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Reductive Dehalogenation vs Substitution in the Polyetherification of Bis(aryl chloride)s Activated by Carbonyl Groups with Hydroquinones: A Potential Competition between SET and Polar Pathways

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ABSTRACT: Aromatic poly(ether ketone)s are frequently synthesized by nucleophilic substitution of the halide of a bis(aryl halide) by a bisphenolate. The bis(aryl halide) is activated toward nucleophilic attack by a carbonyl group. When the bisphenol is hydroquinone, bis(aryl fluoride)s afford high molecular weight polymers, whereas bis(aryl chloride)s often yield low molecular weight polymers. This paper demonstrates that bis(aryl chloride)s and hydroquinones can be condensed to produce high molecular weight polymers. The ability to obtain high molecular weight polymers from bis(aryl chloride)s is dependent on the structure of the bisphenolate and the reaction conditions. The molecular weight that can be achieved in the polyetherification of bis(aryl chloride)s with hydroquinone or substituted hydroquinones can be limited by the occurrence of reductive dehalogenation. Reductive dehalogenation has not been observed in the condensation of bisphenolates which are weaker electron donors (*i.e.*, have less negative oxidation potentials) than the dianion of hydroquinone, such as the bisphenolates of 4,4′-isopropylidenediphenol (Bisphenol A or BPA), 4,4′-oxydiphenol (ODP), 1,1-bis(2-methyl-4-hydroxy-5-*tert*-butylphenyl)ethane (MHBPE), *etc.*, with bis(aryl chloride)s under identical conditions to those used in the polyetherifications involving the hydroquinones. These results strongly suggest that reductive dehalogenation is due to single electron transfer (SET) from the dianion of hydroquinone (or substituted hydroquinones) to the 4-chlorobenzophenone moiety. In many cases, the molecular weights of the polymers synthesized from bis(aryl chloride)s and hydroquinones are not determined by the reactivity of the monomers but by their selectivity. The factors that govern the selectivity between aromatic nucleophilic substitution and reductive dehalogenation are discussed.

Introduction

The aromatic nucleophilic substitution reaction that is used in the synthesis of aromatic poly(ether ketone)s and poly(ether sulfone)s[1] is considered to proceed through an S_NAr mechanism[2] (Figure 1). Bis(aryl halide)s activated by the carbonyl group provide high molecular weight polymers when fluorine is the leaving group and often provide low molecular weight polymers or polymers that contain aberrant structures such as branching when chlorine is the leaving group.[1a,d,3] It is well-established that in S_NAr reactions, the rate constant for substitution of fluorine is much greater than that for chlorine.[4] If the low molecular weight polymers obtained with chlorine are due solely to the lower reactivity of chlorine in relation to fluorine, then it should be possible to produce higher molecular weight polymers from bis(aryl chloride)s at longer reaction times than those used in the polyetherification of bis(aryl fluoride)s. This report will demonstrate that high molecular weight polymers are not always obtainable by simply increasing the reaction time and that in some polymerizations involving hydroquinones as the bisphenolates, the propagating aryl chloride chain is terminated by reductive elimination of chloride which leads to a benzophenone chain end. The extent of reductive elimination for a given pair of electrophilic and nucleophilic monomers is determined by the nature of the solvent and the polymerization temperature. An attempt to explain the aromatic nucleophilic substitution and the reductive dehalogenation reactions based on a competition between polar and single electron transfer (SET) pathways is presented.

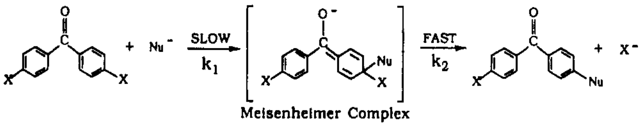

Figure 1. S_NAr mechanism of aromatic nucleophilic substitution.

This paper is an extension of a preliminary communication[5] on the same subject and also compliments our investigations on the mechanism of the polyetherification of 4,4′-dihalodiphenyl sulfones with bisphenolates.[6]

Experimental Section

Commercially available monomers which were used in the polyetherifications were purified as follows. 4,4′-Difluorobenzophenone (DFB, Lancaster Synthesis, 98+%) was used as received. 4,4′-Dichlorobenzophenone (DCB, Aldrich, 99%) was recrystallized from an *n*-hexane/ethanol (70/30 v/v) mixture. 4,4′-Dibromobenzophenone (DBB, Lancaster Synthesis, 98+%) was recrystallized from ethanol. 4,4′-Isopropylidenediphenol (BPA, Bisphenol A, Aldrich, 97%) and *tert*-butylhydroquinone (TBH, Aldrich, 97%) were recrystallized from toluene. The latter was recrystallized under N_2. Hydroquinone (HQ, Aldrich, 99%) was recrystallized from acetone under N_2.

Materials used in the syntheses of 1,3-bis(4-chlorobenzoyl)benzene (1,3-CBB), 1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB), 1,3-bis(4-chlorobenzoyl)-5-*tert*-butylbenzene (1,3-CBTBB), 1,3-bis(4-fluorobenzoyl)-5-*tert*-butylbenzene (1,3-FBTBB), 1,3-bis(benzoyl)-5-*tert*-butylbenzene, 4,4′-oxydiphenol (ODP), 1,1-bis(2-methyl-4-hydroxy-5-*tert*-butylphenyl)ethane (MHBPE), and tetraphenylhydrazine were used as received or purified as follows. 5-*tert*-Butyl-*m*-xylene (98%), 2-*tert*-butyl-5-methylphenol (95%),

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acetaldehyde (99%), $KMnO_4$ (97%), $SOCl_2$ (97%), and $NaBF_4$ (97%) (all from Aldrich) were used as received. Anhydrous $AlCl_3$, pyridine, concentrated HCl (37%), $NaNO_2$, and trifluoroacetic acid (99.8%) (all from Fisher Scientific) were used as received. Diphenylamine (J. T. Baker, reagent grade) and acetic acid (Mallinckrodt, glacial) were used as received. Isophthaloyl dichloride (Aldrich, 98%) was stirred with $SOCl_2$ for 5 h at 60 °C. Then the $SOCl_2$ was distilled off, and finally, the isophthaloyl dichloride was distilled under vacuum. Benzene (Aldrich, 99%), chlorobenzene (Fisher Scientific), and fluorobenzene (Fluka, 99.5%) were distilled from CaH_2. 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 freshly distilled from P_2O_5 under vacuum. Dimethyl sulfoxide (DMSO, Aldrich, 99+%) was vacuum distilled from CaO. Sulfolane (tetramethylene sulfone, Aldrich, 99%) was vacuum distilled from KOH pellets. Toluene was washed successively with concentrated 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. Cu_2O (Ventron) was dried under vacuum at room temperature for 1 day. 18-Crown-6 (Aldrich, 99%) was used as received.

Synthesis of 1,3-Bis(4-chlorobenzoyl)benzene (1,3-CBB). 1,3-Bis(4-chlorobenzoyl)benzene was synthesized by the Friedel-Crafts reaction of isophthaloyl dichloride and chlorobenzene according to a literature procedure.[7] The crude product was recrystallized from toluene to yield white crystals. Yield: 62.0%. Mp: 209–211 °C (lit.[7] mp 210.5–211.5 °C). Purity (DSC): 99.9%. ^{1}H NMR ($CDCl_3$): δ 7.46 (d, 4 H, J = 8.6 Hz, *o* to Cl), 7.63 (t, 1 H, J = 7.7 Hz, 5 position of inner aromatic ring), 7.75 (d, 4 H, J = 8.6 Hz, *m* to Cl), 7.99 (dd, 2 H, J = 7.7, 1.6 Hz, 4 and 6 positions of inner aromatic ring), 8.11 (t, 1 H, J = 1.6 Hz, 2 position of inner aromatic ring).

Synthesis of 1,3-Bis(4-fluorobenzoyl)benzene (1,3-FBB). 1,3-Bis(4-fluorobenzoyl)benzene was synthesized by the Friedel-Crafts reaction of isophthaloyl dichloride and fluorobenzene according to a literature procedure.[7] The crude product was recrystallized from toluene to yield white crystals. Yield: 81.7%. Mp: 176–178 °C (lit.[7] mp 178–179 °C). Purity (DSC): 99.8%. ^{1}H NMR ($CDCl_3$): δ 7.16 (dd, 4 H, $J_H \approx J_F$ = 8.0 Hz, *o* to F), 7.63 (t, 1 H, J = 7.7 Hz, 5 position of inner aromatic ring), 7.85 (dd, 4 H, J_H = 8.0 Hz, J_F = 5.3 Hz, *m* to F), 7.98 (dd, 2 H, J = 7.7, 1.6 Hz, 4 and 6 positions of inner aromatic ring), 8.11 (t, 1 H, J = 1.6 Hz, 2 position of inner aromatic ring).

Synthesis of 5-*tert*-Butylisophthalic Acid. 5-*tert*-Butyl-*m*-xylene (50 g, 0.27 mol) was oxidized with $KMnO_4$ in accordance with a literature procedure.[8] The crude product was recrystallized from glacial acetic acid to yield 62 g (90.6%) of white crystals. Mp >300 °C (lit.[8] mp 343 °C). ^{1}H NMR (CD_3COCD_3): δ 1.41 (s, 9 H, *tert*-butyl), 8.31 (s, 2 H, *o* to *tert*-butyl), 8.54 (s, 1 H, *p* to *tert*-butyl).

Synthesis of 1,3-Bis(4-chlorobenzoyl)-5-*tert*-butylbenzene (1,3-CBTBB). A mixture of 5-*tert*-butylisophthalic acid (25 g, 0.113 mol) and $SOCl_2$ (250 mL) was stirred at reflux for 24 h. The excess $SOCl_2$ was distilled off under vacuum, and the resultant acid chloride was used in the following Friedel-Crafts benzoylation without further purification. Chlorobenzene (250 mL, distilled over CaH_2) was added to the acid chloride, and the solution was cooled in an ice–water bath. Anhydrous $AlCl_3$ (36 g, 0.27 mol) was added slowly such that the temperature did not exceed 5 °C. After addition of all the $AlCl_3$, the resultant red suspension was stirred at room temperature for 16 h and then at 60 °C for 4 h. The reaction mixture was allowed to cool to room temperature and then was poured into a mixture containing ice–water and concentrated HCl. The pale yellow organic layer was separated and successively washed with water, an aqueous solution of $NaHCO_3$ (5%), and water. The organic layer was dried over $MgSO_4$, and the chlorobenzene was evaporated under vacuum. The solid product was recrystallized 2 times from toluene to yield 41.9 g (90.2%) of white flakes. Mp: 182–183 °C. Purity (HPLC): 99.9+%. ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 9 H, *tert*-butyl), 7.46 (d, 4 H, J = 8.8 Hz, *o* to Cl), 7.74 (d, 4 H, J = 8.8 Hz, *m* to Cl), 7.84 (t, 1 H, J = 1.5 Hz, *p* to *tert*-butyl), 8.02 (d, 2 H, J = 1.5 Hz, *o* to *tert*-butyl).

Synthesis of 1,3-Bis(4-fluorobenzoyl)-5-*tert*-butylbenzene (1,3-FBTBB). 1,3-Bis(4-fluorobenzoyl)-5-*tert*-butylbenzene was synthesized using a procedure similar to that employed for the synthesis of 1,3-CBTBB except that fluorobenzene was used instead of chlorobenzene. Yield: 58.3%. Mp: 114.5–115.5 °C. Purity: 99.4%. ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 9 H, *tert*-butyl), 7.15 (dd, 4 H, $J_H \approx J_F$ = 8.0 Hz, *o* to F), 7.84 (m, 5 H, *m* to F, and 1 H, *p* to *tert*-butyl), 8.02 (d, 2 H, J = 1.5 Hz, *o* to *tert*-butyl).

Synthesis of 1,3-Bis(benzoyl)-5-*tert*-butylbenzene. 1,3-Bis(benzoyl)-5-*tert*-butylbenzene was synthesized using a procedure similar to that employed for the synthesis of 1,3-CBTBB except that benzene was used instead of chlorobenzene. Purification of the crude product was accomplished by passage of a chloroform solution of the crude product through a silica gel column. The product was recovered by evaporation of the chloroform under vacuum, and then the product was recrystallized from hexanes. Yield: 23.1%. Mp: 80.5–82.5 °C. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 9 H, *tert*-butyl), 7.47 (t, 4 H, J = 7.5 Hz, *m* to carbonyl in outer aromatic ring), 7.58 (t, 2 H, J = 7.5 Hz, *p* to carbonyl in outer aromatic ring), 7.80 (d, 4 H, J = 7.5 Hz, *o* to carbonyl in outer aromatic ring), 7.90 (t, 1 H, J = 1.5 Hz, 2 position of inner aromatic ring), 8.06 (d, 2 H, J = 1.5 Hz, 4 and 6 positions of inner aromatic ring).

Synthesis of 4,4′-Oxydiphenol (ODP). 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 tetrafluoroborates in refluxing trifluoroacetic acid containing potassium trifluoroacetate.[9a] 4,4′-Oxydiphenol was recrystallized from acetone. Yield: 57.1%. Mp: 168 °C (lit.[10] mp 165–167 °C). Purity (HPLC): 99.2%. ^{1}H NMR (CD_3COCD_3): δ 6.82 (m, 8 H, aromatic protons).

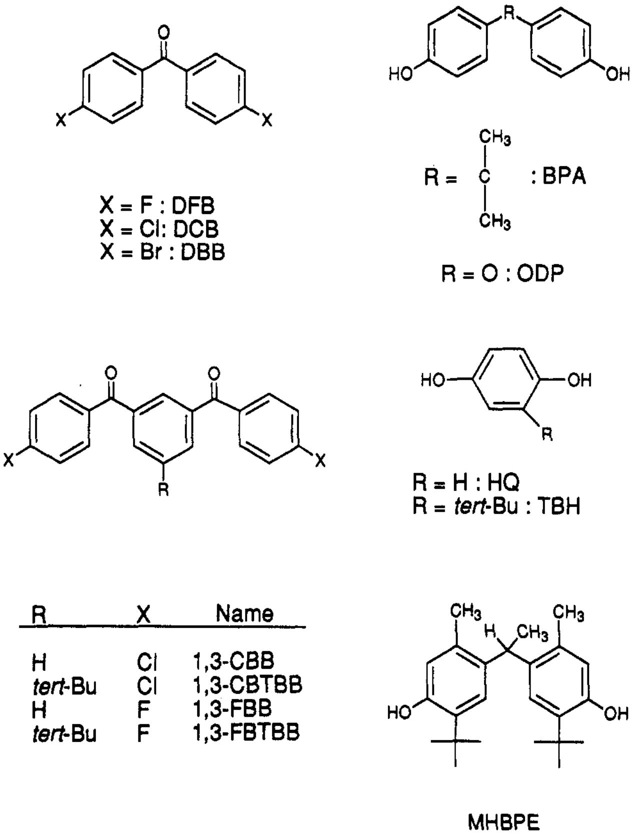
Synthesis of 1,1-Bis(2-methyl-4-hydroxy-5-*tert*-butylphenyl)ethane (MHBPE). MHBPE was synthesized by the condensation of acetaldehyde with 2-*tert*-butyl-5-methylphenol according to a literature procedure.[9b] The reaction product was recrystallized 1 time from methanol and 1 time from toluene. Yield: 12.6%. Mp: 198–201 °C (lit.[9b] mp 201.1–201.5 °C). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 18 H, *tert*-butyl), 1.46 (d, 3 H, J = 7.1 Hz, $CHCH_3$), 2.12 (s, 6 H, $ArCH_3$), 4.21 (q, 1 H, J = 7.1 Hz, $CHCH_3$), 4.48 (s, 2 H, OH), 6.40 (s, 2 H, *o* to OH), 7.01 (s, 2 H, *o* to *tert*-butyl).

Synthesis of Tetraphenylhydrazine. Tetraphenylhydrazine was synthesized by the oxidation of diphenylamine with $KMnO_4$ in acetone at 0 °C according to a literature procedure.[11] The product was recrystallized from an ethanol/acetate (60/40 v/v) mixture. Yield: 57.6%. Mp: 141–145 °C (lit.[11a] mp 144 °C). ^{1}H NMR ($CDCl_3$): δ 6.87 (t, 1 H, J = 7.0 Hz, *p* to hydrazine), 7.25 (m, 4 H, *o* and *m* to hydrazine).

Synthesis of Polyethers. Polymerizations were conducted by a conventional procedure which utilizes K_2CO_3 as the base to form the phenolate in situ.[7,12] 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 DCB (0.9417 g, 3.75 mmol), TBH (0.6233 g, 3.75 mmol), anhydrous K_2CO_3 (1.2750 g, 9.23 mmol), DMAc (7.5 mL), and toluene (3.7 mL). In the polyetherifications in which nitrobenzene, tetraphenylhydrazine, Cu_2O, or 18-crown-6 was added, these compounds were charged with the other reactants. 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 under argon at 157–160 °C for the remainder of the reaction time. 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.

Polymerizations were also carried out in sulfolane in order to investigate higher polymerization temperatures. A similar

Chart 1. Short Names of Monomers



R	X	Name
H	Cl	1,3-CBB
tert-Bu	Cl	1,3-CBTBB
H	F	1,3-FBB
tert-Bu	F	1,3-FBTBB

procedure to that of the polymerizations conducted at 160 °C in DMAc, NMP, and DMSO was used except a more stringent method for oxygen removal was employed as a precaution. The 25-mL, three-neck, round-bottom flask was purged with argon, and then the bis(aryl halide), bisphenol, sulfolane, and toluene were added. The reaction mixture was sparged for 20 min at 40 °C, and then the K_2CO_3 was added. The reaction mixture was sparged for another 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. If a higher polymerization temperature than 160 °C was employed, the temperature was elevated to the desired value over a 30-min period. The reaction was maintained under argon for the remainder of the reaction time.

Model polymers with well-defined chain ends were synthesized by using an excess of the appropriate monomer. The *tert*-butylhydroquinone end-capped polymer of DFB and TBH was obtained from condensation of DFB with a 9% excess of TBH in DMAc. The Bisphenol A end-capped polymer of DCB and BPA was obtained from condensation of DCB with a 9% excess of BPA in DMAc. Likewise, the model polymer with the 4-chlorobenzophenone chain end was synthesized from the condensation of BPA with a 9% excess of DCB in DMAc. The hydroquinone end-capped polymer of 1,3-FBTBB and HQ was obtained from condensation of 1,3-FBTBB with 9% excess of HQ in DMAc.

Techniques. The purities of 1,3-CBTBB, 1,3-FBTBB, and ODP 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 in the case of the higher molecular weight polymers ($M_n > 15\,000$) 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 for these higher molecular weight polymers.

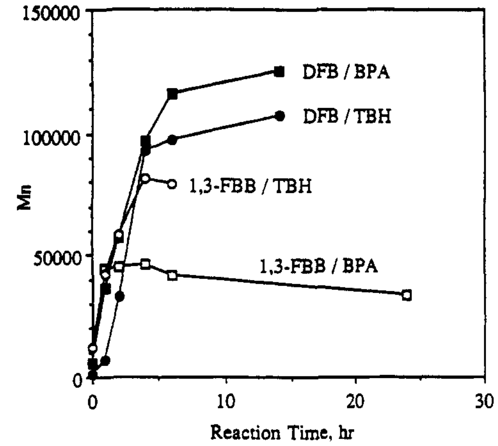


Figure 2. Number-average molecular weight vs reaction time for the polyetherification of DFB and 1,3-FBB with TBH and BPA.

The purities of 1,3-CBB and 1,3-FBB were determined by comparison of the melting curve obtained by differential scanning calorimetry (DSC) to the van't Hoff plot. A Perkin-Elmer DSC-4 equipped with a TADS data station Model 3600 and purity software was used for the purity determinations. Indium was used as the calibration standard. The melting points which are reported for all other compounds were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

The ^1H NMR spectra of 1,3-CBB, 1,3-FBB, 5-*tert*-butylisophthalic acid, 1,3-FBTBB, and ODP were acquired at 200 MHz on a Varian XL-200 spectrometer. ^1H NMR spectra of the polymers, DCB, benzophenone, 1,3-CBTBB, and 1,3-bis(benzoyl)-5-*tert*-butylbenzene in $CDCl_3$ were acquired at 299.95 MHz on a Varian VXR-300 NMR spectrometer. Tetramethylsilane (TMS) was used as the internal standard in both cases. The chain ends of polymers precipitated from chloroform into methanol or acetone were determined by ^1H NMR spectroscopy.[5a,6] In some cases, spectra were also recorded for the polymers after precipitation into water from DMAc and prior to precipitation into methanol from chloroform. These spectra were used to determine the amount of benzophenone chain ends, since they yield a more accurate representation of the total amount of reductive dehalogenation which takes place in the polymerizations. The 2-D COSY spectrum of the polymer formed from 1,3-CBTBB and HQ in sulfolane at 220 °C for 6 h was acquired at 299.95 MHz on a Varian Gemini-300 NMR spectrometer equipped with a $^1H/^{13}C$, 5-mm probe. Phase-sensitive data were collected at ambient temperature without sampling spinning using the method of States et al.[13] Three-hundred twenty fid's were acquired with a 18-μs 90° pulse, 0.658-s acquisition time (1024 points), 1-s relaxation delay, and 777.7-Hz spectral width in f_1 and f_2. Each fid was acquired with 16 transients and 2 dummy pulses for establishing the steady state. Data were processed on a Sun SPARC station using VNMR software with zero filling (4× in f_2 and 4× in f_1) and shifted sine-bell weighting.

Results and Discussion

In the following discussion, monomers will be identified by the acronyms given in the Experimental Section and summarized in Chart 1. Polymers will be identified by the acronyms of the monomers, and the nomenclature will follow the general form bis(aryl halide)/bisphenol. Figure 2 shows the dependence of the number-average molecular weight on the reaction time for the polyetherifications of DFB and 1,3-FBB with BPA and TBH in DMAc at 160 °C. Figure 3 shows the corresponding data for the polyetherifications of DCB and 1,3-CBB with BPA and TBH. The highest molecular weight obtained for each

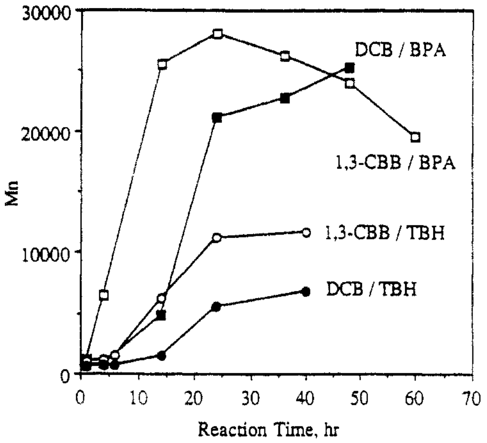


Figure 3. Number-average molecular weight vs reaction time for the polyetherification of DCB and 1,3-CBB with TBH and BPA.

Table 1. Highest Molecular Weights Achieved during Polyetherifications of DXB and 1,3-XBB (X = C, F) with TBH and BPA in DMAc and the Corresponding Reaction Times[a,b]

	monomers			polymer (GPC)	
no.	bis(aryl halide)	bisphenol	rxn time, h	$10^{-3}M_n$	M_w/M_n
1	**DCB**	**TBH**	40	6.8	2.04
2	**1,3-CBB**	**TBH**	40	11.6	3.23
3	**DCB**	**BPA**	48	25.2	2.33
4	**1,3-CBB**	**BPA**	24	28.1	3.10
5	**DFB**	**TBH**	14	107.5	2.56
6	**1,3-FBB**	**TBH**	4	81.6	2.83
7	**DFB**	**BPA**	14	125.0	2.40
8	**1,3-FBB**	**BPA**	4	46.1	3.06

[a] Determined by sampling of polyetherification with time. See Figures 2 and 3 for sampling times. [b] Polyetherification conditions: solvent = DMAc, temperature = 160 °C, total monomer concentration = 1.00 M, 2.5 mol of K_2CO_3/mol of bisphenol.

Table 2. Chain Ends of Polymers from Polyetherifications of DCB, DFB, and 1,3-CBB with TBH and BPA in DMAc[a]

	monomers			polymer chain ends[b]		
no.	bis(aryl halide)	bisphenol	rxn time, h	X	OH	H
9	**DCB**	**TBH**	6	Y	Y	Y
10	**DCB**	**TBH**	14	Y	Y	Y
11	**DCB**	**TBH**	24	Y	Y	Y
12	**DCB**	**TBH**	40	N	Y	Y
13	**1,3-CBB**	**TBH**	40	N	Y	Y
14	**DCB**	**BPA**	24	Y	Y	N
15	**DCB**	**BPA**	60	N	Y	N
16	**1,3-CBB**	**BPA**	24	Y	Y	N
17	**DFB**	**TBH**	14	N	*c*	N

[a] Polyetherification conditions are given in footnote *b* of Table 1. [b] X = 4-halobenzophenone chain end, OH = bisphenol chain end, H = benzophenone chain end. Y = chain end present, N = chain end absent. [c] In the ^{1}H NMR spectrum of **DFB/TBH**, broad resonances exist in the 6.64–6.79 ppm region. These resonances may be due to the *tert*-butylhydroquinone chain end; however, their shape is sufficiently different than the resonances observed for the *tert*-butylhydroquinone chain end of the model polymer that we cannot make a definitive assignment.

polymerization with a bis(aryl fluoride) in DMAc appeared to be determined by the precipitation of the polymer from solution. Table 1 summarizes the highest M_n obtained during the course of each of these polymerizations. Polymer chain ends are summarized in Table 2. In all cases, the polymerization of the bis(aryl fluoride) resulted in a polymer of higher molecular weight than the polymerization of the corresponding bis(aryl chloride). The choice of bisphenolate also affects the molecular weight. Under identical reaction conditions and with the same bis(aryl chloride), BPA yields higher molecular weight polymers than TBH. This can be seen by comparing DCB/TBH with DCB/BPA and 1,3-CBB/TBH with 1,3-CBB/BPA.

In order to gain more insight into the possible reaction mechanism, several other polyetherifications were conducted (Table 3).

Table 4 lists the ^{1}H NMR chemical shifts of the resonances due to the polymer backbones, chain ends, and model compounds. Protons are identified by alphanumeric labels which are given for the polymer backbones in Figure 4 and for the chain ends and model compounds in figures which display their respective ^{1}H NMR spectrum.

^{1}H NMR spectra revealed that DCB/TBH and 1,3-CBB/TBH contain benzophenone chain ends and no 4-chlorobenzophenone chain ends after 40 h at 160 °C in DMAc. Figure 5 shows the aromatic regions of the spectra of the DCB/TBH polymer prepared in DMAc after 40 h at 160 °C (entries 1 and 12), benzophenone, and DCB. No chlorine chain end is present in the polymer, but rather a benzophenone chain end terminates the chain along with some *tert*-butylhydroquinone chain end. A ^{1}H NMR 2-D COSY experiment performed on this polymer also confirmed the presence of the benzophenone chain end.[5a] The protons meta to the carbonyl are *J* coupled to the protons ortho and para to the carbonyl group.[5a]

Samples which were taken from the polymerization of DCB and TBH in DMAc after 6, 14, and 24 h at 160 °C (entries 9–11) were also characterized by ^{1}H NMR spectroscopy. The presence of a small amount of benzophenone chain end can be confirmed as early as 6 h into the polyetherification due to detection of the proton para to the carbonyl group at 7.56 ppm. The aromatic regions of the ^{1}H NMR spectra for the 6- and 14-h samples are shown in Figure 6. The aromatic regions of the ^{1}H NMR spectra of the 24-h sample and the model polymer end capped with *tert*-butylhydroquinone are seen in Figure 7. The relative amount of benzophenone chain end can be determined by integrating the peak area due to the proton para to the carbonyl group, since this area is not overlapped, and comparing it to the peak area from 7.66 to 7.96 ppm which is due to protons ortho to the carbonyl group. The area from 7.66 to 7.96 ppm should remain constant since the protons ortho to the carbonyl group resonate in this range independent of whether chlorine, hydrogen, or phenoxy are in the para position. The amount of benzophenone chain end (which is equivalent to protons para to the carbonyl group) relative to the total amount of benzoyl moieties (each benzophenone moiety is taken to have two benzoyl moieties regardless of substitution in the 4 and 4′ positions, and the amount of benzoyl moiety is equivalent to the protons ortho to the carbonyl group divided by two) is 3, 5, 5, and 6 mol % at 6, 14, 24, and 40 h, respectively.

The polyetherification of DBB with TBH in DMAc for 24 h (entry 18) resulted in oligomers of number-average molecular weight of 808. This molecular weight is much lower than that obtained with DCB and TBH (M_n = 5500) under identical conditions after 24 h. The oligomers from the polymerization of DBB and TBH contained benzophenone chain ends. The polyetherification of DCB and TBH was also conducted in DMSO for 40 h at 160 °C (entry 19). The molecular weight of 8000 is slightly higher than that obtained in DMAc. ^{1}H NMR analysis revealed benzophenone, 4-chlorobenzophenone, and *tert*-butylhydroquinone chain ends.

Table 3. Molecular Weight and Chain End Information for Additional Polyetherifications in Which Monomer, Solvent, or Reaction Conditions Were Changed

					polymer				
	monomers				GPC		chain ends[d]		
no.	bis(aryl halide)	bisphenol	solvent	rxn time, h	$10^{-3}M_n$	M_w/M_n	X	OH	H
18[a]	**DBB**	**TBH**	DMAc	24	0.81	1.20	[e]	Y	Y[e]
19[a]	**DCB**	**TBH**	DMSO	40	8.0	2.24	Y	Y	Y
20[a]	**DCB**	**BPA**	NMP	24	17.7	2.30			
21[b]	**DCB**	**BPA**	NMP	24	4.3	2.12	N	Y	Y
22[b]	**DFB**	**BPA**	NMP	14	66.0	2.56			
23[c]	**DCB**	**MHBPE/BPA**	DMAc	24	1.43	1.73	Y	Y[f]	N

[a] Polyetherification conditions: temperature = 160 °C, total monomer concentration = 1.00 M, 2.5 mol of K_2CO_3/mol of bisphenol. [b] Polyetherification conditions: temperature = 180 °C, total monomer concentration = 1.00 M, 1.4 mol of K_2CO_3/mol of bisphenol. [c] [**DCB**] = 0.5 M, [**MHBPE**] = [**BPA**] = 0.25 M, 2.5 mol of K_2CO_3/mol of bisphenol, temperature = 160 °C. [d] See Table 2 footnote *b* for description of symbols. [e] The aromatic region of the ^{1}H NMR spectrum of **DBB/TBH** is not well-resolved. The resonances for the benzophenone chain end are only resolved for approximately 15% of their peak height. The presence or absence of the 4-bromobenzophenone chain end cannot be determined. [f] The bisphenol chain end is primarily the MHBPE chain end.

The DCB/BPA and 1,3-CBB/BPA polymers prepared in DMAc at 160 °C did not contain benzophenone chain ends. The aromatic regions of the spectra of the DCB/BPA polymers which were obtained by polymerization for 24 h (entry 14) and 60 h (entry 15) in DMAc at 160 °C, the model polymer end capped with 4-chlorobenzophenone, and the model polymer end capped with Bisphenol A are shown in Figure 8. The DCB/BPA polymer contains no benzophenone chain end at either 24 or 60 h. After 24 h, 4-chlorobenzophenone and Bisphenol A chain ends are both present in the polymer. After 60 h, only Bisphenol A chain ends are present. The loss of the 4-chlorobenzophenone chain end does not coincide with the occurrence of the benzophenone chain end in this case. The nonstoichiometry in the amounts of the 4-chlorobenzophenone and Bisphenol A chain ends develops after the polymer has already reached a reasonably high molecular weight. The spectrum of the polymer also has some low intensity resonances which have not been assigned.

Polycondensation of DCB and BPA in NMP at 160 °C (entry 20) provides a polymer of comparable molecular-weight to that achieved in DMAc (entry 3). However, polycondensation of the same two monomers in NMP at 180 °C (entry 21) afforded a polymer of much lower molecular weight (M_n = 4400) which contained benzophenone and Bisphenol A chain ends (Figure 9). Polycondensation of DFB and BPA in NMP at 180 °C (entry 22) yields a high molecular weight polymer.

The presence of the benzophenone chain end correlates with very low molecular weights as can be seen in Tables 1–3. The DBB/TBH (entry 18), DCB/TBH (entry 1), and 1,3-CBB/TBH (entry 2) polymers which were synthesized in DMAc at 160 °C, the DCB/TBH polymer prepared in DMSO at 160 °C (entry 19), and the DCB/BPA (entry 21) polymer synthesized in NMP at 180 °C all are of low molecular weight and contain benzophenone chain ends. Reductive elimination of halide from the 4-halobenzophenone propagating chain results in the unreactive benzophenone chain end.

This side reaction can be explained by reference to the $S_{RN}1$ mechanism.[14] Application of the $S_{RN}1$ mechanism to these polyetherifications is shown in Figure 10. Recently, the ability of phenolates to act as nucleophiles in $S_{RN}1$ reactions has been demonstrated.[14c,15] However, phenolates and aryl iodides or bromides with electron-withdrawing substituents have been shown to undergo carbon–carbon coupling rather than carbon–oxygen coupling upon photostimulation or electrostimulation.[15] The carbanion ortho or para to the oxygen anion of the phenolate displaces the halide of the aryl halide. 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 aryl radical. The soft aryl 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-bromobenzophenone with phenoxide.[15a] Thus, carbon–oxygen bond formation has not been observed for phenolates and activated aryl halides under $S_{RN}1$ conditions. In the case of these polyetherifications, the carbon–carbon coupling products which would be generated by the $S_{RN}1$ propagation steps have not been detected by ^{1}H NMR spectroscopy. Only structural units which would be generated by termination steps, *i.e.*, the benzophenone chain ends, have been detected.

The results of these polyetherifications can be explained by the general mechanism depicted in Figure 11. We propose that these polyetherifications involve a competition between polar and SET pathways. The aryl halide can either react with the phenolate to form the Meisenheimer complex via a polar pathway or accept an electron to form the radical anion via a SET pathway. The radical anion then decomposes to the aryl radical, which yields the benzophenone chain end upon hydrogen abstraction.

In the polycondensation of the 4,4′-dihalobenzophenones with TBH in DMAc, only DFB afforded a high molecular weight polymer. Both DCB and DBB yielded low molecular weight polymers which contained benzophenone chain ends. 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 11, decreases in the order F > Cl > Br > I for oxygen-based nucleophiles.[16] 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.[17,18] Electrochemical reduction of substituted benzophenones in solvents of low proton availability (DMF) has shown

Table 4. ^{1}H NMR Chemical Shifts (see Figures 4–9, 12, 13, 15, 16, and 18 for Chemical Structures)

proton	pattern	δ, ppm
A1	d	7.77
B1	t	7.56
C1	t	7.46
A2	d	7.72
B2	d	7.44
A3	[a]	[a]
B3, C3		6.64–6.79
A4	d	7.70
B4	d	7.43
A5	d	7.08
B5	d	6.74
A6	[a]	[a]
B6	t	7.55
C6	t	7.45
A7	b	7.80[b]
B7	b	7.58[b]
C7	t	7.47
A8	d	7.74
B8	d	7.44
A9	d	6.93
B9	d	6.84
A10	d	6.90
B10	d	6.81
A11, A12	d	7.81
B11, B12	d	7.03
A13	s	7.18
B13, C13	s	6.92
A14	d	7.76
B14	d	7.00
A15	d	7.24
B15	d	6.97
A16	d	7.82
B16	d	7.03
A17	d[c]	7.99
B17	t[c]	7.88
A18	s	7.12
A19	d	7.80
B19	d	7.00
A20	d[c]	7.99
B20	t[c]	7.86
A21, B21	s	7.05
A22	d	7.79
B22	t	7.57
C22	t	7.46
A23	d	7.70
B23	d	7.45
A24	d	7.80
B24	t	7.58
C24	t	7.47
A25	d[c]	8.06
B25	t[c]	7.90
A26	d	7.74
B26	d	7.46
A27	d[c]	8.02
B27	t[c]	7.84
A28, A32, A34	d	7.77
B28, B32, B34	d	7.02
A29	d	7.71
B29	d	7.43
B31	s	6.46
A33	d	7.25
B33	d	6.99
A35	s	7.19
B35	s	6.67

[a] Resonances are overlapped by polymer backbone. [b] Resonances are overlapped by polymer backbone in the case of A7 and side product in the case of B7. Chemical shifts were determined from 2-D COSY spectrum. [c] Splitting pattern is due to long-range coupling with $J \approx 1.5$ Hz.

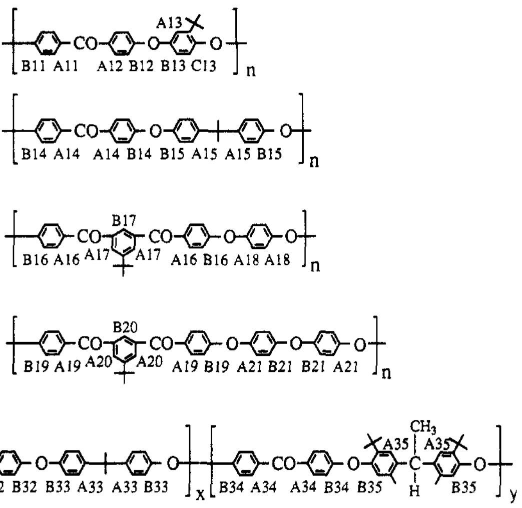


Figure 4. Polymer backbones with alphanumeric labels for identification of ^{1}H NMR chemical shifts in Table 4.

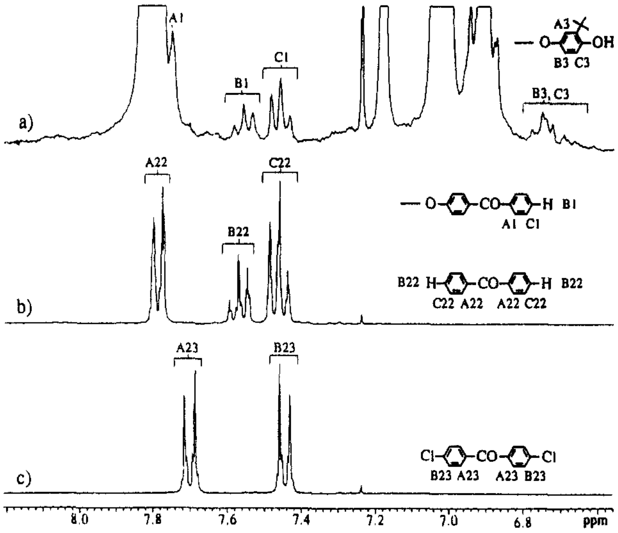


Figure 5. Comparison of the aromatic regions of the ^{1}H NMR spectra of (a) DCB/TBH polymer, 40 h at 160 °C in DMAc, (b) benzophenone, and (c) DCB. The spectra show that the polymer contains benzophenone chain ends. The resonance at 7.24 ppm is due to chloroform. Resonances due to the polymer backbone are off-scale.

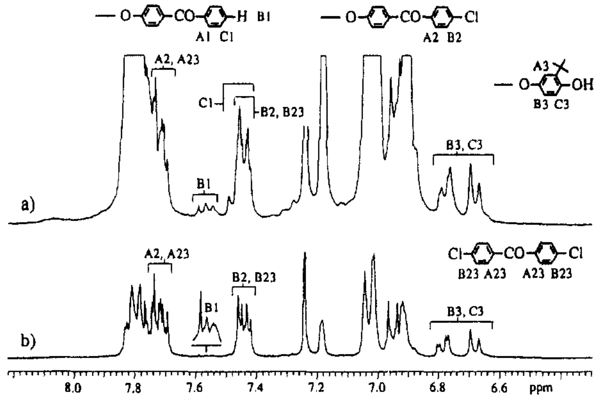


Figure 6. Aromatic regions of the ^{1}H NMR spectra of (a) DCB/TBH polymer, 14 h at 160 °C in DMAc, and (b) DCB/TBH polymer, 6 h at 160 °C in DMAc. The resonance at 7.24 ppm (off-scale) is due to chloroform.

that 4-bromobenzophenone is more easily reduced than 4-chlorobenzophenone, which is more easily reduced than 4-fluorobenzophenone.[18] The ease of reduction is indicated by the reduction potential associated with reduction by the first electron. In fact, polarographic and voltammetric studies indicated a different mechanism for the reductive cleavage of 4-bromo- and 4-chlorobenzophenones compared to that of 4-fluoro-, 4-phenyl-, 4-(dimethylamino)-, 4-methoxy-, 4-methyl-, and 4-(trimethylammonio)-benzophenones. In the case of 4-fluorobenzophenone (and

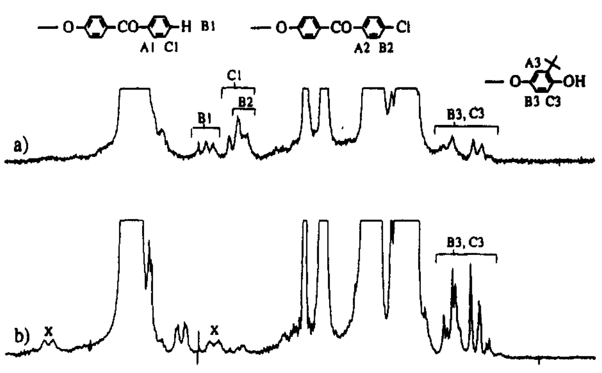


Figure 7. Aromatic regions of the ^{1}H NMR spectra of (a) DCB/TBH polymer, 24 h at 160 °C in DMAc, and (b) model polymer end capped with *tert*-butylhydroquinone. Resonances due to the polymer backbone and chloroform (δ = 7.24 ppm) are off-scale. X indicates ^{13}C satellites.

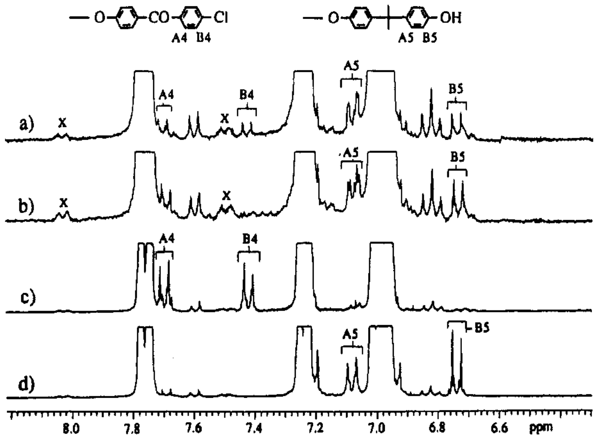


Figure 8. Aromatic regions of the ^{1}H NMR spectra of (a) DCB/BPA polymer, 24 h at 160 °C in DMAc, (b) DCB/BPA polymer, 60 h at 160 °C in DMAc, (c) model polymer end capped with 4,4′-dichlorobenzophenone; and (d) model polymer end capped with Bisphenol A. Resonances due to the polymer backbone are off-scale. X indicates ^{13}C satellites.

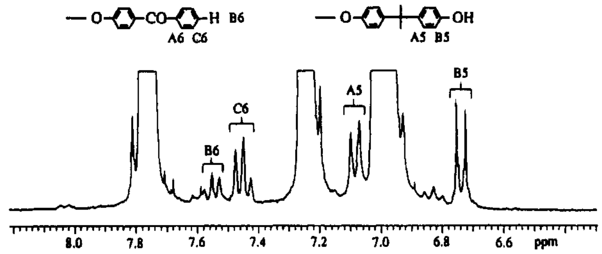


Figure 9. Aromatic region of the ^{1}H NMR spectrum of the DCB/BPA polymer, 24 h at 180 °C in NMP. Resonances due to the polymer backbone are off-scale.

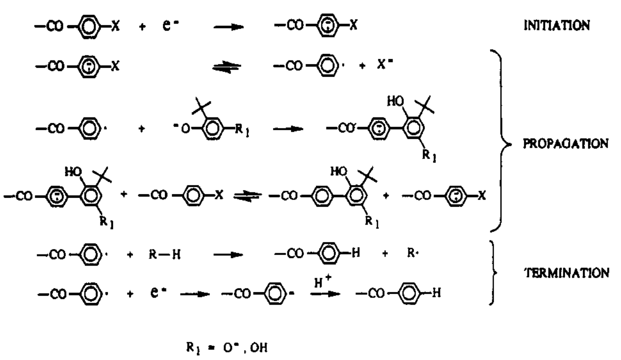


Figure 10. Expected mechanism if the polyetherification of DCB or DBB with TBH was to follow an $S_{RN}1$ mechanism.

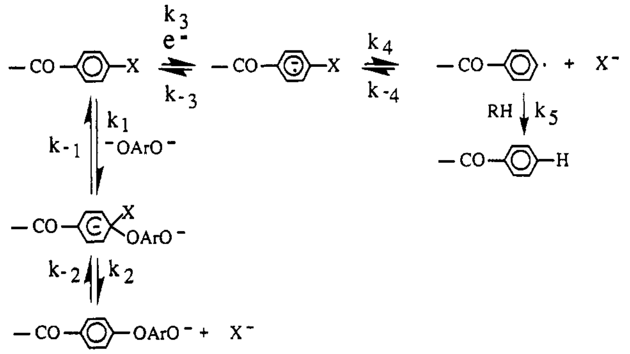


Figure 11. Proposed mechanism for the polyetherification of bis(aryl halide)s that are activated by the carbonyl group with bisphenolates. In the polar pathway, the halide is displaced by the phenolate. The benzophenone chain end is formed via the SET pathway.

the other benzophenones besides 4-bromo and 4-chloro), the first electron reduces the substrate to its radical anion, which is reduced by another electron at a more negative potential (more difficult to reduce than the original 4-fluorobenzophenone) to a dianion. The dianion is then quickly protonated at the carbon bonded to fluorine by acidic impurities such as water or perhaps by the solvent itself. Succeeding or concurrent with protonation, the fluoride leaves, generating benzophenone. In the case of 4-bromo- and 4-chlorobenzophenones, these substrates are reduced by one electron to their radical anions. Then the radical anion decomposes to the aryl radical and halide ion. The aryl radical abstracts a hydrogen atom from the solvent to yield benzophenone.[18] The rate constant for the decomposition of the radical anion of the aryl halide into the aryl radical and halide ion, k_4 in Figure 11, increases with decreasing carbon–halogen bond strength. Therefore, k_4 increases in the order F < Cl < Br < I.[14a,19] As the size of the halogen increases, steric hindrance to covalent bonding increases, and the SET pathway becomes more competitive.[20,21] 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′-dihalobenzophenones with TBH in DMAc are in accord with this expectation.

The occurrence of reductive dehalogenation, which results in low molecular weight polymers, is dependent on the structure of the bisphenolate. This can clearly be seen by comparison of the polyetherifications of TBH and BPA with DCB and 1,3-CBB in DMAc at 160 °C. The polyetherifications of TBH with DCB and TBH with 1,3-CBB afforded polymers with number-average molecular weights of 6800 and 11 600, respectively. Both polymers contained benzophenone chain ends. However, the polyetherifications of BPA with DCB and BPA with 1,3-CBB afforded polymers of higher molecular weight (25 200 and 28 100) which did not contain the benzophenone chain end. These results suggest that the bisphenolate of TBH may act as the electron donor in the SET pathway. TBH is a more probable electron donor than BPA because of two factors. One factor is that the oxidation potential for removal of the first electron of the dianion of TBH is lower (easier to oxidize) than that of the dianion of BPA. This is due to the fact that the two oxygen anions are para to each other on the same aromatic ring in TBH, whereas they are on separate aromatic rings in which conjugation between the rings is broken by the isopropylidene linkage in BPA. Hydroquinone and its derivatives are known to undergo one-electron oxidation to their semiquinones.[22] The other factor is that the *tert*-butyl group sterically

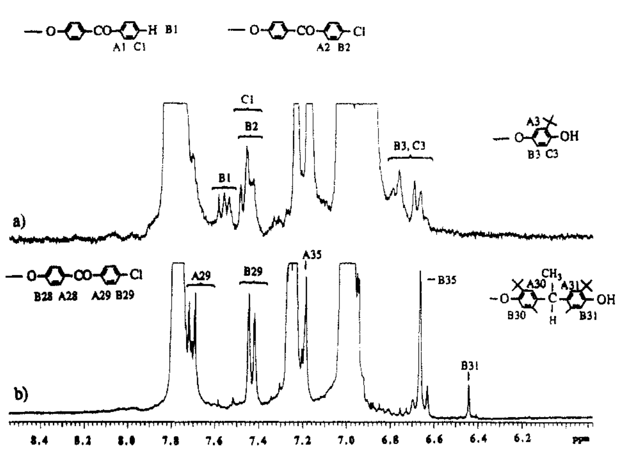


Figure 12. Comparison of the aromatic regions of the ^1H NMR spectra of (a) DCB/TBH polymer, 24 h at 160 °C in DMAc, and (b) DCB/MHBPE/BPA polymer, 24 h at 160 °C in DMAc. The protons responsible for the resonances at A35 and B35 are depicted in Figure 4. Other resonances due to polymer backbone and chloroform ($\delta = 7.24$ ppm) are off-scale.

hinders the displacement of the halide by the phenolate. Steric hindrance has two possible roles. First, it inherently shifts the balance between competitive SET and polar pathways toward the SET pathway. Most nucleophilic substitution reactions follow polar mechanisms due to the lower activation energy of the polar mechanism relative to the SET mechanism.[21] The activation energy of the polar pathway approaches that of the SET pathway as steric hindrance to covalent bond formation increases.[21] This point applies only to the oxygen anion ortho to the *tert*-butyl group and is applicable to both mono- and dianion forms. Second, the role the *tert*-butyl group plays is that of increasing the concentration of the dianion of the bisphenolate relative to the concentration of the monoanion. As discussed previously, the dianion has a lower oxidation potential. The presence of the *tert*-butyl group increases the concentration of the dianion relative to that of the monoanion by slowing the rate of condensation between the phenolate and aryl halide. In a kinetically controlled situation, the concentration of the dianion in relation to that of the monoanion is dependent on the rate of condensation of the phenolate and aryl halide and the rate of deprotonation of the phenol by K_2CO_3. This second factor seems to be less important since the rate of displacement is probably much slower than the establishment of acid–base equilibrium between carbonate and the phenol.

The copolymerization of DCB with MHBPE and BPA in DMAc at 160 °C (entry 23) afforded a very low molecular weight polymer that did not contain benzophenone chain ends. A comparison of the aromatic regions of the ^1H NMR spectra of this polymer and the DCB/TBH polymer (entry 11) formed under identical polymerization conditions is seen in Figure 12. The spectrum of the copolymer which had been precipitated from chloroform into methanol is shown in Figure 12. Both the methanol-soluble and -insoluble fractions of the copolymer do not contain benzophenone chain ends. This copolymerization reflected the same molar ratio of unhindered phenol to hindered phenol (OH ortho to *tert*-butyl group) as in the polymerization of DCB with TBH. However, the dianion of MHBPE is similar to that of BPA in that the oxygen anions are on separate aromatic rings in which conjugation between the rings is broken. *The results of this copolymerization demonstrate that steric hindrance to covalent bond formation is not in itself sufficient for the occurrence of reductive dehalogenation in DMAc at 160 °C. These results strongly suggest that the dianion of TBH is the electron donor in the polyetherifications of DCB and 1,3-CBB with TBH in DMAc at 160 °C and that the oxidation potential of the dianion of the bisphenol is the primary characteristic of the bisphenolate which controls the occurrence of reductive dehalogenation.*

DCB was heated with a mixture of $KHCO_3$, K_2CO_3, and KCl in DMAc at 160 °C for 40 h to determine if reductive dehalogenation occurs in the absence of the bisphenolates. No reductive dehalogenation occurred. *This supports the idea that the bisphenolate of TBH is the electron donor.*

The stability of DCB in NMP is different from that observed in DMAc. When DCB was heated with $KHCO_3$ in NMP at 160 or 180 °C for 24 h, reductive dehalogenation occurred. Other reaction products were also present. Also, DCB underwent reductive dehalogenation in freshly dried NMP at 180 °C after 24 h in the presence of $NaHCO_3$, K_2CO_3, potassium *tert*-butoxide, or the potassium bisphenolate of BPA. Potassium tert-butoxide may induce the reductive elimination of the halide by a mechanism related to that suggested by Bunnett.[19c,d] DCB did not undergo reductive dehalogenation in NMP at 180 °C in the presence of KCl for 24 h. DFB does not undergo reductive dehalogenation in the presence of $KHCO_3$ in NMP at 180 °C after 24 h. However, other products believed to be due to the displacement of fluorine with carbonate were present. The fact that DCB undergoes reductive dehalogenation in NMP in the presence of $KHCO_3$ or K_2CO_3 suggests the reductive dehalogenation observed in the polyetherification of DCB and BPA in NMP at 180 °C (entry 21) may not occur via the proposed SET mechanism in which the phenolate of BPA is the electron donor. *The apparent enhanced 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; S_NAr, $S_{RN}1$, and cation-radical mechanisms have been proposed.[1g,6]

The behavior of other bisphenols such as hydroquinone (HQ) and 4,4′-oxydiphenol (ODP) in these polyetherifications is of interest; however, the condensation of these bisphenolates with DCB or 1,3-CBB only forms oligomers in DMAc at 160 °C due to the insolubility of the oligomers under these reaction conditions. However, when 1,3-CBTBB and 1,3-FBTBB were condensed with bisphenolates such as HQ and ODP, soluble polymers formed. These polymers are also soluble in chloroform, tetrahydrofuran, *etc.* The results of the polyetherification of 1,3-CBTBB and 1,3-FBTBB with TBH, HQ, and ODP are presented in Table 5. Polycondensation of 1,3-CBTBB with TBH and HQ (entries 24 and 25) under conditions identical to those used for the polyetherifications in Table 1 afforded polymers with molecular weights of 17 600 and 15 000, respectively. ^1H NMR analysis indicated that the polymer based on 1,3-CBTBB and TBH contained 4-chlorobenzophenone, benzophenone, and *tert*-butylhydroquinone chain ends. The polymer based on 1,3-CBTBB and HQ only had 4-chlorobenzophenone chain ends. Since the polymer based on HQ did not contain benzophenone chain ends, it was considered that the molecular weight may be limited by the solubility of the polymer and/or the phenolate of HQ. Therefore, the total monomer concentration was reduced from 1.0 to 0.625 M, and 1,3-CBTBB was polymerized with HQ to yield a polymer of molecular weight of 51 900 (entry 27). 1,3-CBTBB was also poly-

Table 5. Results of Polyetherification of 1,3-CBTBB and 1,3-FBTBB with Various Bisphenolates[a]

	monomers						polymer				
							GPC		chain ends[c]		
no.	bis(aryl halide)	bisphenol	concn,[b] mol/L	solvent	rxn temp, °C	rxn time, h	$10^{-3}M_n$	M_w/M_n	X	OH	H
24	**1,3-CBTBB**	TBH	1.00	DMAc	160	24	17.6	2.21	Y	Y	Y
25	**1,3-CBTBB**	HQ	1.00	DMAc	160	24	15.0	2.63	Y	N	N
26[d]	**1,3-CBTBB**	HQ	1.00	DMAc	160	24	7.7	2.34	N	Y	N
27	**1,3-CBTBB**	HQ	0.625	DMAc	160	24	51.9	2.69			
28	**1,3-FBTBB**	HQ	0.625	DMAc	160	6	73.2	2.14			
29	**1,3-CBTBB**	ODP	0.625	DMAc	160	24	67.3	2.09			
30	**1,3-CBTBB**	HQ	0.625	$TMSO_2$	160	24	25.5	2.42	Y	N	N
31	**1,3-CBTBB**	HQ	1.00	$TMSO_2$	160	24	21.6	2.74	Y	N	N
32	**1,3-CBTBB**	HQ	1.00	$TMSO_2$	220	6	8.0	2.54	N	Y	Y
33	**1,3-CBTBB**	HQ	1.00	$TMSO_2$	250	6	1.2	1.68	N	Y	Y
34	**1,3-CBTBB**	ODP	1.00	$TMSO_2$	220	6	20.9	2.74	N	Y	N
35	**1,3-FBTBB**	HQ	1.00	$TMSO_2$	220	6	19.4	2.88	N	Y	N

[a] Polyetherification conditions: 2.5 mol of K_2CO_3/mol of bisphenol. [b] Total monomer concentration ([bis(aryl halide)] + [bisphenol]). [c] See Table 2, footnote *b* for description of symbols. [d] 1.0 mol of 18-crown-6/mol of **HQ**.

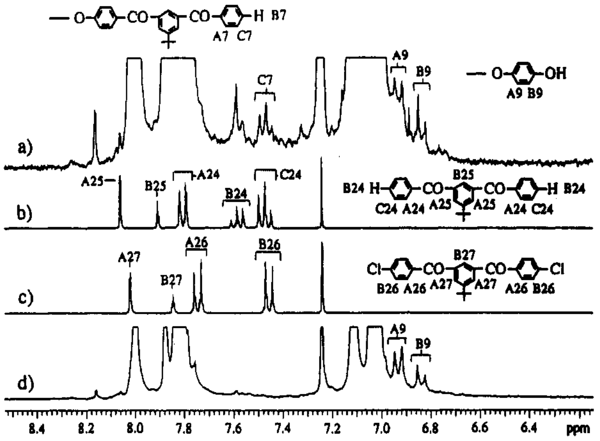


Figure 13. Comparison of the aromatic regions of the ^1H NMR spectra of (a) 1,3-CBTBB/HQ polymer, 6 h at 220 °C in sulfolane, (b) 1,3-bis(benzoyl)-5-*tert*-butylbenzene, (c) 1,3-CBTBB, and (d) model polymer end capped with hydroquinone. Resonances due to the polymer backbone and chloroform (δ = 7.24 ppm) are off-scale.

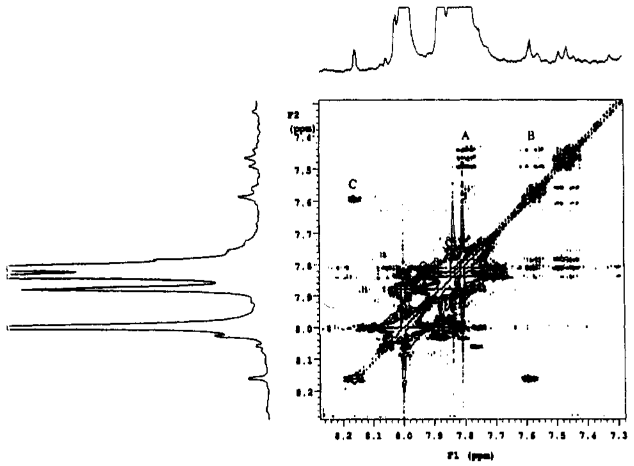


Figure 14. 2-D COSY spectrum of the 1,3-CBTBB/HQ polymer, 6 h at 220 °C in sulfolane.

merized with ODP to yield a polymer with a number-average molecular weight of 67 300 (entry 29).

Polycondensations were also conducted in sulfolane in order to investigate a wider range of polymerization temperatures. Polyetherification of 1,3-CBTBB with HQ in sulfolane at 160 °C with total monomer concentrations of 1.0 and 0.625 M (entries 31 and 30) afforded similar results to the polyetherifications conducted in DMAc at 160 °C. No reductive dehalogenation was observed, and the more dilute polyetherification provided the higher molecular weight polymer. The polyetherifications at 1.0 and 0.625 M provided polymers with number-average molecular weights of 21 600 and 25 500, respectively. *At a polymerization temperature of 220 °C and a total monomer concentration of 1.0 M, polyetherification of 1,3-CBTBB and HQ resulted in a lower molecular weight polymer (M_n = 8000) than that obtained at 160 °C, and the polymer contained benzophenone and hydroquinone chain ends (entry 32).* The ^1H NMR spectra of the aromatic regions of this polymer, 1,3-bis(benzoyl)-5-*tert*-butylbenzene, 1,3-CBTBB, and the model polymer end capped with hydroquinone are presented in Figure 13. In the spectrum of the polymer, the triplet at 7.47 ppm corresponds to the protons on the terminal aromatic ring of the benzophenone chain end which are meta to the carbonyl group. Unfortunately, the resonances due to the protons ortho and para to the carbonyl group are overlapped by other resonances. Crosspeaks A and B in the 2-D COSY spectrum of the polymer (Figure 14) indicate the meta protons are *J* coupled to protons with resonances at 7.80 and 7.58 ppm, respectively. These are the chemical shifts expected for the protons ortho and para to the carbonyl group in the terminal aromatic ring of the benzophenone chain end as can be seen from the spectrum of 1,3-bis(benzoyl)-5-*tert*-butylbenzene in Figure 13 and the chemical shifts given in the Experimental Section and Table 4. The resonance at 7.58 ppm which is due to the para proton of the benzophenone chain end is overlapped by another resonance at 7.59 ppm. The presence of crosspeak C in the 2-D COSY spectrum indicates that the resonance at 7.59 ppm is coupled to a resonance at 8.16 ppm. The coupled resonances at 7.59 and 8.16 ppm are present in polymers formed from both 1,3-CBTBB and 1,3-FBTBB. The chemical structure responsible for the resonances at 7.59 and 8.16 ppm has yet to be determined. *Polyetherification of 1,3-CBTBB and ODP at 220 °C (entry 34) provided a polymer with a number-average molecular weight of 20 900, which did not contain benzophenone chain ends.* The ^1H NMR spectrum of this polymer along with that of the 1,3-CBTBB/HQ polymer synthesized under identical conditions is shown in Figure 15. *The results of the polyetherification of 1,3-CBTBB with HQ and 1,3-CBTBB with ODP at 220 °C clearly demonstrate that the occurrence of reductive dehalogenation of the bis(aryl chloride) requires the presence of the dianion of hydroquinone. Steric hindrance is not a factor in these polyetherifications.*

The extent of reductive dehalogenation relative to substitution of the halide by the phenolate increases with temperature. This result is in accord with a higher activation energy for reductive dehalogenation relative to

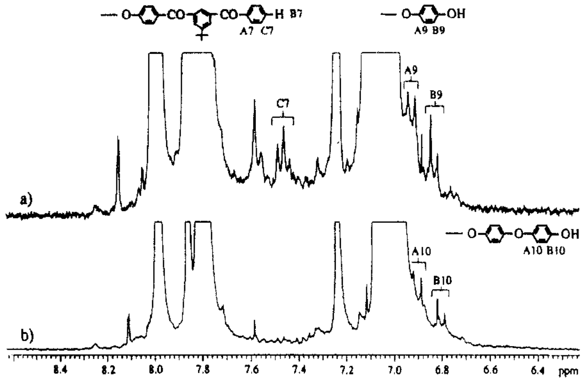


Figure 15. Aromatic regions of the ^{1}H NMR spectra of (a) 1,3-CBTBB/HQ polymer, 6 h at 220 °C in sulfolane, and (b) 1,3-CBTBB/ODP polymer, 6 h at 220 °C in sulfolane. Resonances due to the polymer backbones and chloroform (δ = 7.24 ppm) are off-scale.

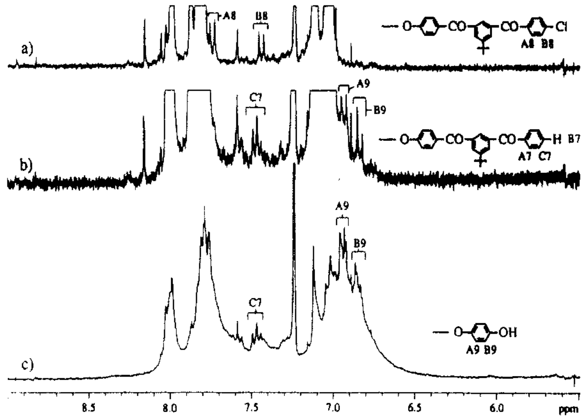


Figure 16. Aromatic regions of the ^{1}H NMR spectra of (a) 1,3-CBTBB/HQ polymer, 24 h at 160 °C in sulfolane, (b) 1,3-CBTBB/HQ polymer, 6 h at 220 °C in sulfolane, and (c) 1,3-CBTBB/HQ polymer, 6 h at 250 °C in sulfolane. Resonances due to the polymer backbone and chloroform (δ = 7.24 ppm) are off-scale.

aromatic nucleophilic substitution. In the polyetherification of 1,3-CBTBB with HQ in sulfolane, no reductive dehalogenation was observed at 160 °C. At 220 and 250 °C, reductive dehalogenation yielded 7% and 30% (based on ^{1}H NMR) of benzophenone moiety relative to benzoyl moiety (two benzoyl moieties per 1,3-CBTBB), respectively. Only oligomers were obtained at 250 °C. The ^{1}H NMR spectra of the polymers formed in the polyetherification of 1,3-CBTBB with HQ in sulfolane at 160, 220, and 250 °C (entries 31–33) are presented in Figure 16. Polycondensation of 1,3-FBTBB and HQ in sulfolane at 220 °C (entry 35) afforded a polymer which did not contain benzophenone chain ends. The polymer had a number-average molecular weight of 19 400 after 6 h; however, this is not the highest molecular weight obtainable. The viscosity of the reaction mixture becomes very high after 1 h and then decreases substantially after 6 h. This decrease in viscosity and presumably molecular weight may be due to transetherification reactions.[23] Polyetherification of 1,3-CBTBB with a more extensive group of bisphenolates and under a wider range of reaction conditions to produce high molecular weight polymers is reported in a separate article.[24]

All the experimental observations regarding the polyetherifications of the bis(aryl halide)s, which are activated by the carbonyl group, with TBH and HQ support the concept that the reductive elimination of the halide from the 4-halobenzophenone moiety occurs via a SET mechanism in which the 4-halobenzophenone moiety is the electron acceptor and the dianion of TBH or HQ is the electron donor. The ability of benzophenones to act as electron acceptors is well-established,[18,19a,25,26] and that of phenolates to act as electron donors toward inorganic oxidizing agents and their coupled quinones is well-recognized.[27] Not as well-known is the single electron transfer between the dianion of HQ and nitrobenzene in which both the radical anions of nitrobenzene and HQ were observed by ESR.[28] The extent of electron transfer from the phenolate of 2,2-di-*tert*-butyl-4-methylphenol to nitrobenzene was greatly diminished in relation to that observed between the dianion of HQ and nitrobenzene.[28] 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.[29] Also, the proposed SET reactions involving enolates as electron donors may be pertinent to these polyetherifications. Enolates and iodobenzene[26,30] and enolates and diazines[31] 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.[32] Also, EPR studies of aldol condensation reactions between enolates and benzophenones support a SET mechanism in which the enolate donates an electron to the benzophenone.[33]

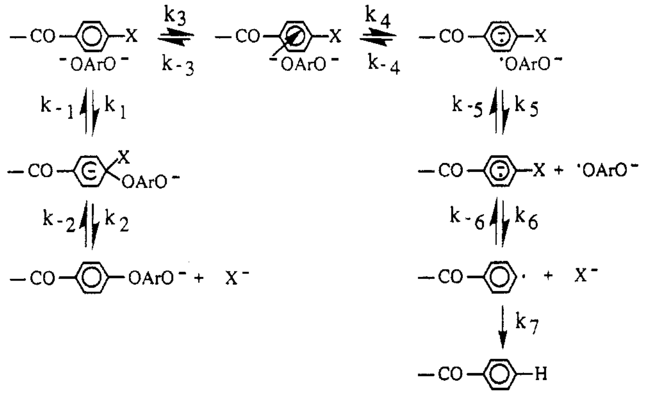


Figure 17. Proposed mechanism for the polyetherification of bis(aryl halide)s that are activated by the carbonyl group with bisphenolates. In the polar pathway, the aryl halide and bisphenolate act as an electrophile and nucleophile, respectively. In the SET pathway, the aryl halide and bisphenolate act as an electron acceptor and electron donor, respectively.

Incorporation of the phenolate as the electron donor into the mechanism is depicted in Figure 17. The two 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 aryl radical and the halide ion. The aryl 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 benzophenone chain end.

The relationship between polar and SET pathways is a very active area of research. Some have proposed that many polar reactions involve simultaneous, or nearly simultaneous, occurrence of single electron transfer and bond formation. In this context, one can envision that the formation of the Meisenheimer complex results from the rapid collapse of the radical anion–radical pair (charge-transfer complex). These concepts are discussed in greater detail in ref 6 and the references cited therein. Our data do not allow differentiation between these varying views of the polar pathway.

The feasibility that the proposed single electron transfer from the dianion of TBH to the 4-chlorobenzophenone moiety can account for the formation of the benzophenone chain end was tested by the same procedure used in an earlier paper.[6] The error in this procedure is quite large; however, it does allow us to judge whether a SET reaction is at least feasible or if it is improbable. Since 3% of the 4-chlorobenzophenone moieties are converted to benzophenone moieties in 6 h, a minimum value of 1.3×10^{-6} M^{-1} s^{-1} for the apparent rate constant of the SET reaction can be calculated. This calculation neglects depletion of the 4-chlorobenzophenone moiety and the dianion of TBH by the polar pathway. Also, the calculation assumes that all the TBH is in the form of the dianion, and all the dianion is in solution.

The apparent rate constant for a SET reaction between an electron donor and an acceptor can be estimated by eq 1 (see ref 6 and references cited therein). Equation 1 is

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

only expected to be accurate to within a few orders of magnitude due to the approximations which were made in its formulation.[6] Using a value of −1.55 V (vs saturated calomel electrode, SCE) for the standard reduction potential, E°_{red}, of the 4-chlorobenzophenone moiety and an estimated value of −0.55 V (vs SCE) for the standard oxidation potential, E°_{ox}, of the dianion of TBH, the apparent rate constant, k_{app}, is calculated to be $\sim 10^{-2}$ M^{-1} s^{-1}. The value of −1.55 V is based on literature values for E°_{red} of 4-chlorobenzophenone.[18,34] The estimated value of −0.55 V for E°_{ox} is based on literature values for tetramethylhydroquinone.[22] The estimated value for k_{app} of 10^{-2} M^{-1} s^{-1} is much greater than the minimum value of 1.3×10^{-6} M^{-1} s^{-1}. *Therefore, the proposed single electron transfer between the dianion of TBH and the 4-chlorobenzophenone moiety is a plausible explanation for the formation of the benzophenone chain end.*

The feasibility of electron transfer from the phenolate to any benzophenone unit along the polymer (or oligomer) backbone was also considered. This electron would be exchanged among various benzophenone units until it is accepted by one which has a chlorine (or bromine or iodine) in the 4 position. The rate of electron exchange among the benzophenone units is much faster than the rate of electron transfer from the dianion of TBH to the benzophenone moiety. Once a 4-chlorobenzophenone unit accepts the electron, the halide leaves and the benzophenone chain end is formed. A value of −1.7 V for E°_{red} of the internal benzophenone unit was estimated from a correlation of E°_{red} of substituted benzophenones and the Hammett constants, σ, of the substituents.[18] Values of 0.05 and −0.03 have been reported in the literature[35] for the Hammett constant of *p*-phenoxy. Their use yields a reduction potential of approximately −1.7 V. An apparent rate constant calculated from eq 1 for electron transfer between the dianion of TBH and an internal benzophenone unit is estimated to be 53 times slower than that for the electron transfer between the dianion of TBH and the 4-chlorobenzophenone moiety. Thus, reductive dehalogenation occurs via direct electron transfer from the dianion of the hydroquinone to the 4-chlorobenzophenone moiety. However, as the concentration of the 4-chlorobenzophenone moiety decreases, indirect electron transfer via internal benzophenone units becomes relatively more important.

Table 6. Results of the Polyetherification of DCB and TBH in DMAc in the Presence of Electron Acceptors and Radical Scavengers[a]

		quantity, mol/mol	rxn	polymer				
				GPC		chain ends[c]		
no.	additive[b]	DCB	time, h	$10^{-3}M_n$	M_w/M_n	Cl	OH	H
36	NB	0.30	40	2.7	1.38	Y	N	N
37	TPH	0.02	40	4.9	1.39	Y	Y	Y
38	Cu_2O	0.005	27	5.2	1.26	Y	Y	Y

[a] Polyetherification conditions are given in footnote *b* of Table 1. [b] NB = nitrobenzene, TPH = tetraphenylhydrazine. [c] Cl = 4-chlorobenzophenone chain end, OH = bisphenol chain end, H = benzophenone chain end. Y = chain end present, N = chain end absent.

While a phenolate with a structure based on hydroquinone is necessary for the occurrence of reductive dehalogenation under the conditions employed here (an exception being polyetherifications conducted in NMP at 180 °C), the substituents on the hydroquinone play an important role as evidenced by the difference in behavior of HQ and TBH. As was discussed in more detail previously, polyetherification of 1,3-CBTBB with HQ in DMAc at 160 °C (entry 25) did not result in the formation of benzophenone chain ends, whereas polyetherification with TBH under the same conditions (entry 24) did result in the formation of benzophenone chain ends. These results indicate that the *tert*-butyl substituent is critical for the occurrence of reductive dehalogenation in the polyetherification of TBH with 1,3-CBTBB, 1,3-CBB, and DCB in DMAc at 160 °C (entries 1, 2, 9–13, and 24). Several factors may account for the effect of the *tert*-butyl group. The *tert*-butyl group increases the activation energy of the polar pathway due to steric hindrance, while it has little effect on the SET pathway. The rate of condensation of the first oxygen anion of the dianion of TBH (which is the only relevant rate to be compared) will be approximately a factor of 2 slower than the rate of condensation of the first oxygen anion of the dianion of HQ. The factor of 2 is due simply to the fact that the dianion of HQ has two very reactive sites and TBH only has one. At the same time, the *tert*-butyl group is electron donating, and therefore, the oxidation potential of the dianion of TBH is expected to be slightly lower than that of HQ. Values for the oxidation potentials of the dianions of TBH and HQ are not available in the literature. The only relevant values available are −0.29 and −0.19 V for the oxidations of 2,4,6-tri-*tert*-butylphenolate and 2,6-di-*tert*-butylphenolate to their respective phenoxy radicals.[36] Assuming the oxidation potential of the dianion of TBH is 0.10 V lower than the oxidation potential of the dianion of HQ translates into an apparent rate constant for electron transfer which is approximately 10 times greater for the dianion of TBH than the dianion of HQ. This estimate is based on calculation of the apparent rate constants by use of eq 1. Another factor is that the *tert*-butyl group may help to solubilize the dianion, and thus the concentration of the dianion of TBH is greater than that of HQ. To determine if the higher solubility of the TBH dianion accounts for the difference in behavior of TBH and HQ, a large amount of 18-crown-6 was added to the polyetherification of 1,3-CBTBB and HQ in DMAc at 160 °C (entry 26). The resultant polymer had a number-average molecular weight of 7700 and did not contain benzophenone chain ends. This demonstrates that the difference in solubility of the two dianions is not responsible for their different chemical behavior.

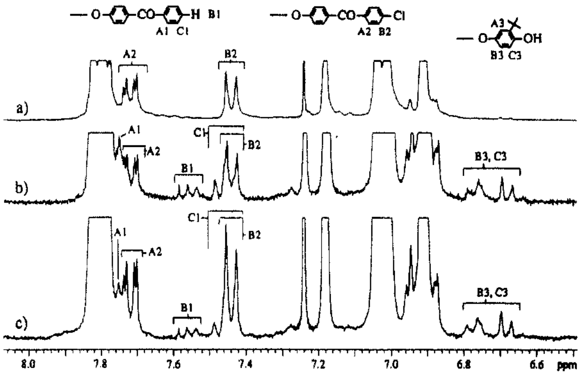


Figure 18. Aromatic regions of the ^{1}H NMR spectra of polymers synthesized from DCB and TBH in DMAc at 160 °C with the addition of (a) nitrobenzene, (b) tetraphenylhydrazine, and (c) Cu_2O. Resonances due to the polymer backbone and chloroform (δ = 7.24 ppm) are off-scale.

Radical scavengers and electron acceptors have also been used to provide support for $S_{RN}1$ mechanisms.[37] The results of the polyetherification of DCB with TBH in DMAc at 160 °C in the presence of nitrobenzene, tetraphenylhydrazine, and Cu_2O are summarized in Table 6, and the ^{1}H NMR spectra of the polymers are shown in Figure 18. The addition of nitrobenzene (an electron acceptor) to the polyetherification resulted in a polymer of number-average molecular weight of 2700 containing only 4-chlorobenzophenone chain ends. This is in contrast to the polymer obtained in the absence of any electron acceptor or radical scavenger which had a number-average molecular weight of 6800 and contained *only benzophenone* and a small amount of *tert*-butylhydroquinone chain ends. Since nitrobenzene is a better electron acceptor than the 4-chlorobenzophenone moiety, the nitrobenzene, rather than the 4-chlorobenzophenone moiety, accepts the electron from the donor, or if the radical anion of the 4-chlorobenzophenone moiety is formed, the nitrobenzene oxidizes it before the chloride can leave. The lower molecular weight polymer obtained in the presence of nitrobenzene is most likely due to an increase in the amount of oxidation of the phenolate, since nitrobenzene is a stronger electron acceptor than the 4-chlorobenzophenone moiety. However, the addition of tetraphenylhydrazine to the polyetherification had very little effect. The resulting polymer contained 6 mol % benzophenone chain ends based on the benzoyl moiety, and there was no evidence of diphenylamino chain ends. Copper salts have been claimed to increase the molecular weights obtainable in the polycondensation of carbonyl-activated bis(aryl chloride)s with bisphenolates.[38] Addition of Cu_2O afforded a polymer of number-average molecular weight of 5200 with only 2 mol % benzophenone chain ends. The rest were 4-chlorobenzophenone and *tert*-butylhydroquinone chain ends. Therefore, Cu_2O appears to have diminished the amount of reductive dehalogenation.

In an earlier paper[6] on the mechanism of polyetherification of 4,4′-dihalodiphenyl sulfones with TBH, BPA, and ODP in DMAc at 160 °C, fluoro, chloro, and bromo derivatives afforded high molecular weight polymers with all bisphenolates. Only the polycondensation of 4,4′-diiododiphenyl sulfone and TBH yielded a low molecular weight polymer which contained diphenyl sulfone chain ends. The polycondensations of 4,4′-diiododiphenyl sulfone with BPA or ODP yielded high molecular weight polymers. Thus, 4,4′-diiododiphenyl sulfone behaves very similarly to DCB. The sulfone group is more electron withdrawing than the carbonyl group in terms of the S_NAr reaction. Also, benzophenone is reduced more easily than diphenyl sulfone. *Therefore, the ability of 4,4′-dichlorodiphenyl sulfone and 4,4′-dibromodiphenyl sulfone to provide high molecular weight polymers with TBH while DCB and DBB can only provide low molecular weight polymers due to reductive dehalogenation is in accord with the proposed mechanism (Figure 17) for these polyetherifications.*

The balance between the polar and SET pathways is dependent on the chemical structure of the bis(aryl halide). The reduction potential of the bis(aryl halide) and the electron density at the aromatic carbon bonded to the halogen nucleofuge determine the balance between the two pathways. The electron-withdrawing group and the halogen-leaving group affect both the reduction potential and the electron density at the carbon bonded to the halogen. The more electronegative the halogen, the lower the electron density at the aromatic carbon and the lower (more negative) the reduction potential [*i.e.*, the bis(aryl halide) is more difficult to reduce]. Thus, the balance shifts toward the polar pathway in going from iodine to fluorine. The affect of the electron-withdrawing group is not as straightforward. As the electron-withdrawing ability increases, the electron density at the carbon bonded to the leaving group decreases, and thus, the rate constant for the first and rate-limiting step of the polar reaction increases. The Hammett constant, σ_p^-, is indicative of the electron-withdrawing strength.[35a,b,39] The sulfone group is a stronger electron-withdrawing group than the carbonyl group. In general, the reduction potential increases (becomes less negative) as the electron-withdrawing strength increases, and therefore, the more reactive substrates in terms of the polar or S_NAr reaction are also the substrates which are more easily reduced. However, there does not appear to be an exact correlation between electron-withdrawing ability in terms of reactivity in the S_NAr reaction and reduction potential. Indeed, the phenylsulfonyl group has a larger value for σ_p^- [35a] and activates aromatic substrates toward nucleophilic attack[40] more so than the benzoyl group; however, diphenyl sulfone appears to have a lower reduction potential for one-electron reduction to the radical anion than that of benzophenone. Values reported in the literature for the reduction potentials of diphenyl sulfone and benzophenone are approximately −2.1[41] and −1.75 V[18,34b,c] (vs SCE), respectively. As a consequence, the polar pathway is favored to a greater extent in the case of sulfone activation compared to carbonyl activation. The ability to compare other electron-withdrawing groups is more difficult. For example, the nitro group is a stronger electron-withdrawing group than both the sulfone and carbonyl groups, and nitrobenzene is more easily reduced than both diphenyl sulfone and benzophenone.[42] Therefore, the affect of the nitro group on the balance between the polar and SET pathways relative to the affect of the sulfone and carbonyl groups cannot be predicted by the same qualitative approach.

The reaction conditions also affect the balance between the polar and SET pathways. Only a small percentage of the reactants need to follow the SET pathway for the molecular weight of the resulting polymer to be significantly decreased. The effect of temperature has been discussed previously. Other factors which may affect the balance between the polar and SET pathways are solvent, ion pairing, and solubility or heterogeneity of the reactants.

Factors which affect the amount of the dianion relative to the amount of the monoanion of the hydroquinone are expected to influence the extent of reductive dehalogenation and, therefore, the polymer molecular weight. Lower basicity of the polymerization media or protection of the phenol groups followed by slow deprotection during the polyetherification should increase the molecular weights.

Conclusions

Reductive dehalogenation has been shown to limit the polymer molecular weight obtainable in the polyetherification of bis(aryl chloride)s and bis(aryl bromide)s that are activated by the carbonyl group with bisphenolates based on hydroquinone. The occurrence of reductive dehalogenation is dependent on the nature of the substituent of the hydroquinone and the polymerization temperature. A mechanism involving single electron transfer from the dianion of the hydroquinone to the 4-chloro- or 4-bromobenzophenone moiety has been proposed for the reductive dehalogenation reaction. Therefore, these polyetherifications involve a competition between polar and SET pathways. The aromatic nucleophilic substitution reaction constitutes the polar pathway, whereas the reductive dehalogenation reaction proceeds via a SET pathway.

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