Poly(aryl ether ketone) synthesis via competing S_NAR and $S_{RN}1$ reactions: 1. Polymers derived from 1,3-bis(*p*-chlorobenzoyl)benzene and 1,3-bis(*p*-fluorobenzoyl)benzene with hydroquinone and 4,4′-isopropylidenediphenol

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Poly(aryl ether ketone)s were synthesized by the reaction of 1,3-(bischlorobenzoyl)benzene or the corresponding fluoro analogue with bisphenoxides derived from either hydroquinone or 4,4′-isopropylidenebiphenol (bisphenol-A). With the stronger nucleophile, obtained from bisphenol-A, and either of the dihalides, high molecular weight polymers are formed exclusively via a nucleophilic aromatic substitution (S_NAR) reaction. A similar reaction leads to the formation of a high molecular weight polymer when the weaker nucleophile, derived from hydroquinone, is allowed to react with the bisfluoride. On the other hand, oligomeric products are obtained when the bischloride is treated with this weaker nucleophile. In this case, both S_NAR and $S_{RN}1$ (substitution, radical-nucleophilic, unimolecular) mechanisms are operative for the replacement of the chlorine atoms. The $S_{RN}1$ pathway, which is responsible for the formation of oligomeric products, can be eliminated by the addition of a suitable radical scavenger. High molecular weight poly(aryl ether ketone) is then formed via the S_NAR mechanism.

(**Keywords: poly(aryl ether ketone)s; 1,3-bis(*p*-chlorobenzoyl) benzene; 1,3-bis(*p*-fluorobenzoyl)benzene; competing S_NAR and $S_{RN}1$ mechanisms; radical scavenger; oligomer; high molecular weight polymer**)

INTRODUCTION

Poly(aryl ether ketone)s belong to a class of materials known as engineering thermoplastics[1,2]. During the past decade ICI has commercialized an aromatic poly(aryl ether ketone)[3–5], PEEK™, **1**, which has contributed to the enhanced scientific interest in this class of materials. Poly(aryl ether ketone)s exhibit many desirable characteristics including exceptional thermooxidative and dimensional stability, resistance against radioactive irradiation and excellent mechanical properties. The introduction of crystallinity into a poly(aryl ether ketone) backbone provides improvement in the solvent resistance and modulus. PEEK exhibits a high degree of crystallinity and a high melting point (T_m) of 335°C. On the other hand, PEEK suffers from poor creep behaviour above its relatively low glass transition temperature[6] (T_g) of 145°C. Therefore, attempts have been made to either increase the glass transition temperatures of semicrystalline poly(aryl ether ketone)s in general or to introduce crosslink sites into the PEEK backbone[7–10]. In an attempt to achieve higher glass transition temperatures and/or higher melting points, two carbonyl groups (in contrast to PEEK which contains one carbonyl group) have been introduced into the polymer repeat unit structures (e.g. **2a** and **2b**)[11,12].

Polymer **2a** was synthesized by the reaction of bisphenol-A with either 1,4-bis(*p*-fluorobenzoyl) benzene (1,4-FBB), **3a**, or 1,3-bis(*p*-fluorobenzoyl) benzene (1,3-FBB), **3b**, via nucleophilic aromatic substitution (S_NAR) reactions[13]. The reaction of bisphenol-A with 1,3-bis(*p*-chlorobenzoyl) benzene (1,3-CBB), **3c**, to synthesize high molecular weight poly(aryl ether ketone) has been previously reported[14]. Surprisingly, an equally common bisphenol, hydroquinone, was not used along with 1,3-CBB to synthesize high molecular weight polymers. Our attempts to synthesize the same polymer resulted in the formation of oligomeric products only[15]. This was intriguing in the light of the fact that both bisphenol-A and hydroquinone react with 4,4′-difluorobenzophenone to afford high molecular weight polymers, and only oligomeric products are obtained when 4,4′-dichlorobenzophenone is used[4,16]. Thus, both bisphenols exhibit a parallel reactivity pattern with the dihalobenzophenone but fail to do so with 1,3-CBB. This prompted us to undertake an extensive investigation in order to gain a fundamental understanding of the mechanism of

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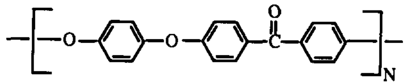
poly(aryl ether ketone) synthesis with particular emphasis on 1,3-CBB and 1,3-FBB.



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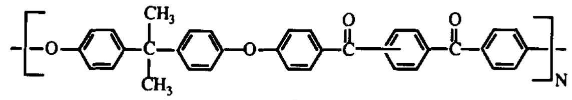
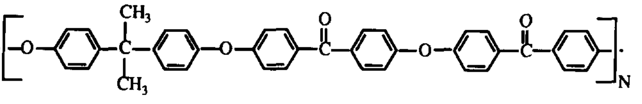


2a



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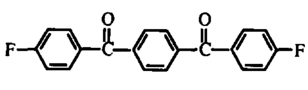
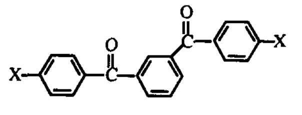


3a



3 b, X= F

c, X= Cl

Our findings suggest that both S_NAR and $S_{RN}1$[17,18] reactions are responsible for the replacement of the chlorine atoms when the weaker nucleophile (bisphenoxide from hydroquinone) and 1,3-CBB are used. The $S_{RN}1$ pathway, which is responsible for the formation of the oligomeric products in these reactions, can be eliminated by the addition of a catalytic amount of a suitable radical scavenger to afford high molecular polymer via the S_NAR mechanism. We present experimental evidence in support of our findings and report herein model reactions of phenol and 4-tert-butylphenol with 1,3-CBB and 1,3-FBB with or without the presence of a radical scavenger and the corresponding polymerization studies with bisphenol-A and hydroquinone. The thermal, spectral characteristics and molecular weight nature of polymers synthesized in the presence or absence of the radical scavenger have been compared. At the completion of our work and while this manuscript was in preparation, a somewhat similar preliminary report has appeared[19].

EXPERIMENTAL

Materials

Dimethylacetamide (DMAc) (Aldrich) was dried over calcium hydride and then distilled at reduced pressure. Diphenyl sulphone (DPS) (Aldrich) was recrystallized from acetone. Toluene was used as received.

4,4′-Isopropylidenebiphenol (bisphenol-A) (Dow Chemical Co.), was purified by recrystallization from toluene and dried at reduced pressure at 80°C for 24 h. Hydroquinone (Eastman Kodak) was recrystallized from deoxygenated acetone. Thionyl chloride (Aldrich) was stirred over triphenyl phosphite and distilled at normal pressure prior to use. Anhydrous potassium carbonate (Fisher) was dried in an oven overnight at 100°C. All other reagents were used without further purification.

General procedure for model compound synthesis

A three-necked, 100 ml, round-bottomed flask fitted with a nitrogen inlet, a thermometer, and a Dean-Stark trap fitted with a condenser was charged with 1 mmol of 1,3-CBB (0.354 g) or 1,3-FBB (0.322 g), 2 mmol of the desired phenol (4-tert-butylphenol or phenol) (*Table 1*), 7.0 g (~six-fold excess) of anhydrous potassium carbonate, 35 ml of DMAc and 20 ml of toluene. For reactions involving the use of a catalytic amount of radical scavenger, tetraphenylhydrazine (TPH) (0.004 mmol, 0.0135 g) was also added to the reaction mixture. The reaction mixture was heated at solvent reflux (145°C), and water, the byproduct of the reaction, was removed by azeotropic distillation. The reaction mixture was heated to 160°C for 16 h and then cooled to room temperature. It was distilled under reduced pressure to remove all solvents. The residue was dissolved in methylene chloride and the resulting solution was filtered to remove residual salts. The filtrate was washed repeatedly with water, dried over anhydrous magnesium sulphate and the solvent removed by rotary evaporation at reduced pressure. For those cases in which the crude product consisted of only a single compound, the desired model ether was obtained after crystallization. On the other hand, the mixture of compounds present in the crude product from the reactions of phenol and 1,3-CBB in the absence of TPH, were separated on a silica gel column (40% hexane/methylene chloride).

Table 1 Intrinsic viscosity data of polymers **4** and **5**

Polymer	Bishalide	Bisphenol	Additive	$[\eta]$ (dl g^{-1})
4a	1,3-CBB	Bisphenol-A	–	0.41[a]
4b	1,3-FBB	Bisphenol-A	–	0.47[a]
5a	1,3-CBB	Hydroquinone	–	0.17[b]
5b	1,3-FBB	Hydroquinone	–	0.43[b]
5c	1,3-CBB	Hydroquinone	TPH	0.47[b]

[a] Solvent, chloroform

[b] Solvent, concentrated H_2SO_4

General procedure for polymer synthesis

A typical synthesis of poly(aryl ether ketone) was conducted in a 500 ml, four-necked, round-bottomed flask equipped with a nitrogen inlet, a thermometer, an overhead stirrer and a Dean-Stark trap. A detailed synthetic procedure used to prepare the bisphenol-A functional polymer is provided. The flask was charged with 5.7 g (25 mmol) of bisphenol-A and 25 mmol of the desired bishalide from Teflon-coated weighing pans. The weighing pans were carefully washed with 125 ml of DMAc with solvent flowing directly into the reaction vessel. Anhydrous potassium carbonate, 10 g (~six-fold excess) was added followed by 45 ml of toluene. In reactions involving the use of the radical scavenger, 0.05 mmol (0.168 g) of TPH was then added. The reaction mixture was heated until solvent began to reflux at 140°C. Water (byproduct of the reaction) was continuously removed via the Dean-Stark trap. The reflux temperature was maintained for 4 to 6 h until the accumulation of water was no longer evident in the Dean-Stark trap. The reaction mixture acquired a light yellow colour at the initial stage of the reaction due to the formation of the phenoxide and slowly deepened to brown with time. The reaction temperature was gradually raised to 165°C by removing toluene from the Dean-Stark trap. The reaction mixture was heated at that temperature for a period of 18 h. An additional amount (20 ml) of DMAc was added to reduce the high viscosity of the reaction mixture and the heating at 165°C was continued for an additional 6 h.

The viscous reaction mixture was allowed to cool to room temperature, diluted with 100 ml of DMAc and filtered to remove inorganic salts. The filtrate was acidified with several drops of glacial acetic acid to neutralize the phenoxide end groups and the polymer was precipitated with a 10-fold volume of methanol. The polymer was then dried at reduced pressure at 50°C for 8 to 10 h. It was redissolved in the appropriate solvent, the solution was filtered, acidified with glacial acetic acid, and the polymer coagulated in methanol. The fibrous solid was dried as before. In reactions involving hydroquinone (25 mmol), 45 g of DPS was added in addition to the solvents mentioned earlier. These reactions were carried out at 140°C for 2 h and the temperature of the reaction mixture was allowed to increase to 180°C by removing toluene and DMAc via the Dean-Stark trap. The temperature was maintained at 180°C for 18 h. The reaction vessel was heated further and the reaction was stirred at 220°C for 4 h and finally at 230°C for an additional 2 h. The polymer was coagulated by pouring the reaction mixture while still hot (160°C) into a 10-fold volume of acetone. The coagulated polymer was then extracted with acetone, water and acetone, in that order, using a Soxhlet apparatus. The polymer was then dried as before.

Characterization

^{1}H and ^{13}C n.m.r. spectra of the model compounds and the polymers were recorded using a General Electric QE-300 instrument. The n.m.r. spectra of the semicrystalline polymers were obtained in trifluoromethanesulphonic acid solution. Deuterium oxide (D_2O) in a sealed capillary tube was used as the lock solvent. I.r. spectra were obtained with a Nicolet DxB *FT*i.r. spectrophotometer. Mass spectra were obtained on a HP Model 5995 A g.c.–m.s. spectrometer. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured either with a DuPont DSC 2100 or a Perkin-Elmer DSC-7 at a heating rate of 10°C min^{-1}. The same instruments were used to measure the melting points of the semicrystalline polymers. Melting points were taken as the peak maxima. Thermogravimetric analysis (t.g.a.) of the polymer samples was conducted at a heating rate of 10°C min^{-1} in nitrogen. Intrinsic viscosity measurements for the semicrystalline and the amorphous polymers were determined by using a Cannon-Ubbelohde dilution viscometer in either concentrated sulphuric acid or chloroform (25°C), respectively.

RESULTS AND DISCUSSION

Monomer synthesis

The monomers, 1,3-CBB and 1,3-FBB, were prepared according to a reported procedure[11]. The purity of these compounds was of critical importance, in order to attain high molecular weight polymers and to establish the mechanisms of chloro group replacement reactions without ambiguities. The compounds were therefore crystallized repeatedly from toluene and d.s.c. analysis was utilized to ascertain the purity of the monomers (*Figure 1*). An examination of *Figure 1* clearly indicates that the monomers are of very high purity. This is of great importance to the present study which deals with the mechanisms of poly(aryl ether) synthesis.

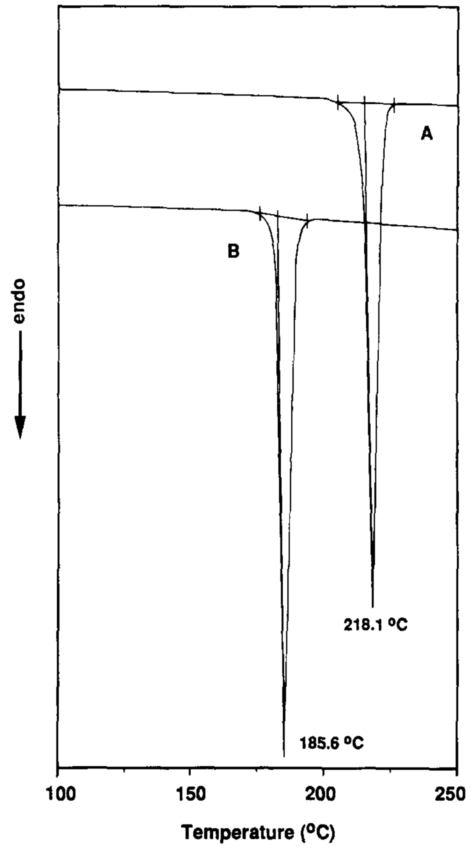
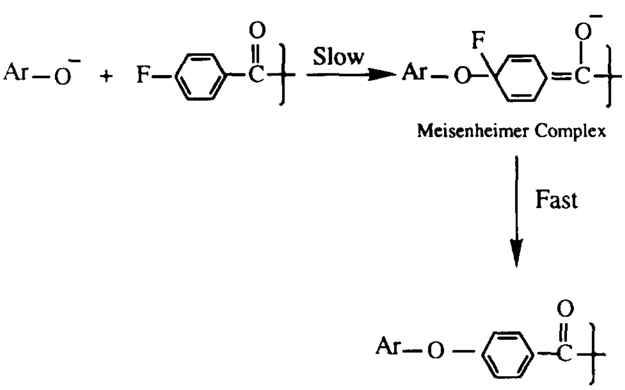


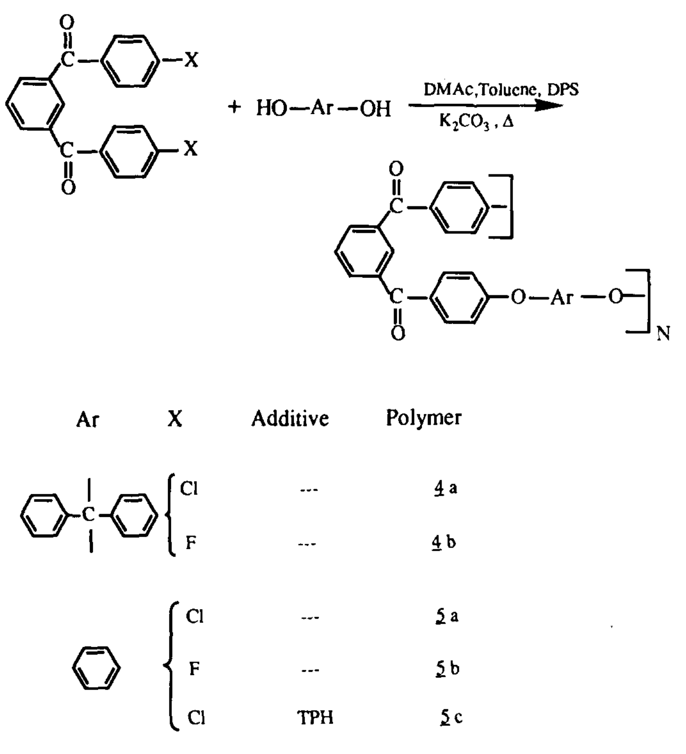
Figure 1 D.s.c. thermograms; A, 1,3-bis(*p*-chlorobenzoyl)benzene; B, 1,3-bis(*p*-fluorobenzoyl)benzene

Polymer synthesis

High molecular weight poly(aryl ether ketone)s were synthesized by the reaction of a suitable bisphenoxide with a bisarylfluoride activated by keto groups. The reaction proceeds through the S_NAR mechanism[20]. The ether linkages are formed via the slow formation of the Meisenheimer complex, followed by the fast elimination of the fluoride anions (*Scheme 1*). The corresponding bisarylchlorides are thought to be insufficiently reactive for the synthesis of high molecular weight polymers under the same reaction conditions. For example, 4,4′-difluorobenzophenone is used for the preparation of PEEK and other poly(aryl ether ketone)s[23]. On the other hand, under similar reaction conditions, 4,4′-dichlorobenzophenone is thought to be an unsuitable monomer for poly(aryl ether) synthesis[3]. This has been attributed to the low reactivity of a chlorine substituent, due to its



Scheme 1



Scheme 2

lower electronegativity as compared to that of a fluorine atom.

In contrast, bischlorides, such as 1,3-CBB, have been shown to be reactive enough to obtain high molecular weight polymers with bisphenol-A. High molecular weight amorphous polymers, **4a** and **4b**, could be synthesized by the reaction of bisphenol-A with either 1,3-CBB or 1,3-FBB (*Scheme 2*). These reactions were carried out in DMAc in the presence of anhydrous potassium carbonate at 165°C. In both instances, clear, finger-nail creasable films could be obtained upon compression moulding or solution casting from chloroform. The high molecular weight nature of **4a** and **4b** was further confirmed by measuring intrinsic viscosities in chloroform (*Table 1*). The identical repeat unit structures of these two polymers were verified by ^{13}C n.m.r. analysis. The ^{13}C n.m.r. of polymer **4a** is shown in *Figure 2*. The observed peak positions are in agreement with calculated chemical shifts[21]. With the available instrumentation, it was not possible to resolve the absorbances due to C-1 and C-12 which appear at the same position. Furthermore, owing to the high molecular weight of the polymer, additional absorbances due to the terminal units were not observed.

The reaction of 1,3-CBB with hydroquinone resulted in the formation of low molecular weight oligomeric products which precipitated from the reaction mixture

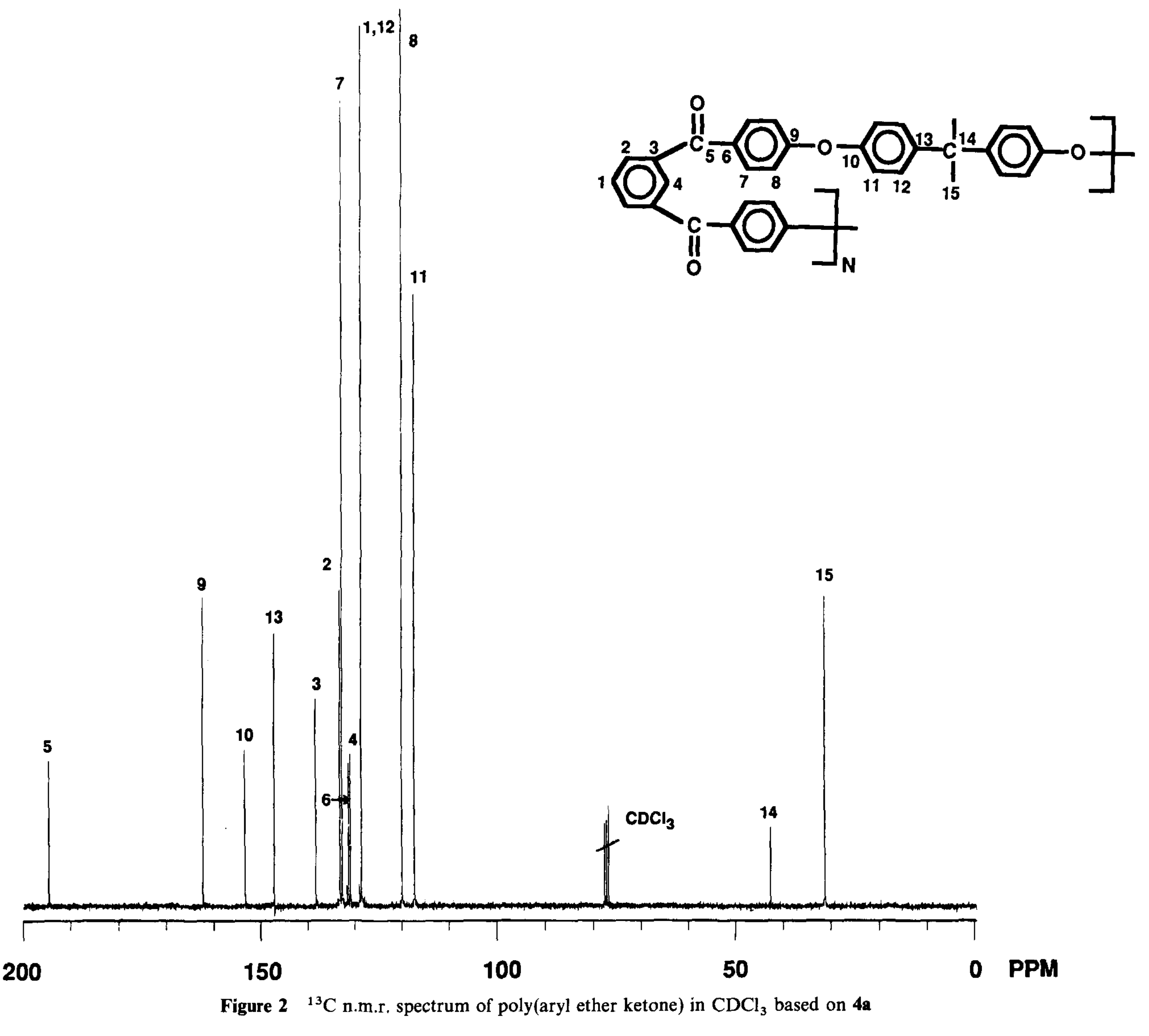
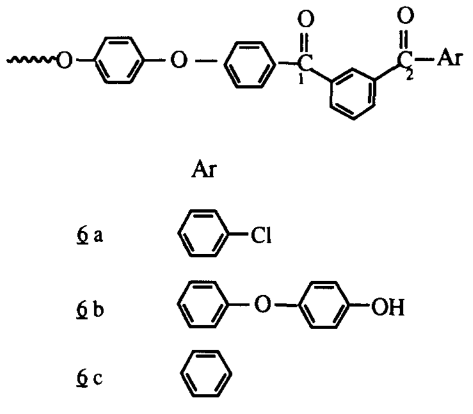


Figure 2 ^{13}C n.m.r. spectrum of poly(aryl ether ketone) in $CDCl_3$ based on **4a**

in refluxing DMAc (*Scheme 2*). In order to circumvent the problems associated with product insolubility and the resulting low molecular weight nature polymer, DPS was used as the solvent (see Experimental). DPS has proven to be an excellent solvent for the synthesis of high molecular weight semicrystalline poly(aryl ether ketone)s with high melting points[3,9]. It was anticipated that at a higher reaction temperature the enhanced solubility of the oligomers would be maintained and the formation of high molecular weight product would be possible. The reaction was carried out at 230°C for a period of 5 h. The reaction mixture remained fairly homogeneous at this elevated temperature. The polymer, **5a**, was precipitated with acetone. Residual salts and DPS were removed from the coagulated polymer by extracting with acetone, water and acetone, in that order, in a Soxhlet apparatus. The resulting product was powdery in nature, indicative of low molecular weight, and its solubility behaviour was typical of semicrystalline poly(aryl ether ketone)s. It was insoluble in hot chlorinated solvents, tetrahydrofuran and a variety of dipolar aprotic solvents including DMAc and *N*-methylpyrrolidione. It was only soluble in strong protic acids such as concentrated aqueous sulphuric acid solution and trifluoromethanesulphonic acid. The low molecular weight of the polymer was verified by intrinsic viscosity measurements in concentrated sulphuric acid at 25°C ($\eta = 0.17\,\mathrm{dl\,g^{-1}}$) (*Table 1*). The semicrystalline nature of the oligomeric product was further confirmed by d.s.c. The d.s.c. thermogram of the oligomer showed a melting point endotherm, T_m, at 270°C in the first heat and a crystallization exotherm, T_c, at 197°C on slow cooling. Upon second heating, a glass transition temperature, T_g, at 127°C, a T_c at 195°C and a T_m at 280°C are observed. In the final heating after quench cooling, the polymer exhibits a T_g, a T_c and a T_m at 128°C, 207°C and 281°C, respectively. This suggested that a higher molecular weight polymer could be obtained by conducting the polymerization reaction at a temperature above 230°C and approaching that of the oligomer melting point, 270°C. The reaction was therefore carried out at 270°C for a period of 5 h. Unfortunately only oligomeric products could be isolated. In sharp contrast, the reaction of hydroquinone with 1,3-FBB, conducted at 230°C for a period of 5 h, resulted in the formation of a high molecular weight polymer, **5b** (*Scheme 2*). Polymer **5b** was fibrous in nature in contrast to the powdery nature of **5a** and its solubility behaviour was identical to that of **5a**. Polymer **5b** exhibited a significantly higher intrinsic viscosity value ($\eta = 0.43\,\mathrm{dl\,g^{-1}}$) than that of **5a** ($\eta = 0.17\,\mathrm{dl\,g^{-1}}$) in the same solvent, concentrated aqueous sulphuric acid solution (*Table 1*). This was indicative of the higher molecular weight nature of **5b** than that of **5a**. D.s.c. analysis of **5b** revealed similar yet non-identical thermal behaviour to that of **5a**. An analysis of the d.s.c. thermograms of **5b** shows a melting point endotherm in the first heating at 282°C. The polymer did not recrystallize upon slow cooling, unlike **5a**. In the subsequent heating cycles only well defined glass transition temperatures at 140°C could be observed. This is due to the fact that **5b** exhibits a lower tendency to recrystallize than **5a**, possibly because of the apparent molecular weight differences.

^{13}C n.m.r. analysis of 5a and 5b

The solution (trifluoromethanesulphonic acid) ^{13}C n.m.r. spectra of the polymers **5a** and **5b** are shown in *Figures 3a* and *b* respectively. The spectrum of **5b** exhibits a total of 11 absorbances, consistent with the repeat unit structure, which contains 11 different carbon atoms. Except for the most downfield absorbance at 199.6 ppm, which was assigned to the carbonyl carbon atom[21], assignments for the remaining 10 absorbances due to the carbon atoms of the benzene moieties, could not be made. This is due to the fact that the necessary substituent chemical shift (SCS) values, in trifluoromethanesulphonic acid solvent system for various benzene ring substituents, are not readily available. An examination of the spectrum of polymer **5a** (*Figure 3a*), reveals the presence of a greater number of absorbances than the expected total of 11 peaks. As mentioned earlier, polymer **5a** is of lower molecular weight than **5b**. Therefore, the concentration of the chain ends will be significantly higher in case of **5a** than of **5b**. Thus, it is not inappropriate to conclude that the additional absorbances in the ^{13}C spectrum of **5a** must be due to the carbon atoms present in the chain terminal moieties. It was possible, however, to assign the absorbances at 199.2, 199.6 and 206.8 ppm to three different carbonyl carbon atoms[21]. Furthermore, based on the carbonyl carbon atom assignment for the higher molecular weight polymer **5b**, the absorbance at 199.6 ppm for **5a**, could be assigned to the in-chain carbonyl carbon atom, C-1 (*Scheme 3*). The remaining two absorbances at 199.2 and 206.8 ppm must therefore be due to the carbonyl carbon atoms at the chain terminal moieties. Since the polymerization reactions were carried out using the bisphenol and the bishalide in 1:1 stoichiometry, it may be expected that some of the chains of oligomeric **5a** will be terminated with the halide, namely a 1,3-CBB fragment, **6a**, and a fraction of the chains will be terminated with phenolic groups, **6b** (*Scheme 3*). The ^{13}C n.m.r. of 1,3-CBB in trifluoromethanesulphonic acid exhibits an absorbance at 206.7 ppm due to the carbonyl carbon atoms. This led to the initial conclusion that the peak at 206.8 ppm in the ^{13}C spectrum of **5a** must be due to the chain termini with the 1,3-CBB fragment. In order to further verify the presence of chloro groups at the chain terminus, the i.r. (KBr) spectra of 1,3-CBB and the oligomer **5a** were compared. The C–Cl bond in 1,3-CBB absorbs strongly[22] at $1088\,\mathrm{cm^{-1}}$. Such an absorption is absent in the i.r. spectrum of **5a**. Although not very conclusive, this suggested that, contrary to the initial expectation, the chain termini of **5a** are devoid of chlorine atoms and **6a** does not exist. Therefore the assignment of the ^{13}C absorbance at 206.8 ppm to the



Scheme 3

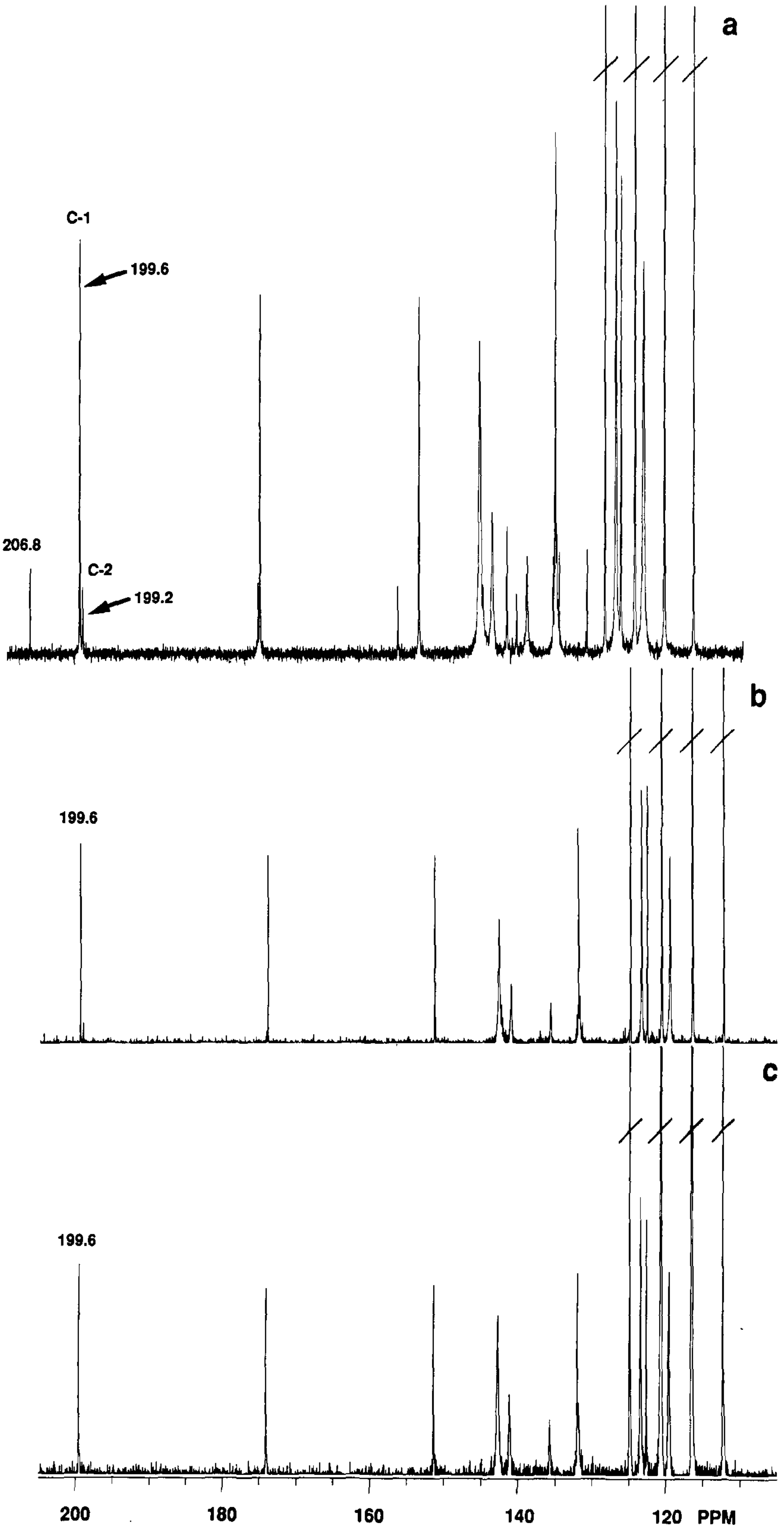


Figure 3 ^{13}C n.m.r. spectrum of poly(aryl ether ketone) in trifluoromethanesulphonic acid based on (a) **5a**, (b) **5b** and (c) **5c**

chain terminal carbonyl carbon atoms with 1,3-CBB fragment of **5a** had to be modified. We were unable to make any further assignment of this absorbance at this point of the investigation. The remaining absorbance at 199.2 ppm was assigned to the carbonyl carbon atom, C-2, present in the chain end **6b**. This is not unreasonable, if the similar yet slightly different chemical environments of the in-chain carbonyl carbon atom, C-1 ($\delta = 199.6$), and that of C-2 are considered. Although the ^{13}C n.m.r. analysis was helpful, it was not conclusive. The peak at 206.8 ppm contained in the spectrum of **5a** due to one type of carbonyl carbon atom of the chain terminal moieties, remained to be assigned. In order to understand the nature of these carbonyl groups and to further understand the different reactivity patterns of 1,3-CBB with hydroquinone and bisphenol-A, model compound studies were undertaken.

Model compound studies

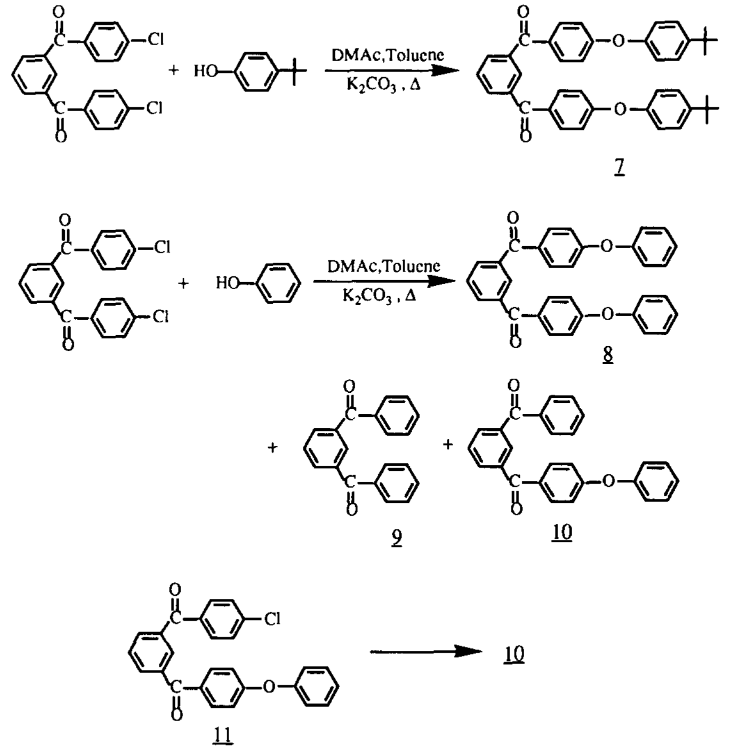
The bishalides, 1,3-CBB and 1,3-FBB, were treated with phenol and 4-tertbutylphenol to synthesize a series of model compounds. All reactions were carried out in DMAc in the presence of anhydrous potassium carbonate (see Experimental). Model bisether **7** could be obtained in quantitative yield by the reaction of 4-tertbutylphenol with 1,3-CBB and 1,3-FBB (*Scheme 4*). The ^{13}C n.m.r. spectra of **7** (obtained from these two reactions) in $CDCl_3$ were identical and consistent with the expected structure. Similarly, the reaction of phenol with 1,3-FBB went to completion and the desired bisether, **8**, could be isolated in quantitative yield. The model reactions discussed so far proceed by S_NAR mechanisms (*Scheme 1*)[13]. Analytical data for various model compounds are shown in *Table 2*.

The reaction of phenol with 1,3-CBB, on the other hand, was complicated by the presence of two additional major products, **9** and **10** ($\sim$50%), in addition to the desired bisether, **8** ($\sim$50%) (*Scheme 4*). An examination of the nature of the products **9** and **10** indicates that **9** is obtained from dehalogenation of 1,3-CBB. Dehalogenation of monophenoxy substituted 1,3-CBB, **11**, results in the formation of **10**. Compound **9** was prepared independently by Friedel–Crafts acylation of benzene with isophthaloyl chloride in the presence of anhydrous aluminium chloride according to a standard procedure. The i.r. and solution ^{13}C n.m.r. absorbances, the m.s. fragmentation patterns and the melting points of **9**, obtained from the two reaction sources agreed very well indeed. The solution ^{13}C n.m.r. spectrum of **9** in trifluoromethanesulphonic acid is shown in *Figure 4*. An examination of the figure shows a total of nine absorbances. Once again, except for the most downfield absorbance it was not possible to make any other assignments for reasons alluded to earlier. The most downfield absorbance at 208.6 ppm, was assigned to the carbonyl carbon atom, C-5 (*Figure 4*). This is of crucial importance to the present discussion, because, as stated earlier, polymer **5a**, derived from hydroquinone and 1,3-CBB, exhibits an absorbance at 206.8 ppm. Therefore, it readily became very clear that polymer **5a** must also contain chain terminus **6c** (*Scheme 3*) in addition to **6b**, the presence of which has been confirmed earlier. ^{13}C n.m.r. analysis of the polymers coupled with the model compound studies led to the following conclusions. First, dehalogenation reactions become operative when 1,3-CBB is allowed to react with either the phenoxide derived from phenol or the bisphenoxide from hydroquinone (during polymerization). A direct consequence of dehalogenation during polymerization is the loss of 1:1 stoichiometry between the halide and the bisphenoxide resulting in the formation of oligomeric products. Second, S_NAR mechanisms (*Scheme 1*), which can account for the formation of the bisether, cannot explain the dehalogenation processes. Third, the reactions of 1,3-CBB with 4-tertbutylphenoxide or the bisphenoxide from bisphenol-A proceed to completion without dehalogenation via an S_NAR mechanism. Finally, all reactions of 1,3-FBB discussed so far follow the same S_NAR mechanism.

Table 2 Analytical data for model compounds 7–9

Compound	Phenol	Bishalide	Yield (%)	M.p. (°C)	I.r. (KBr) (cm^{-1})	^{13}C n.m.r. (δ)[a]	Mass spectrum (m/e) relative intensities
7	4-tertbutylphenol	1,3-CBB	89	131–133	2960, 1644, 1585, 1494, 1311, 1245	31.34, 34.32 116.83, 119.87 126.78, 128.30 130.63, 130.86 132.37, 132.80 138.03, 147.58 152.68, 162.23 194.37	585 (16) 582 (29) 568 (40) 567 (100) 511 (16) 453 (10) 341 (18)
8	Phenol	1,3-CBB	91	91–93	1651, 1586, 1499, 1402, 1245	119.35, 120.38 121.92, 127.31 130.57, 131.48 131.79, 135.54 140.13, 142.49 152.61, 174.88 198.41	471 (25) 470 (64) 198 (14) 197 (100) 141 (16)
9	–	–	–	100–102	1658, 1599, 1448, 1317, 1251	129.05, 131.19 131.54, 132.03 137.52, 139.86 144.48, 144.97 208.28	286 (48) 209 (32) 181 (14) 105 (100)

[a] Solvent: 7, $CDCl_3$; **8** and **9**, trifluoromethanesulphonic acid



Scheme 4

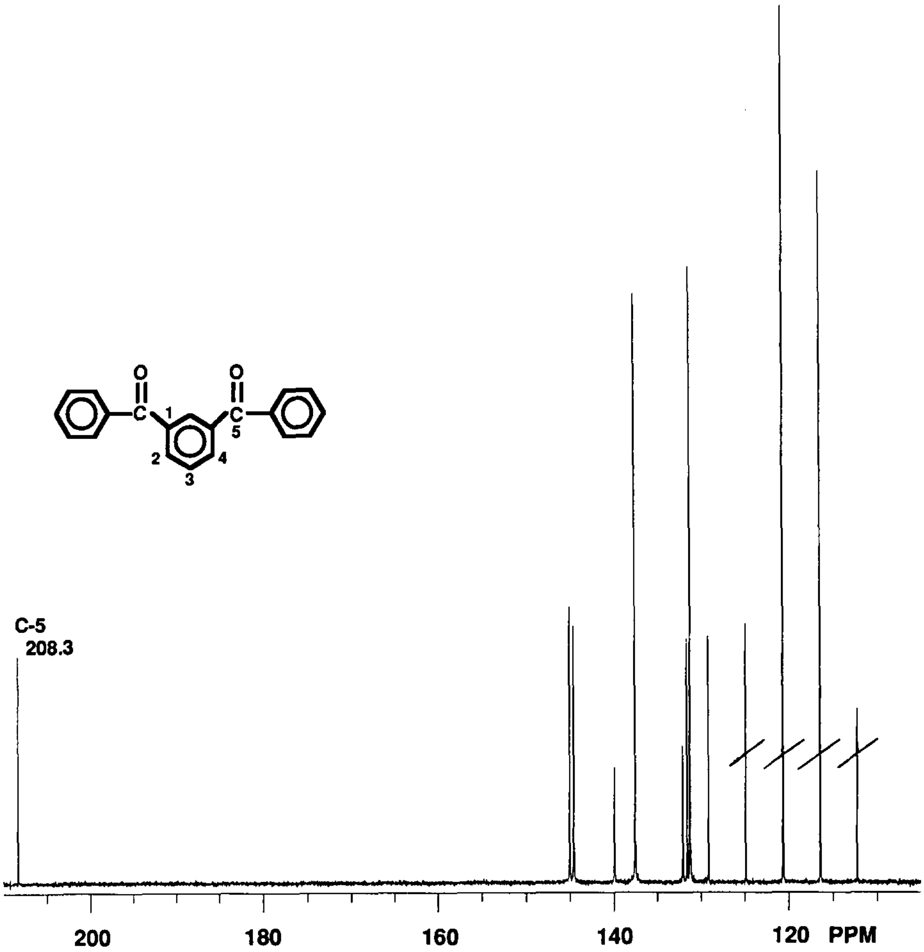
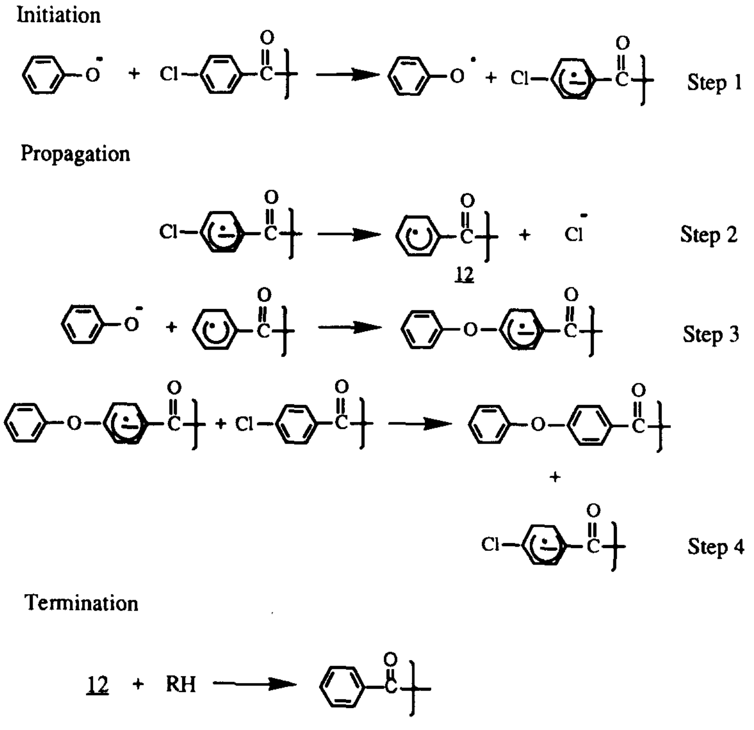


Figure 4 ^{13}C n.m.r. spectrum of model compound **9** in trifluoromethanesulphonic acid

Competing S_NAR and $S_{RN}1$ process

The difference in reactivity of 1,3-CBB towards the phenoxides derived from phenol and 4-tertbutylphenol must arise from the relative nucleophilicities of the anions[22]. The required set of nucleophilicity values to permit this comparison is not available. However, it is possible to correlate the order of basicity of the phenoxide anions with their relative nucleophilicity. That this can be done is due to the relatively small size of the oxygen anionic centre and also due to the fact that the attacking atom is the same (oxygen) in both the cases[23-25]. A comparison of the relative acidity constants for phenol and 4-tertbutylphenol reveals the following order: 4-tertbutylphenol < phenol[26]. It therefore follows that the order of the conjugate base strength and nucleophilicity is $\text{Ph-O}^- < 4\text{-}(CH_3)\text{C-Ph-O}^-$. Thus it is not surprising that the weaker phenoxide derived from phenol can show different reactivity patterns with 1,3-CBB and 1,3-FBB. In the case of the more reactive bisfluoride, fluoride displacement reactions by the weaker nucleophile take place by the S_NAR pathway, whereas a different mechanism, alone or in addition to the S_NAR mechanism, must be operative when the weaker nucleophile is allowed to react with the less reactive 1,3-CBB. The more strongly nucleophilic anion derived from 4-tertbutylphenol displaces the halogen atoms by the S_NAR pathway irrespective of the reactivities of the bishalides.

$S_{RN}1$ reactions involving phenoxides at high reaction temperatures for the formation of aromatic ethers have been well documented[18,27-30]. In addition, nucleophilic replacement of the halogen atoms of 4-chlorobenzophenone[31,32] and halopyridines[33-35], by $S_{RN}1$ mechanisms are well known. Furthermore, reductive dehalogenation reactions of 4-chlorobenzophenone leading to the formation of benzophenone during $S_{RN}1$ substitution reactions have also been observed[31,32]. This suggested that in the present case (reactions of 1,3-CBB with the phenoxide from phenol or from hydroquinone), $S_{RN}1$ processes might account for the reductive dehalogenation reactions. Either $S_{RN}1$ alone or in competition with the S_NAR pathway could account for the formation of bisether. These reactions are illustrated in *Scheme 5*. Initiation (step 1) is provided by the electron transfer, presumably from the phenoxide anion, to form the radical anion of the halogenated aromatic ketone, 1,3-CBB. In the second step, the radical anion expels the chloride ion to form a radical, which combines in the third step with a phenoxide anion to form a radical anion again. In the fourth step, this newly formed radical anion transfers an electron to the halogen-bearing nucleus of 1,3-CBB to form an ether linkage and a new radical anion. Steps 2, 3 and 4, which can repeat themselves, are the propagation steps. The situation is further complicated by the presence of DMAc and toluene as the solvent system. It is highly likely that the radical, **12**, formed in the second step can abstract a hydrogen atom from either of these two solvents and compounds such as **9** and **10** can form. Since the amount of toluene is expected to be exceedingly low at a reaction temperature of 165°C, it is highly likely DMAc serves as the major source of hydrogen atom to terminate **12**. Since dimethylacetamide is present in excess as the solvent, the formation of bisether **8**, and the monoether, **10**, by the reaction of the radical **12** with the phenoxide anion would have been expected to be very low and the completely dehalogenated compound **9** to have been the major product. However, as stated earlier, the bisether was isolated in ~50% yield. Therefore, the ether formation may be occurring via both $S_{RN}1$ and S_NAR competing reactions. Under these circumstances, if the $S_{RN}1$ pathway can be suppressed, then the bisethers would be formed only by the S_NAR reaction. It follows, therefore, that it would be possible to synthesize high molecular weight polymers by the reaction of hydroquinone and 1,3-CBB via the S_NAR reaction by eliminating the $S_{RN}1$ processes. The validity of these contentions is dependent on one tacit assumption, namely, the energetics of the reactions of **12** with DMAc or toluene and the phenoxy anions are not significantly different.



Scheme 5

Additional experimental evidence will be presented in the following section in support of these assumptions.

Suppression of $S_{RN}1$ processes in the presence of a radical scavenger

A wide variety of organic and inorganic additives have been used as inhibitors to suppress the $S_{RN}1$ reaction by scavenging the radical formed in step 2. These radical scavengers include 1,1-diphenylethylene, azoxybenzene, nitrobenzene, 2,2′-dinitrobiphenyl, copper(II) chloride[35], di-tertbutyl nitroxide[33], and tetraphenylhydrazine[36]. Tetraphenylhydrazine (TPH) was used in the present set of experiments as the reagent of choice to suppress the $S_{RN}1$ reaction. Phenol was allowed to react with 1,3-CBB in dimethylacetamide in the presence of anhydrous potassium carbonate and a catalytic (0.02 mol% of phenol) amount of tetraphenylhydrazine (under reaction conditions similar to *Scheme 4*). The derived bisether, **8**, was isolated as the sole product in quantitative yield. Formation of the dehalogenated products, **9** and **10**, was not evident. The reactions of 4-tertbutylphenol with 1,3-CBB or 1,3-FBB or the reactions of phenol with 1,3-FBB, which are known to proceed via the S_NAR mechanism, remained unaffected by the addition of a catalytic or a 10-fold excess of tetraphenylhydrazine.

The polymerization reactions of hydroquinone and 1,3-CBB in presence of a catalytic amount (0.05 mol% of the phenolic hydroxyl groups) of TPH resulted in the formation of high molecular weight semicrystalline polymer **5c** (*Table 1*). The high molecular weight nature of the polymer was verified by intrinsic viscosity measurements in concentrated aqueous sulphuric acid solution at 25°C ($\eta = 0.47\,\mathrm{dl\,g^{-1}}$). High molecular weight polymer also resulted when the same reaction was carried out in the presence of a 10-fold excess of TPH. The structure of the repeat unit of **5c** was verified by ^{13}C n.m.r. analysis. An examination of the n.m.r. spectrum of **5c** (*Figure 3c*) reveals that it is identical in all respects with that of polymer **5b** (*Figure 3b*), derived from hydroquinone and 1,3-FBB via S_NAR reaction. Furthermore, polymer **5c** exhibited parallel thermal behaviour to **5b**. These experiments established the following facts. First, tetraphenylhydrazine is highly effective in eliminating the $S_{RN}1$ process. Second, in the absence of the $S_{RN}1$ pathway, the reactions of phenol or hydroquinone proceed exclusively via the S_NAR mechanism. This results in the quantitative formation of the bisether in case of the monofunctional phenol and the formation of high molecular weight polymer in the case of hydroquinone. The latter event becomes possible because, in the absence of the $S_{RN}1$ process, dehalogenation reactions of 1,3-CBB or the chain-end halogen moieties do not occur and the initial 1:1 stoichiometry is maintained throughout the course of the reaction. This eventually results in the formation of high molecular weight polymer. Finally, the S_NAR process, which does not involve radical intermediates, remains unaffected by the addition of the radical scavenger, TPH. This was further verified by conducting polymerization reactions of bisphenol-A with 1,3-FBB (which is known to proceed via the S_NAR pathway) in the presence of a catalytic amount of TPH. High molecular weight, amorphous polymers were prepared in this case. These observations confirm parallel findings[19] that, depending on the nature of the bisphenol–bishalide pair, both $S_{RN}1$ and S_NAR processes compete for the formation of poly(aryl ether ketone)s.

Our understanding as to how TPH in catalytic amount prevents the $S_{RN}1$ process from occurring, is meagre. It is known, however, that TPH first dissociates into linear[37] diphenylamino radicals[38]. The resulting diphenylamino radical then possibly accepts an electron from the radical anion formed in the first step (*Scheme 5*) and transfers it to the phenoxy radical to reform the phenoxy anion. This eliminates the subsequent propagation steps (steps 2, 3 and 4). Therefore, halogen replacement occurs via the only slightly more energetically demanding S_NAR pathway.

This investigation raises a series of fundamental questions. First, are competing mechanisms operative for all 'non-reactive' halide nucleophilic replacement reactions? Second, what is the impact of increasing or decreasing solvent polarity on the relative importance of the two competing reactions, since changing solvent polarity is likely to affect the nucleophilicity of the attacking anion? Third, is TPH unique or can other radical trapping agents be used to eliminate the $S_{RN}1$ process? Finally, what is the fate of TPH (which appears to remain unaffected) during the reaction? These and other related questions, including whether TPH plays a role in the first step alone or in the termination step or both, are being addressed at present.

CONCLUSIONS

The mechanisms of the polymerization reactions of hydroquinone with 1,3-CBB and 1,3-FBB have been investigated. The former reaction proceeds via competing $S_{RN}1$ and S_NAR reaction pathways. The $S_{RN}1$ reaction is responsible for dehalogenation of 1,3-CBB and halogen-bearing chain termini. This results in the formation of low molecular weight polymer. By the addition of a catalytic amount of a suitable radical scavenger the $S_{RN}1$ pathway can be eliminated and high molecular weight semicrystalline polymer can be obtained exclusively via S_NAR mechanism. The reaction of hydroquinone with 1,3-FBB, which proceeds via the S_NAR pathway and remains unaffected by the presence or the absence of a radical scavenger, results in the formation of high molecular weight semicrystalline polymer.

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