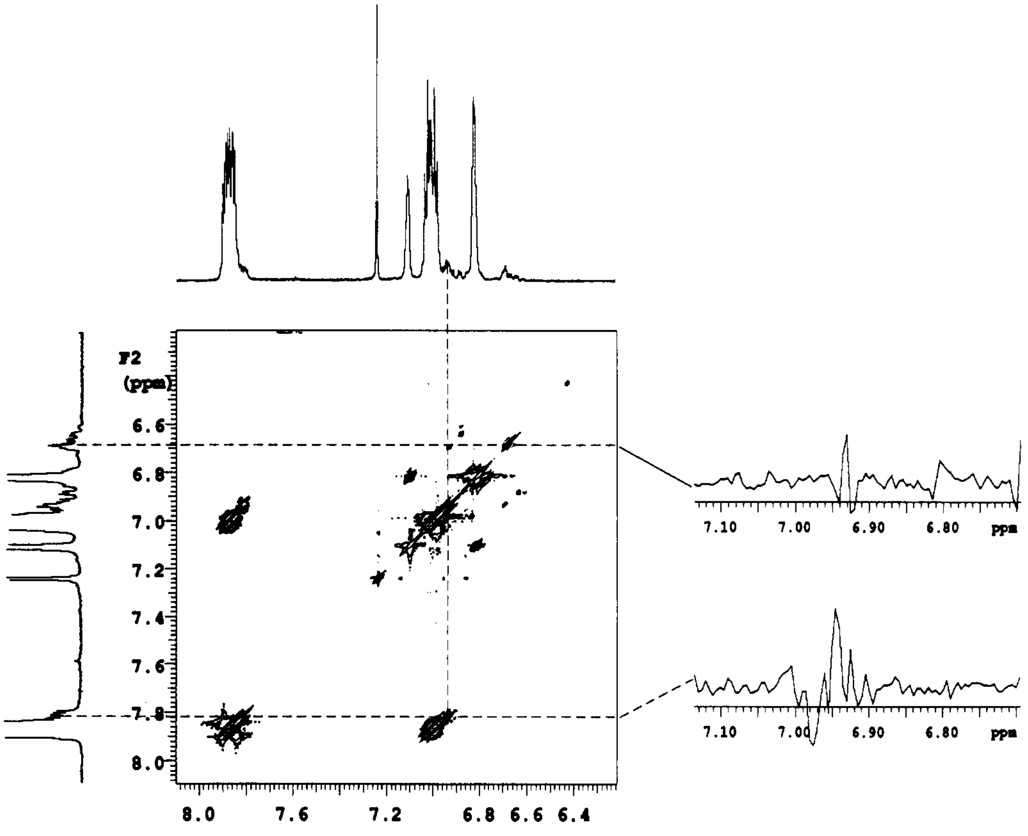

Figure 3. COSY 2-D NMR spectrum of the model polymer with *tert*-butylhydroquinone chain ends.

I < Br < Cl < F.[12] Thermolysis, or homolytic cleavage, generates a phenyl radical, which upon hydrogen abstraction from a hydrogen donor results in the diphenyl sulfone chain end. The other possible explanation for the generation of the diphenyl sulfone chain end is that it forms via a SET mechanism which is presented in Figure 4. In this mechanism, the 4-iododiphenyl sulfone moiety accepts an electron from an electron donor to form a radical anion. Then the radical anion decomposes to the phenyl radical and iodide ion. The phenyl radical can either abstract a hydrogen from a hydrogen donor, such as the solvent, or the phenyl radical can accept another electron and then

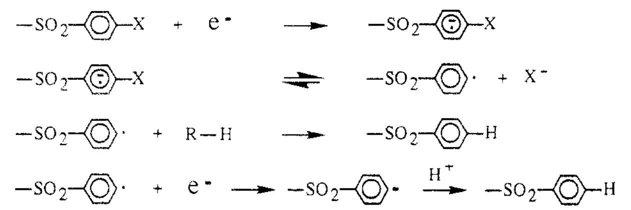

Figure 4. Formation of diphenyl sulfone chain end via a SET mechanism.

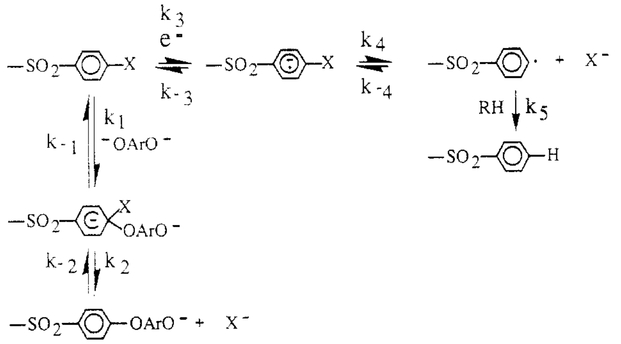

Figure 5. Proposed mechanism for the polyetherification of 4,4′-dihalodiphenyl sulfones with bisphenolates. In the polar pathway, the halide is displaced by the phenolate. The diphenyl sulfone chain end is formed via the SET pathway.

be protonated. Either step leads to the formation of the diphenyl sulfone chain end. All the steps in this mechanism are common to the $S_{RN}1$ mechanism.[11] However, not all the steps, specifically, most of the propagation steps, of a typical $S_{RN}1$ reaction are present in this mechanism.

To differentiate between thermolysis and a SET mechanism, 4,4′-diiododiphenyl sulfone was heated under conditions similar to those used in the polymerization, except that the phenolate was not present. 4,4′-Diiododiphenyl sulfone was heated with KI, $KHCO_3$, and K_2CO_3 in DMAc at 160 °C for 18 h. The reaction was worked-up in an identical manner as that of the polymerization. Only 4,4′-diiododiphenyl sulfone was recovered. No dehalogenation had occurred as determined by ^1H NMR spectroscopy. Therefore, thermolysis is not responsible for the formation of the diphenyl sulfone chain ends which are present in the polymer synthesized from 4,4′-diiododiphenyl sulfone and *tert*-butylhydroquinone.

A SET mechanism is proposed for the generation of the diphenyl sulfone chain ends. A general mechanism for this polyetherification is depicted in Figure 5. The activated aryl halide can either react with the phenolate to form the Meisenheimer complex via a polar reaction or accept an electron to form the radical anion via a SET reaction. In the polymerizations of 4,4′-dihalodiphenyl sulfones with *tert*-butylhydroquinone in DMAc, only 4,4′-diiododiphenyl sulfone underwent significant reductive elimination of the halogen. Use of 4,4′-difluorodiphenyl sulfone, 4,4′-dichlorodiphenyl sulfone, and 4,4′-dibromodiphenyl sulfone resulted in high molecular weight polymers. These results can be rationalized in terms of well-established trends in reactivity for the halogen nucleofuges in S_NAr and $S_{RN}1$ reactions. In S_NAr reactions, in which the aryl halide is activated toward nucleophilic attack by an electron-withdrawing group, the rate limiting step is typically the formation of the Meisenheimer complex. The rate constant, k_1 in Figure 5, decreases in the order F > Cl > Br > I for oxygen-based nucleophiles.[12] This is attributed to the electronegativity of the halogen. As the electronegativity increases, the electropositive character of the aromatic carbon bonded to the halogen increases, and the rate of nucleophilic attack increases. The transfer of a single electron to a substrate is more favorable for substrates that are easily reduced. Thus, k_3 increases in the order F < Cl < Br < I.[13] The rate constant for the decomposition of the radical anion of the aryl halide into the phenyl radical and halide ion, k_4, increases with decreasing carbon–halogen bond strength. Therefore, k_4 increases in the order F < Cl < Br < I.[11a,14] As the size of the halogen increases, steric hindrance to covalent bonding increases, and the SET pathway becomes more competitive.[15,16] All these trends indicate that the amount of reductive elimination of the halide relative to the amount of condensation between the aryl halide and the phenolate should increase in the order F < Cl < Br < I. The polycondensations of the 4,4′-dihalodiphenyl sulfones with *tert*-butylhydroquinone in DMAc are in accord with this expectation.

The source of the electron has not been established unequivocally. The fact that reductive elimination of iodide from the 4-iododiphenyl sulfone moiety does not occur in DMAc when the phenolate is not present and that the occurrence of reductive elimination is dependent on the chemical structure of the phenolate suggests that the phenolate is the electron donor. The other possible electron donors are the iodide anion, the Meisenheimer complex,[17] and species generated from the decomposition of the solvent. The iodide anion can be ruled out based on the results of the experiment previously described in which 4,4′-diiododiphenyl sulfone, KI, $KHCO_3$, and K_2CO_3 were heated at 160 °C for 18 h. The 4,4′-diiododiphenyl sulfone was unaffected by this treatment. The possibility that the Meisenheimer complex is the electron donor can be discarded since this does not account for the effect of the phenolate structure on the occurrence of reductive elimination. Also, the lifetime and steady-state concentration of the Meisenheimer complex are dependent on the leaving group of the electrophile. The lifetime and steady-state concentration of the Meisenheimer complex should decrease in the order F > Cl > Br > I. This is a consequence of k_1 being the smallest and k_2 the greatest (refer to Figure 1) when iodine is the leaving group. The possibility that products from the decomposition of the solvent act as the electron donors is viable, since reductive elimination is only observed in the case where the S_NAr reaction is slow. Therefore, the solvent is subjected to higher degrees of basicity for longer times since the phenolate remains in solution and does not condense with the aryl halide as quickly. However, the reductive elimination of iodide is not solvent specific. It occurs in DMAc, DMSO, and NMP. The only common reaction to all these solvents which produces a potential electron donor is the deprotonation of the carbon α to the electron-withdrawing group. However, the basicity of the reaction rules against this possibility, since the K_a of phenolates is approximately 15 orders of magnitude larger than the K_a of these carbanions.[18] While the generality of products from the decomposition of the solvent acting as electron donors seems unlikely, there may be specific cases where the solvent or a product derived from the solvent is the electron donor. This may be the case in some polyetherifications conducted in NMP.

We have found that polyetherifications conducted in NMP are quite sensitive to the dryness of the NMP and the polymerization temperature. Reductive dehalogenation in NMP is also very sensitive to these two parameters. In fact, unlike the behavior found in DMAc and DMSO, reductive dehalogenation of 4,4′-dichlorodiphenyl sulfone occurs in NMP with $KHCO_3$ at 180 °C. No phenolate is necessary. The results obtained from the polyetherifications conducted at 160 °C in NMP, which was freshly vacuum distilled from P_2O_5, are presented in Table I. The results are similar to those obtained for the polyetherifications conducted in DMAc and DMSO at 160 °C. Only the polymer obtained from the polycondensation of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone contained diphenyl sulfone chain ends. However, when NMP which was distilled over P_2O_5 and stored in a sealed container for 1 month was used as the solvent, polycondensations of 4,4′-difluorodiphenyl sulfone, 4,4′-dichlorodiphenyl sulfone, 4,4′-dibromodiphenyl sulfone, and 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone resulted in low molecular weight polymers. The polymers from the chloro, bromo, and iodo derivatives all contained diphenyl sulfone and *tert*-butylhydroquinone chain ends. The amount of *tert*-butylhydroquinone chain ends is greater than the amount of diphenyl sulfone chain ends. This contrasts the results obtained in the polycondensations of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone in DMAc, DMSO, and freshly dried NMP at 160 °C. In these cases, the polymer had predominantly diphenyl sulfone chain ends and no or very little *tert*-butylhydroquinone chain ends. We have observed similar results in the synthesis of poly(ether ketone)s. 4,4′-Dichlorobenzophenone undergoes reductive dehalogenation in even freshly dried NMP at 180 °C in the presence of $KHCO_3$, $NaHCO_3$, K_2CO_3, potassium *tert*-butoxide, or the potassium phenolate of 4,4′-isopropylidenediphenol. Reductive dehalogenation was also observed in freshly dried NMP at 160 °C in the presence of $KHCO_3$, while no reductive dehalogenation was observed in DMAc under identical conditions. 4,4′-Dichlorobenzophenone does not undergo reductive dehalogenation in NMP at 180 °C in the presence of KCl. The mechanism responsible for reductive dehalogenation in NMP is not known. Two different mechanisms may be operative. One involving electron transfer from the phenolate which is dominant in dry NMP at lower temperatures, and the other involving decomposition of NMP which is dominant at higher water contents and higher temperatures. The rate of hydrolysis of NMP to potassium 4-(*N*-methylamino)butanoate would be expected to increase with higher water contents and higher temperatures under basic conditions. However, a detailed investigation of the cause of the dehalogenation in NMP has not been undertaken. The apparent ability of aryl halides to undergo reductive dehalogenation in NMP may be significant in other reactions where NMP is the preferred solvent, such as in the synthesis of polyphenylene sulfide from *p*-dichlorobenzene and sodium sulfide. The mechanism of this polymerization is not completely agreed upon, and S_NAr,[19] $S_{RN}1$,[20] and cation-radical[21] mechanisms have been proposed.

All the experimental observations regarding the polyetherifications conducted in DMAc and DMSO at 160 °C support, but do not prove, the concept that the reductive elimination of iodode from the 4-iododiphenyl sulfone moiety occurs via a SET mechanism in which the 4-iododiphenyl sulfone moiety is the electron acceptor and the phenolate of *tert*-butylhydroquinone is the electron donor. The ability of aryl iodides to act as electron acceptors is well established.[11a,b,g,h,14b] The electron-withdrawing sulfone group enhances the ability of the aryl iodide to accept an electron. The ability of phenolates to act as electron donors toward inorganic oxidizing agents and their coupled quinones is well recognized.[22] Perhaps not as well-known is the single electron transfer between the dianion of 1,4-hydroquinone and nitrobenzene in which both the radical anions of nitrobenzene and hydroquinone were observed by ESR.[23] Also, 5-halogeno-2*H*,3*H*-benzo[*b*]thiophene-2,3-diones were reduced to their radical anions in the presence of phenoxide. The chloro, bromo, and iodo derivatives all underwent reductive dehalogenation.[24]

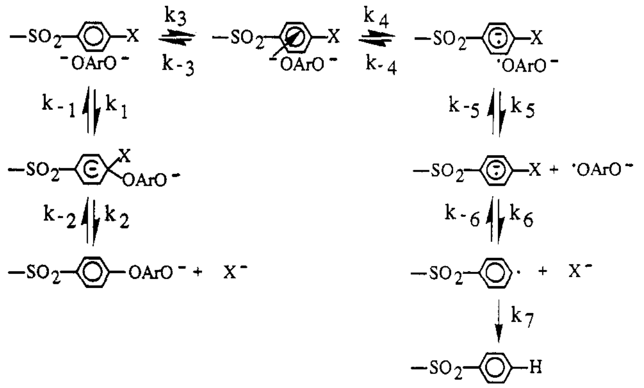

Figure 6. Proposed mechanism for the polyetherification of 4,4′-dihalodiphenyl sulfones with bisphenolates. The activated aryl halide can act as an electrophile or an electron acceptor. The phenolate can act as a nucleophile or an electron donor.

Incorporation of the phenolate as the electron donor into the mechanism is depicted in Figure 6. In the polyetherifications, the reactants can proceed either through a polar or SET pathway. In the polar pathway, the phenolate reacts with the aryl halide to form the Meisenheimer complex, which subsequently loses a halide anion to form the substitution product. In the SET pathway, the phenolate and aryl halide form a π complex. Within the π complex, the phenolate donates an electron to the aryl halide to form a charge transfer complex or radical anion–radical pair. The radical anion–radical pair dissociates into the radical anion of the aryl halide and phenoxy radical. Then the radical anion decomposes to the phenyl radical and the halide ion. The phenyl radical can abstract a hydrogen from a hydrogen donor, or it can accept an electron to form an anion which can be protonated, thus forming the unreactive diphenyl sulfone chain end.

In most organic reactions, the polar pathway is followed due to its lower free energy of activation, which is a consequence of bonding interactions. However, steric and electronic factors can cause the polar and SET pathways to become competitive.[16] As steric hindrance to bonding increases, the free energy of activation for the polar pathway approaches that of the SET pathway.[16] The ability to stabilize unpaired electrons (free radicals) also affects this competition. Electrophiles and nucleophiles with an even number of electrons result in species with an unpaired electron upon single electron transfer from the nucleophile to the electrophile. SET is more competitive when the electrophile and nucleophile are better able to stabilize unpaired electrons.[16] In the case of aromatic nucleophilic substitution between an activated aryl halide and phenolate, both reactants are able to stabilize an unpaired electron through resonance in the aromatic rings and, in some cases, through resonance with the electron-withdrawing group.

In the polyetherification of the 4,4′-dihalodiphenyl sulfones with the bisphenolates, the reaction pathway which is followed is dependent on the spatial and electronic properties of the reactants, and the reaction conditions. As discussed previously, in the polymerizations of 4,4′-dihalodiphenyl sulfones with *tert*-butylhydroquinone in DMAc, only 4,4′-diiododiphenyl sulfone underwent significant reductive elimination of the halide. Use of 4,4′-

difluorodiphenyl sulfone, 4,4′-dichlorodiphenyl sulfone, and 4,4′-dibromodiphenyl sulfone resulted in high molecular weight polymers. These results can be rationalized in terms of well-established trends in reactivity for the halogen nucleofuges in S_NAr and $S_{RN}1$ reactions.

The role steric hindrance plays in the competition between the polar and SET pathways is clearly demonstrated in the polyetherifications of 4,4′-diiododiphenyl sulfone with 4,4′-isopropylidenediphenol, 4,4′-oxydiphenol, and *tert*-butylhydroquinone in DMAc. In the polycondensations of 4,4′-diiododiphenyl sulfone with 4,4′-isopropylidenediphenol and 4,4′-oxydiphenol, polymers with number average molecular weights of 40 000 and 59 000, respectively, were obtained. However, polycondensation with *tert*-butylhydroquinone afforded a low molecular weight polymer (M_n = 8900) which had diphenyl sulfone chain ends. The polycondensation of 4,4′-diiododiphenyl sulfone with either 4,4′-isopropylidenediphenol or 4,4′-oxydiphenol proceds through the polar pathway. However, in the condensation of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone, the bulky *tert*-butyl group sterically hinders covalent bond formation between the aryl iodide and the phenolate. Thus, the free energy of activation of the polar pathway increases and approaches that of the SET pathway. Aryl iodides and phenolates which proceed via the SET pathway form the unreactive diphenyl sulfone chain end by reductive elimination of iodide from the aryl halide.

Electronic factors also play a very important role in the polycondensations of 4,4′-diiododiphenyl sulfone with 4,4′-isopropylidenediphenol, 4,4′-oxydiphenol, and *tert*-butylhydroquinone. One factor is that the oxidation potential for the removal of the first electron of the dianion of *tert*-butylhydroquinone is lower (easier to oxidize) than that of the dianions of 4,4′-isopropylidenediphenol and 4,4′-oxydiphenol. This is due to the fact that the two oxygen anions are para to each other on the same aromatic ring in *tert*-butylhydroquinone, whereas they are on separate aromatic rings in which conjugation between the rings is broken by the isopropylidene or oxygen linkage in 4,4′-isopropylidenediphenol or 4,4′-oxydiphenol. Dianions of hydroquinones are known to undergo one electron oxidation to their semiquinones.[25] The concentration of the dianion of *tert*-butylhydroquinone is dependent on the rate of deprotonation of the phenol by K_2CO_3 and the rate of condensation between the phenolate and aryl halide. Slower condensations may result in higher concentrations of the dianion.

Another important factor is that phenolates are ambident ions. The principal resonance forms place the negative charge on the oxygen atom and the carbon atoms ortho and para to the oxygen. Reaction at oxygen is usually favored since reaction at carbon requires the aromaticity to be destroyed as the reaction proceeds. The competition between C- and O-alkylation in S_N2 reactions has been studied and reported in the literature.[26-28] O-Alkylation is predominant; however three factors have been shown to increase the amount of C-alkylation. Bulky substituents ortho to the oxygen anion sterically hinder O-alkylation and, subsequently, increase C-alkylation.[26] Heterogeneous reactions conditions in which the phenolate is not totally solubilized favor C-alkylation.[27] The addition of species such as water, phenol, and trifluoroethanol which are capable of hydrogen bonding to the oxygen anion decrease the reactivity of the oxygen anion and increase the amount of C-alkylation.[28] In the case of *tert*-butylhydroquinone, the bulky *tert*-butyl group may give the phenolate significant carbanion character, and its chemistry may be similar to that of the enolates. This is of interest because enolates and iodobenzene[29] and enolates and diazines[30] are known to undergo $S_{RN}1$ reactions in the dark without any external source of electrons. The initiation is a thermal process, and it has been postulated that the enolate and iodobenzene form a charge transfer complex in which the enolate donates an electron to the iodobenzene.[31] Therefore, the *tert*-butylhydroquinone may be more predisposed to be an electron donor than 4,4′-isopropylidenediphenol and 4,4′-oxydiphenol.

The overall reaction rates of $S_{RN}1$ reactions which occur in the dark are increased by photostimulation.[29a,30,32] Photostimulation increases the rate of initiation. In the case of acetone enolate and iodobenzene, photostimulation has been shown to result in electron transfer between the acetone enolate and iodobenzene within an excited charge transfer complex.[31,32] The excited charge transfer complex decomposes to the radical anion of iodobenzene which then begins the propagation cycle.

Photostimulation of the polyetherification of 4,4′-dibromodiphenyl sulfone and *tert*-butylhydroquinone (see Experimental Section) in DMAc afforded a polymer with a number average molecular weight of 7200. ^{1}H NMR analysis of the polymer revealed the presence of diphenyl sulfone chain ends. This is in contrast to the polymer which results from the polycondensation of the same monomers without photostimulation. In the polycondensation without photostimulation, the resulting polymer has a number average molecular weight of 37 000, and no diphenyl sulfone chain ends were observed. The aromatic regions of the ^{1}H NMR spectra for these two polymers are presented in Figure 7. Photostimulation of the polycondensation increases the amount of electron transfer between the phenolate of *tert*-butylhydroquinone and the 4-bromophenyl sulfone moiety. This can occur by electron transfer within an excited charge transfer complex as discussed for acetone enolate and iodobenzene[31] or by photoejection of electrons from excited state anions.[32] Phenolates in aqueous solution are known to eject electrons upon irradiation with ultraviolet light.[33] Also, the aryl halide may be excited upon irradiation, and then the aryl halide in an excited state may accept an electron from a donor.[32,34] The products recovered from the polyetherification which was photostimulated included 14.9 wt % of a chloroform-insoluble material in addition to the polymer described above. This material was also insoluble in methanol and water. The insoluble material may be due to cross-linking. Cross-linking could occur by the carbon–carbon coupling of phenoxy radicals or carbon–carbon coupling of the 4-bromophenyl sulfone moiety and phenolate. Phenolates and aryl iodides and bromides have been shown to undergo carbon–carbon coupling upon photostimulation or electrostimulation.[35] The carbanion ortho or para to the oxygen anion of the phenolate displaces the halide of the aryl halide via a $S_{RN}1$ mechanism. These results are consistent with a mechanism in which photostimulation or electrostimulation initiates the reaction by forming the radical anion of the aryl halide. The radical anion then decomposes to the phenyl radical. The soft phenyl radical couples with the soft carbanion of the phenolate, rather than the hard oxygen anion, to form the radical anion of the carbon–carbon coupling product. Transfer of an electron from this radical anion to an aryl halide yields the carbon–carbon coupling product and the radical anion of the aryl halide, which starts the chain reaction over again. Besides the carbon–carbon coupling products, reductive dehalogenation has been observed in the case of the electrostimulated reaction of 4-bromoben-

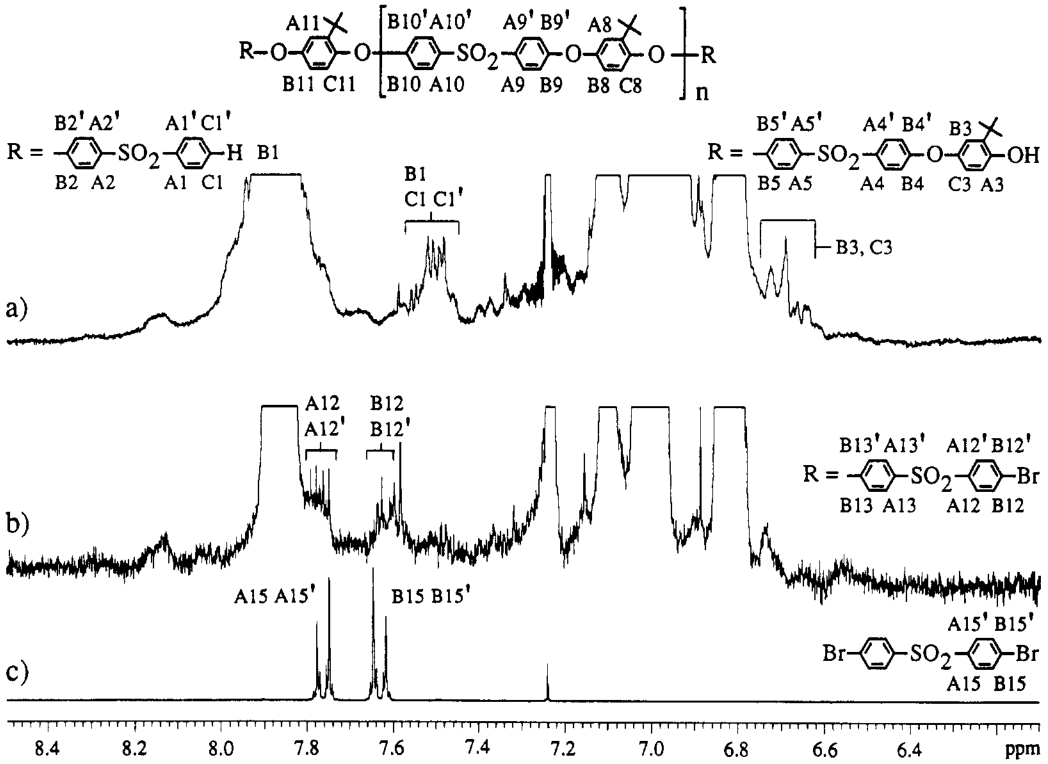

Figure 7. Comparison of the aromatic regions of the ^{1}H NMR spectra of (a) polymer from 4,4′-dibromodiphenyl sulfone and *tert*-butylhydroquinone irradiated with UV light (polymer 7, see Table I), (b) polymer from 4,4′-dibromodiphenyl sulfone and *tert*-butylhydroquinone (polymer 3, see Table I), and (c) 4,4′-dibromodiphenyl sulfone. The resonance at 7.24 ppm is due to chloroform.

zophenone with phenoxide.[35a] Both carbon–carbon coupling of phenoxy radicals or carbon–carbon coupling of the 4-bromophenyl sulfone moiety and phenolate could generate branch points in the soluble portion of the polymer. However, as of yet, analyses to prove or disprove these possibilities have not been undertaken.

Nitrobenzene is often used to inhibit reactions which involve single electron transfer to substrates which are weaker electron acceptors than nitrobenzene.[11e,h,36] However, the addition of nitrobenzene to these polyetherifications provides very unusual results. The addition of nitrobenzene (30 mol % based on 4,4′-diiododiphenyl sulfone) to the polyetherification of 4,4′-diiododiphenyl sulfone and *tert*-butylhydroquinone in DMAc increases the amount of reductive elimination of iodide at the expense of the condensation of 4,4′-diiododiphenylsulfone with the bisphenolate of *tert*-butylhydroquinone. Only oligomers were obtained. The ^{1}H NMR spectrum of the products from this polyetherification is presented in Figure 8 and shows the presence of a large amount of diphenyl sulfone chain ends. While this result is quite unusual, very similar results have been reported for the $S_{RN}1$ reaction of iodobenzene with pinacolone enolate in the dark without any external source of electrons.[29a] The reaction rate of this $S_{RN}1$ reaction is initially inhibited by the addition of nitrobenzene, but after an induction period, the reaction rate becomes greater than when nitrobenzene is not present.[29a] In this polyetherification, the role of nitrobenzene is not yet well understood. The effect of nitrobenzene is most probably due to its ability to act as an electron acceptor and is not likely due to a solvent effect since nitrobenzene is only 1.6% by volume in relation to DMAc. A possible explanation for the effect of nitrobenzene is depicted in Figure 9. Nitrobenzene is a better electrophile than the 4-iododiphenyl sulfone moiety, and consequently, more of the phenolate undergoes reaction with nitrobenzene. We expect that a Meisenheimer complex is formed and that the phenolate leaves to regenerate the starting nitrobenzene and phenolate. No direct evidence that a Meisenheimer complex is formed between the nitrobenzene and phenolate is available owing to the relative instability of this Meisenheimer complex. However, studies of the reaction of 1,3-trinitrobenzene with alkoxides indicate the formation of 2-Meisenheimer complexes.[37] The reaction of the phenolate with the nitrobenzene to form the Meisenheimer complex has no effect on the final reaction products since this pathway simply regenerates the phenolate and nitrobenzene. However, the nitrobenzene and phenolate can also form the radical anion of nitrobenzene and the phenoxy radical via a SET pathway. This is supported by the study of the interaction of the dianion of 1,4-hydroquinone and nitrobenzene by ESR.[23] Both the radical anions of nitrobenzene and hydroquinone were observed. Upon formation of the radical anion of nitrobenzene, an equilibrium involving electron transfer between nitrobenzene and the 4-iododiphenyl sulfone moiety is established. This equilibrium strongly favors the formation of the nitrobenzene radical anion ($k_{-10} > k_{10}$). However, once the 4-iododiphenyl sulfone radical anion forms, its decomposition to the phenyl radical and iodide ion is competitive enough with single electron transfer back to nitrobenzene to allow for extensive reductive elimination.

The addition of the same amount of nitrobenzene to the polyetherification of 4,4′-dichlorodiphenyl sulfone and *tert*-butylhydroquinone affords lower molecular weight polymer (M_n = 5000) than that obtained from the same polyetherification without the addition of nitrobenzene (M_n = 38 000). ^{1}H NMR analysis of the polymer (Figure 10) indicates the presence of the 4-chlorodiphenyl sulfone chain end. No diphenyl sulfone and *tert*-butylhydroquinone chain ends were observed. The higher molecular weight of this polymer compared to the oligomers obtained in the polyetherification of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone in the presence of nitrobenzene is simply due to the greater rate of condensation of

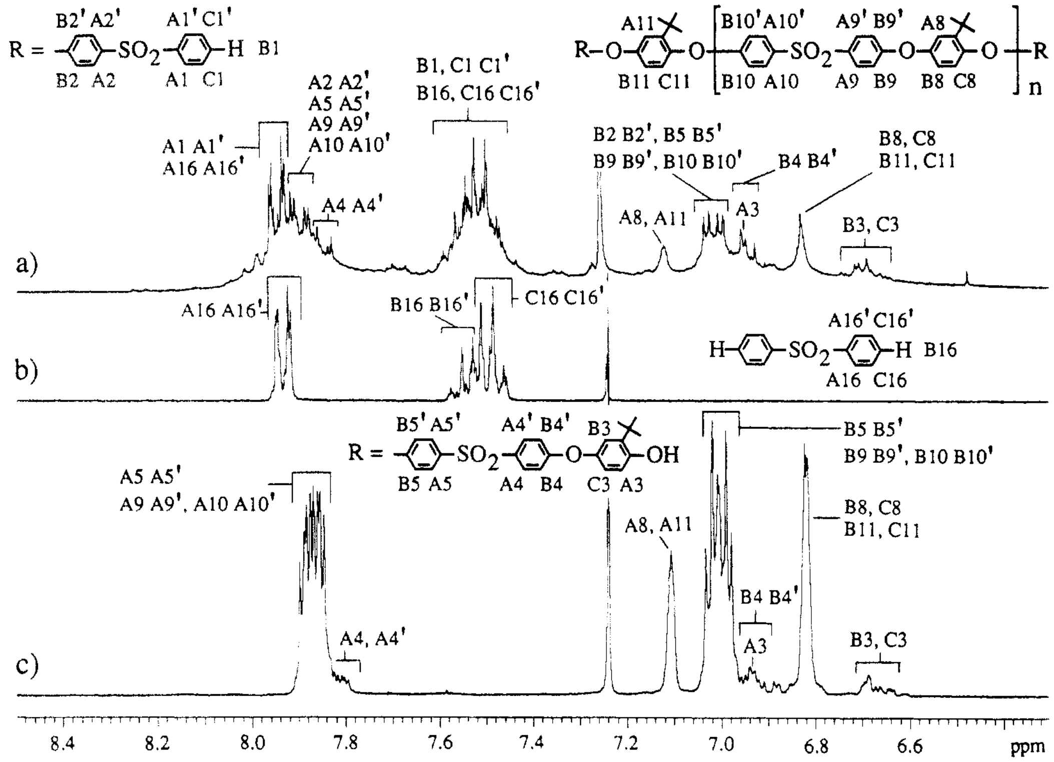

Figure 8. Comparison of the aromatic regions of the ^1H NMR spectra of (a) oligomers from 4,4'-diiododiphenyl sulfone and *tert*-butylhydroquinone with nitrobenzene (polymer 9, see Table I), (b) diphenyl sulfone, and (c) model polymer end capped with *tert*-butylhydroquinone. The resonance at 7.24 ppm is due to chloroform.

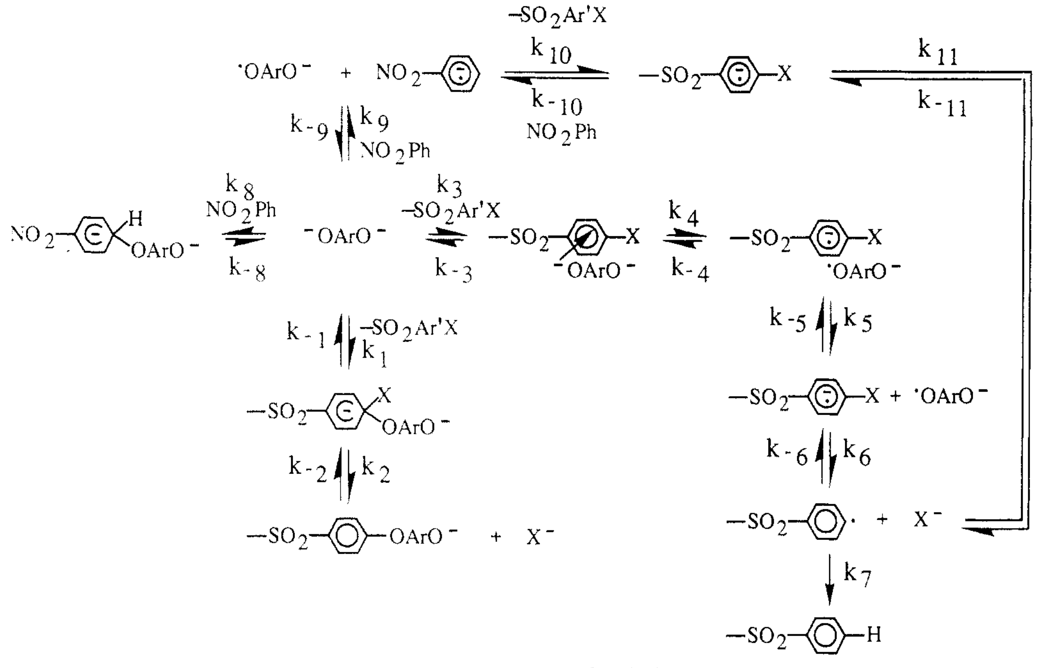

Figure 9. Role of nitrobenzene in the polyetherifications of 4,4'-diiododiphenyl sulfone with *tert*-butylhydroquinone and 4,4'-dichlorodiphenyl sulfone with *tert*-butylhydroquinone.

the 4-chlorodiphenyl sulfone moiety with the phenolate to form the Meisenheimer complex in comparison to the rate of condensation of the 4-iododiphenyl sulfone moiety with the phenolate. The molecular weight of the polymer formed from the polyetherification of 4,4'-dichlorodiphenyl sulfone and *tert*-butylhydroquinone in the presence of nitrobenzene is lower than the molecular weight of the polymer formed from the same monomers in the absence of nitrobenzene. This is due to the fact that some of the phenolate donates an electron to nitrobenzene to form the phenoxy radical and the radical anion of nitrobenzene. An equilibrium involving electron transfer between nitrobenzene and the 4-chlorodiphenyl sulfone moiety is established. The equilibrium strongly favors the formation of the nitrobenzene radical anion. Decomposition of the radical anion of the 4-chlorodiphenyl sulfone moiety is much slower than that of 4-iododiphenyl sulfone, and the electron is transferred back to the nitrobenzene before decomposition of the radical anion of the 4-chlorodiphenyl sulfone moiety can occur ($k_{-10} > k_{11}$). A small amount of 4-chlorodiphenyl sulfone chain ends is present due to the stoichiometric imbalance between the 4-chlorodiphenyl sulfone moiety and phenolate which develops as a result of the electron transfer from the phenolate to the nitrobenzene. The resultant phenoxy radical most likely undergoes further reactions, such as carbon–carbon cou-

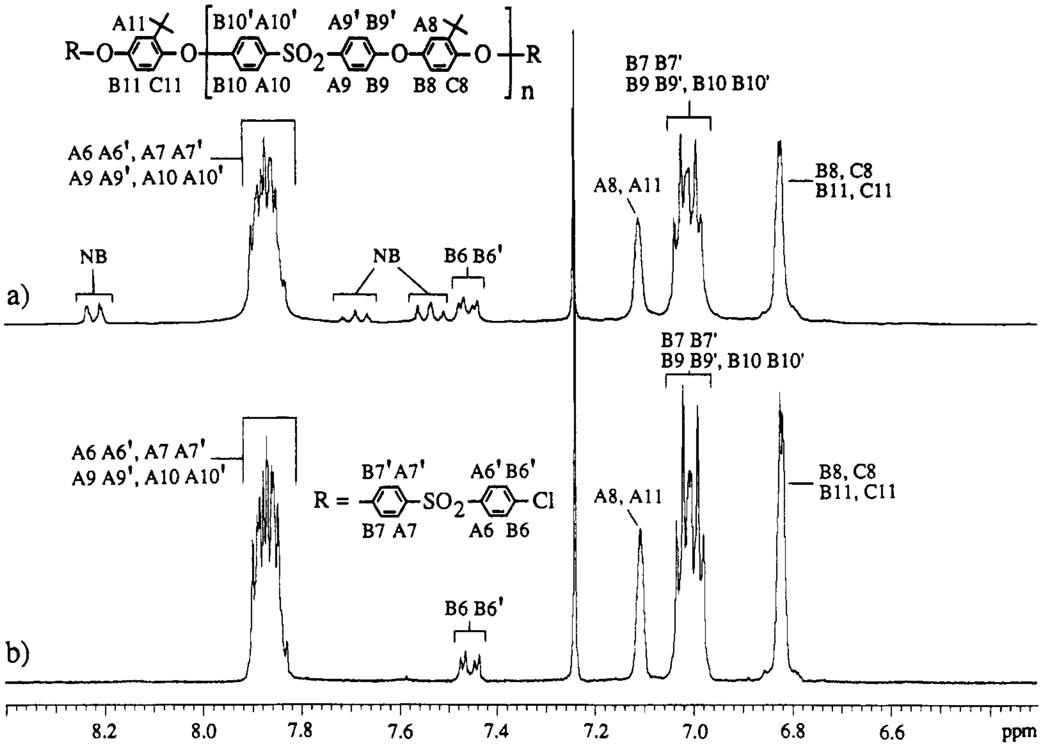

Figure 10. Comparison of the aromatic regions of the ^{1}H NMR spectra of (a) polymer from 4,4′-dichlorodiphenyl sulfone and *tert*-butylhydroquinone with nitrobenzene (polymer 8, see Table I), and (b) model polymer end capped with 4-chlorodiphenyl sulfone. NB indicates resonances due to nitrobenzene. The resonance at 7.24 ppm is due to chloroform.

pling with other phenoxy radicals.

The experimental results show that of the bisphenolates condensed with 4,4′-diiododiphenyl sulfone only *tert*-butylhydroquinone leads to reductive dehalogenation. *tert*-Butylhydroquinone differs from 4,4′-isopropylidenediphenol and 4,4′-oxydiphenol in that its dianion is oxidized much more easily than those of 4,4′-isopropylidenediphenol and 4,4′-oxydiphenol and that one of its oxygen anions is sterically hindered by the *tert*-butyl group. As was discussed previously, both these factors may shift the reaction of *tert*-butylhydroquinone with 4,4′-diiododiphenyl sulfone toward the SET pathway in relation to the reactions of 4,4′-isopropylidenediphenol and 4,4′-oxydiphenol with 4,4′-diiododiphenyl sulfone. However, the experimental results do not indicate whether only one factor or both are necessary for the occurrence of reductive dehalogenation. This raises the question of whether the dianion of *tert*-butylhydroquinone or the monoanion of the *tert*-butylhydroquinone chain end with the *tert*-butyl group ortho to the unreacted oxygen anion is the electron donor.

Eberson[38] has developed a treatment to test the feasibility that an organic reaction can occur via an outer sphere[39] single electron transfer process. A modified, and admittedly less accurate, version of this treatment was used to determine the feasibility that single electron transfer from a phenolate to the 4-iododiphenyl sulfone group can account for the formation of the diphenyl sulfone chain end. The dianion of *tert*-butylhydroquinone, the monoanion of the *tert*-butylhydroquinone chain end, and the dianion of 4,4′-isopropylidenediphenol were all considered. The error in this analysis is quite large; however the analysis does allow us to judge whether a reaction is at least feasible or if it is improbable.

The molecular weight and ^{1}H NMR characterization of the polymer formed from 4,4′-diiododiphenyl sulfone and *tert*-butylhydroquinone in DMAc indicate that approximately 4% of the 4-iododiphenyl sulfone groups have undergone reductive dehalogenation to form the diphenyl sulfone moiety. Assuming 4% conversion in 18 h, an apparent rate constant for the proposed SET reaction can be calculated using the rate equation

$$d[P]/dt = k_{\mathrm{appl}}[A][D] \tag{1}$$

where

[P] = concentration of diphenyl sulfone moiety

[A] = concentration of 4-iododiphenyl sulfone moiety

[D] = concentration of phenolate

Neglecting depletion of the 4-iododiphenyl sulfone moiety and phenolate by the polar pathway and assuming all the phenol is converted to phenolate and is in solution allows eq 1 to be solved easily and a minimum boundary is obtained for k_{appl}. Substituting eq 2 into eq 1 yields eq 4.

$$X = [P] \tag{2}$$

$$dX/dt = k_{\mathrm{appl}}([A]_0 - X)([B]_0 - X) \tag{3}$$

$$[A]_0 = [D]_0 = 1\ \mathrm{M}$$

$$dX/dt = k_{\mathrm{appl}}(1 - X)^2 \tag{4}$$

Solving eq 4 based on 4% conversion of the 4-iododiphenyl sulfone moiety to the diphenyl sulfone moiety in 18 h yields $k_{\mathrm{appl}} = 6.4 \times 10^{-7}\ \mathrm{M^{-1}\,s^{-1}}$. Thus, the apparent rate constant for the proposed SET reaction between the phenolate and the 4-iododiphenylsulfone moiety must be greater than $6.4 \times 10^{-7}\ \mathrm{M^{-1}\,s^{-1}}$.

The rate limiting step in the formation of the diphenyl sulfone chain end is assumed to be the single electron transfer from the phenolate to the 4-iododiphenyl sulfone moiety. As will be seen, this is a very reasonable assumption given the large free energy of activation for this step. Assuming the kinetic scheme shown in eq 5 in which the reactants diffuse together to form an encounter complex which then undergoes an electron transfer step

Table III. Reduction Potentials from the Literature

compound	E°_{red} (V vs SCE[a])	conditions	ref
diphenyl sulfone	−2.16	DMF	42a
4-bromophenyl methyl sulfone	−1.87	DMF	42a,b

[a] Saturated calomel electrode.

Table IV. Oxidation Potentials from the Literature

phenolate of	E°_{ox} (V vs SCE[a])	conditions	ref
tetramethylhydroquinone (dianion)	−0.44 to −0.59	$11 < pH < 13.5$ H_2O/pyridine	25
2,6-di-*tert*-butyl-4-methoxyphenol	−0.45	acetonitrile	43
2,4,6-tri-*tert*-butylphenol	−0.28	acetonitrile	43
2,6-di-*tert*-butylphenol	−0.19	acetonitrile	43
2,6-dimethylphenol	−0.07	acetonitrile	43

[a] Saturated calomel electrode.

with rate constant k_{el}, an expression for the observed or apparent rate constant, k_{app2}, can be formulated (eq 6).[38]

$$A + D \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [A\cdots D] \xrightarrow{k_{el}} \text{products} \tag{5}$$

$$k_{app2} = k_d/\{1 + C \exp[\Delta G^{\ddagger}/RT]\} \tag{6}$$

$$\text{where } C = (k_{-d}/k_d)(k_d/Z) \text{ and } Z = \text{collision frequency}$$

In the formulation of eq 6, the steady-state approximation was applied to [A···D], and k_{el} was put in terms of the free energy of activation, $\Delta G^{\ddagger}$, by use of the Eyring equation.[38,40] Eberson then substitutes the Marcus expression for the free energy of activation, eq 7, into eq 6.[38]

$$\Delta G^{\ddagger} = (\lambda/4)(1 + \Delta G^{\circ\prime}/\lambda)^2 + W \tag{7}$$

The Coulombic free energy term, W, is zero since the 4-iododiphenyl sulfone moiety is uncharged. Unfortunately, the reorganization free energy, λ, is unknown for the proposed SET process in these polyetherifications and therefore the Marcus expression was not used to determine the feasibility of the proposed SET process. However, a rough approximation of the free energy of activation, $\Delta G^{\ddagger}$, is that it is equivalent to the standard free energy change, ΔG°, under the prevailing reaction conditions. Note that the electrostatic free energy change upon transfer of the electron in the transition state is zero in the case of the monoanion of the phenolate and negligible in comparison to ΔG° in the case of the dianion of *tert*-butylhydroquinone, and thus $\Delta G^{\circ\prime} \approx \Delta G^\circ$. ΔG° is related to the reduction potential of the electron acceptor and the oxidation potential of the electron donor by eq 8.

$$\Delta G^\circ(\text{kcal mol}^{-1}) = -23.06[E^\circ_{red}(\text{V}) - E^\circ_{ox}(\text{V})] \tag{8}$$

Substituting ΔG° for $\Delta G^{\ddagger}$ and using typical values of 10^9 M^{-1} s^{-1} for k_d[38,41] and 0.2 for C,[38] eq 6 is converted to eq 9. Equation 9 was then used to estimate k_{app2} for potential SET reactions between 4-iododiphenyl sulfone moiety and the phenolates.

$$k_{app2} = 10^9/\{1 + 0.2 \exp[(-23.06(E^\circ_{red} - E^\circ_{ox}))/RT]\} \tag{9}$$

Since the reduction potential of the 4-iododiphenyl sulfone moiety and the oxidation potentials of the phenolates under conditions similar to the polyetherification are not available in the literature, we have chosen values based on the best available data from the literature for similar compounds. These data are available in Tables III and IV. The error in the values of k_{app2} determined by this method are quite large due to the approximations made in formulating eq 9 and the use of oxidation and reduction potentials which are not specific for the species and conditions present in the polyetherifications. The calculation only yields rough approximations of the apparent rate constant which are expected to be within a few orders of magnitude of the true value.

Table V. Estimated Standard Free Energy Change and the Estimated Apparent Rate Constant Associated with Single Electron Transfer from the Phenolates to the 4-Iododiphenyl Sulfone Moiety

phenolate of	ΔG° (kcal mol^{-1})	k_{app2} (M^{-1} s^{-1})
tert-butylhydroquinone (dianion)	31.1	$\approx 10^{-6}$
tert-butylhydroquinone chain end	41.5	$\approx 10^{-11}$
4,4′-isopropylidenediphenol (dianion)	41.5	$\approx 10^{-11}$

Using a value of −1.90 V for the reduction potential of the 4-iododiphenylsulfone moiety and oxidation potentials of −0.55, −0.10, and −0.10 V for the phenolates of *tert*-butylhydroquinone (dianion), *tert*-butylhydroquinone chain end (*tert*-butyl group ortho to the unreacted oxygen anion), and 4,4′-isopropylidenediphenol (dianion), respectively, yields estimates of the apparent rate constants for the potential SET reactions. These estimated rate constants appear in Table V. The only value of k_{app2} which is greater than the minimum boundary value of 6.4×10^{-7} M^{-1} s^{-1} is that for the SET reaction between the dianion of *tert*-butylhydroquinone and the 4-iododiphenyl sulfone moiety. The rate of electron transfer from the monoanion of the *tert*-butylhydroquinone chain end or the dianion of 4,4′-isopropylidenediphenol appears too slow to account for the formation of the diphenyl sulfone chain ends. *These calculations suggest that in the polyetherification of 4,4′-diiododiphenyl sulfone, the lower oxidation potential of the dianion of tert-butylhydroquinone is necessary for the occurrence of reductive dehalogenation.* However, the *tert*-butyl group also has an important role. Since it is electron donating, it lowers the oxidation potential of *tert*-butylhydroquinone. However, this effect is not as important as the resonance between the para oxygens in the hydroquinone structure.[25] Also, the *tert*-butyl group slows the polar pathway and helps solubilize the dianion.

The results of the polyetherifications of the 4,4′-dihalodiphenyl sulfones with the bisphenolates highlight the role spatial and electronic properties play in determining the balance between the polar and SET pathways. We feel the results can be rationalized in terms of two possible scenarios which describe the nature of the polar and SET pathways and their relationship to each other. One scenario views the polar and SET pathways as separate and distinct pathways with common starting reactants but no common intermediates. The other scenario views the polar reaction as the simultaneous occurrence, or nearly simultaneous occurrence, of single electron transfer and bond formation, and consequently, the polar and SET pathways are very similar in nature.

In the scenario in which the polar and SET pathways are separate and distinct, the polar pathway involves direct attack of the oxygen anion of the phenolate at the carbon bonded to the halogen leaving group to form the covalent bond. At not point in the polar reaction profile are radical or radical–anion species generated. In the SET pathway, an electron is donated from the phenolate to the π^* orbital of the aryl halide. We feel that the dichotomy represented by the polar and SET pathways can in some ways be related to hard soft acid base (HSAB) principles.[44] The hard oxygen anion of the phenolate prefers to react with a more electropositive carbon, which is bonded to the halogen, in the polar pathway. Whereas, in the SET pathway, perhaps the soft carbanion of the phenolate donates an electron to the soft π^* orbital of the aryl halide.

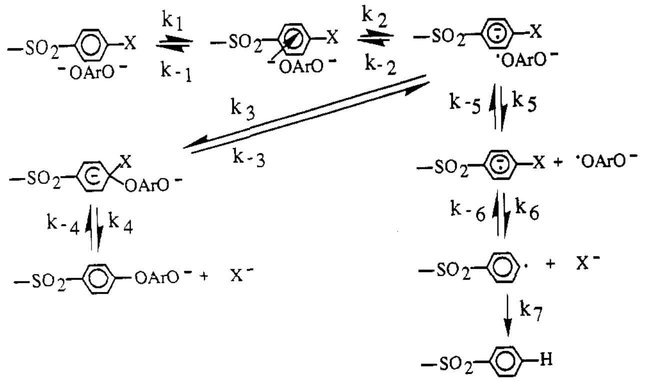

Figure 11. Mechanism illustrating the concept that substitution of the halide by the phenolate occurs via a single electron transfer to form the radical anion–radical pair and then coupling of this pair to form the Meisenheimer complex. Reductive dehalogenation requires dissociation of the radical anion–radical pair.

The other scenario views the polar reaction as the simultaneous occurrence of single electron transfer and bond formation. In regards to aromatic nucleophilic substitution, the concept of the nucleophile acting as an electron donor and the electrophile as an electron acceptor in a SET step is precedented. Several reactions have been shown to involve formation of free radicals by ESR or radical trapping experiments.[45] However, it has not been definitively established that these radical anions and radicals lie on the reaction pathway for the formation of the Meisenheimer complex. Some of the most compelling evidence in support of coupling of the radical anion–radical pair to form the Meisenheimer complex is the study of the reactions of some nitroarenes with hydroxide ion in DMSO/H_2O mixtures by stopped-flow spectrometry and NMR line broadening techniques.[46] The relationship between polar and SET pathways in organic chemistry has recently been addressed by Pross.[16] Application of these concepts to aromatic nucleophilic substitution is depicted in eq 10.

$$\underset{\text{reactant configuration}}{\mathrm{ArX} + \bar{:}\mathrm{Nu}} \rightarrow \underset{\text{product configuration}}{(\mathrm{ArX})^{\bar{\cdot}}\cdot\mathrm{Nu}} \qquad (10)$$

This reaction involves electron transfer or a single electron shift from the nucleophile to the electrophile. If bond formation between the nucleophile and electrophile and the single electron shift occur simultaneously, then the product configuration in eq 10 represents the Meisenheimer complex, and the reaction has proceeded via a polar pathway. In this context, the polar pathway is equivalent to an inner sphere SET pathway.[47] This view of the polar pathway is in contrast to the commonly held belief that two spin paired electrons of the nucleophile form the bond between the nucleophile and electrophile resulting in the formation of the Meisenheimer complex. Conversely, if the single electron shift occurs prior to or without bond formation, then the product configuration represents a radical anion–radical pair (change transfer complex), and the reaction has proceeded via a SET pathway. The radical anion–radical pair can couple in a subsequent step to form the Meisenheimer complex via a SET pathway, or the pair can dissociate into a radical anion and a radical. Application of this mechanistic view to the polyetherification of 4,4′-dihalodiphenyl sulfones with bisphenolates is depicted in Figure 11. Factors such as steric hindrance to coupling and the electronic properties of the radical anion and radical determine the partitioning of the radical anion–radical pair between collapse to the Meisenheimer complex and dissociation to the separated radical anion and radical.[16,46b,c] In this context, the formation of the Meisenheimer complex via the polar pathway is conceptually the same as its formation via the SET pathway. The only difference is that the delay between electron transfer and bond formation, and therefore the lifetime of the radical anion–radical pair, both approach zero in the polar pathway. In practice, a reaction is deemed polar or SET depending on our ability to detect free radicals. Therefore, a reaction is polar if bond formation occurs on a time scale too fast to allow detection of free radicals, or in other words the lifetime of the charge transfer complex approaches zero. Both views concerning the relationship between the polar and SET pathways are feasible. However, much more understanding of this relationship is needed before a more definitive explanation of the polyetherification mechanism can be offered.

Conclusion

The polycondensation of 4,4′-dihalodiphenyl sulfones with *tert*-butylhydroquinone in DMAc at 160 °C afforded poly(ether sulfone)s of high molecular weight when the leaving group was fluoride, chloride, and bromide. However, when the leaving group was iodide, a low molecular weight polymer was obtained. The polycondensation of 4,4′-diiododiphenyl sulfone with 4,4′-isopropylidenediphenol (Bisphenol A) and 4,4′-oxydiphenol resulted in high molecular weight polymers. The results were similar in DMSO and NMP at 160 °C.

The low molecular weight polymer obtained from 4,4′-diiododiphenyl sulfone and tert-butylhydroquinone contained diphenyl sulfone chain ends. A SET pathway has been proposed for the formation of the diphenyl sulfone chain end. The addition of nitrobenzene to the polyetherification of 4,4′-diiododiphenyl sulfone with *tert*-butylhydroquinone and the UV irradiation of the polyetherification of 4,4′-dibromodiphenyl sulfone with *tert*-butylhydroquinone enhance the amount of reductive dehalogenation. These results are similar to those reported in the literature for the thermally initiated $S_{RN}1$ reactions between enolates and iodo- and bromobenzenes.[29a] *The source of the electron in the proposed SET pathway for these polyetherifications has not been unequivocally established. However, all the data support the concept that the dianion of tert-butylhydroquinone is the electron donor in the polyetherification of 4,4′-diiododiphenyl sulfone with tert-butylhydroquinone in DMAc and DMSO at 160 °C.* Unlike the polyetherifications in DMAc and DMSO, polyetherifications conducted in NMP are complicated by the fact that reductive dehalogenation can occur in the absence of the phenolate.

We propose that in the polyetherification of 4,4′-dihalodiphenyl sulfones and bisphenolates in DMAc and DMSO at 160 °C, a competition exists between polar and SET pathways. The polar pathway leads to the displacement of the halide by the oxygen anion of the phenolate and, as such, represents continuation of the step growth polymerization. The SET pathway leads to the formation of a radical anion–radical pair, which upon dissociation eventually leads to the formation of diphenyl sulfone chain ends. The formation of the diphenyl sulfone chain ends terminates the chain growth. The electronic and spatial properties of the aryl halide and bisphenolate govern the balance between the polar and SET pathways.

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