Competing reactions for poly(aryl ether ketone) synthesis:
2. Preparation of high molecular weight polymer from hydroquinone and 1,3-bis(4-chlorobenzoyl)benzene*

A. Bhatnagar, R. S. Mani, B. King and D. K. Mohanty†
Department of Chemistry and Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859, USA

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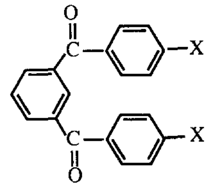
High molecular weight semicrystalline poly(aryl ether ketone)s have been prepared from hydroquinone and 1,3-bis(4-chlorobenzoyl)benzene in diphenylsulfone and anhydrous potassium carbonate with or without toluene. The use of this solvent system, instead of a combination of dimethylacetamide, diphenylsulfone and toluene, results in the elimination of $S_{RN}1$ (radical nucleophilic, unimolecular substitution) processes and the formation of high molecular weight polymer takes place entirely via S_NAR (nucleophilic aromatic substitution) reactions.

(Keywords: reactions; poly(aryl ether ketone); synthesis)

Introduction

Hydroquinone, a common bisphenol, has been used extensively for the preparation of poly(aryl ether)s[1–3]. In particular, a commercially important poly(aryl ether ketone), PEEK, can be prepared from hydroquinone and 4,4′-difluorobenzophenone, in the presence of a base[4]. The successive formation of ether linkages proceeds via nucleophilic aromatic substitution (S_NAR) reactions, presumably through the formation of a Meisenheimer complex[5,6]. This mechanism operates for the formation of high molecular weight semicrystalline polymer from 1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB), **1**, and hydroquinone[7]. Recently[8], the same polymer was prepared by the reactions of hydroquinone and 1,3-bis(4-chlorobenzoyl)benzene (1,3-CBB), **2**.



X = F, 1
X= Cl, 2

These reactions were carried out in dimethylacetamide (DMAc), diphenylsulfone (DPS) and toluene, in the presence of anhydrous potassium carbonate and a catalytic amount of tetraphenyl hydrazine (TPH). In contrast to 1,3-FBB, the reactions of 1,3-CBB with hydroquinone proceed via both S_NAR and radical nucleophilic, unimolecular substitution ($S_{RN}1$) processes[9] in the absence of TPH[8]. The latter pathway is responsible for dehalogenation during the reaction. This results in the loss of 1:1 stoichiometry between the reactants, and oligomeric products are formed. It was possible to eliminate the $S_{RN}1$ reactions with TPH and to obtain high molecular weight polymers via S_NAR pathway[8]. The S_NAR and $S_{RN}1$ processes have been termed[10,11], more appropriately, as polar and single electron transfer (SET) processes, respectively, following the suggestions by Pross[12]. The objective of this investigation was to modify the previously used solvent system (DMAc/DPS/toluene) for the polymerization reactions of hydroquinone and 1,3-CBB and to achieve high molecular weight polymers.

Experimental

Materials. The monomers, 1,3-CBB and 1,3-FBB, were synthesized according to a previously reported procedure[7]. The purification procedures for the other reagents have been described earlier[8].

Model compound synthesis. The model compounds were prepared in a 100 ml three-necked, round-bottomed flask fitted with a magnetic stirrer, a thermometer and a Dean–Stark trap. Phenol (0.940 g, 0.01 mol), 1,3-CBB (1.775 g, 0.005 mol), anhydrous potassium carbonate (2 g, excess) and DPS (13 g) were added to the reaction vessel. The reaction mixture was heated to 140°C and the reaction was allowed to continue at that temperature for 2 h under a constant purge of nitrogen. The temperature was gradually raised to 220°C over a period of 1 h. The reaction mixture was kept at that temperature for 30 h. It was then cooled, diluted with 30 ml of dichloromethane, filtered, and the residue was washed with 20 ml of dichloromethane. The filtrate was distilled to remove dichloromethane. The residue was eluted on a silica gel column (60% hexane/dichloromethane) to separate the desired bisether from DPS.

Polymerization. The polymerization reactions were carried out in a four-necked, 250 ml round-bottomed flask fitted with an overhead stirrer, a thermometer, a nitrogen inlet and a Dean–Stark trap. The flask was charged with hydroquinone (1.3750 g, 0.0125 mol),

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* For part 1 see reference 8
† To whom correspondence should be addressed

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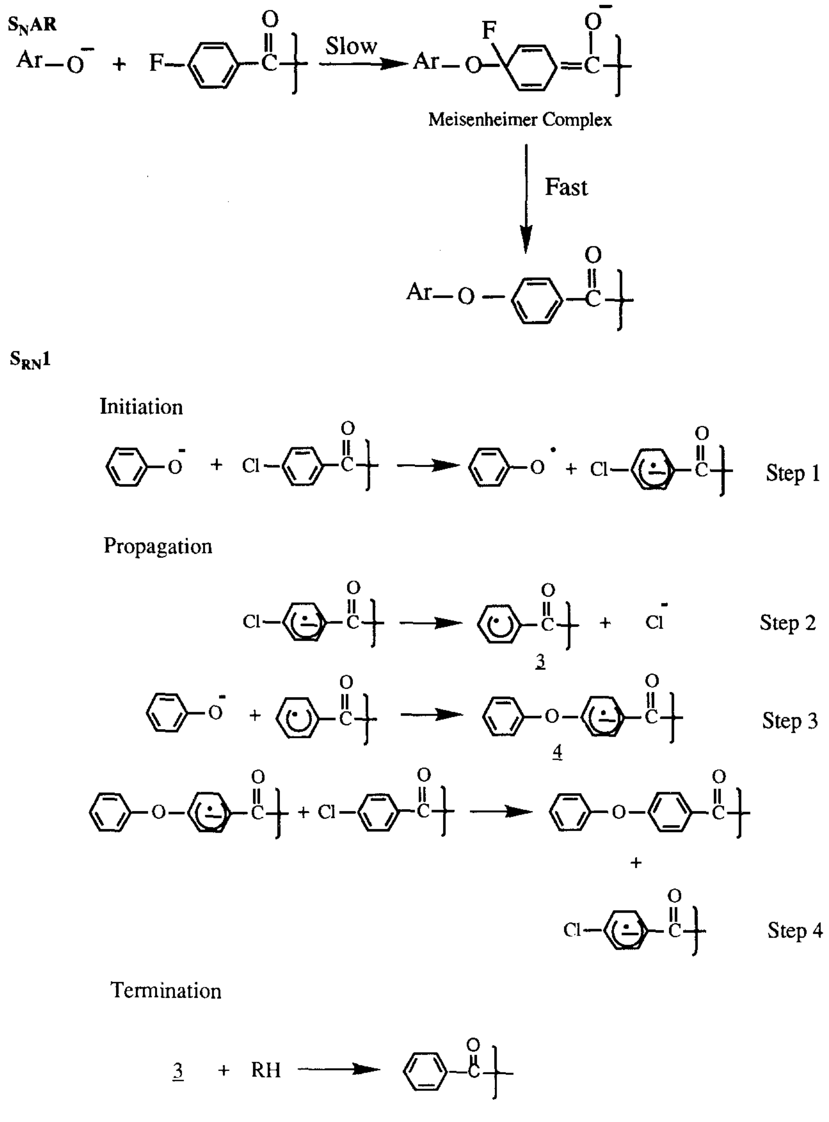
1,3-CBB (4.4375 g, 0.0125 mol), anhydrous potassium carbonate (7 g, excess) and DPS (30 g). The Teflon-coated pans used for weighing and transfers were washed with toluene (45 ml) with the solvent flowing directly into the reaction vessel. For reactions which were conducted in the absence of toluene, anhydrous diethyl ether (15 ml) was used for the washing. The reaction vessel was heated externally by an oil bath until toluene began to reflux at 130°C. The reaction was allowed to continue at this temperature for 3 h. Toluene was removed via the Dean–Stark trap until the reaction temperature rose to 150°C. The colour of the reaction mixture turned bright yellow. After 1 h at that temperature, toluene was removed continuously from the trap and the reaction temperature rose to 230°C. The reaction mixture was heated at that temperature for an additional 30 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 extracted with acetone, water, and acetone, in that order, using a Soxhlet apparatus. The polymer was then dried at 50°C at reduced pressure. For reactions conducted in the absence of toluene, anhydrous diethyl ether (used for washing the weighing pans) was removed from the reaction vessel through the Dean–Stark trap at early stages of the reaction.

Measurements. The ^{1}H and ^{13}C n.m.r. spectra were obtained on a General Electric QE-300 instrument. A solution of the polymer in trifluoromethanesulfonic acid was used to obtain n.m.r. spectra. Deuterium oxide in a sealed capillary tube was used as the lock solvent. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured either with a Du Pont DSC 2100 or a Perkin–Elmer DSC-7 instrument at a heating rate of 10°C min^{-1}. Melting points, taken as the peak maxima, were also measured using the same instruments. The intrinsic viscosities of the semicrystalline polymers were determined by using a Cannon–Ubbelhode dilution viscometer in concentrated aqueous sulfuric acid solutions (25°C).

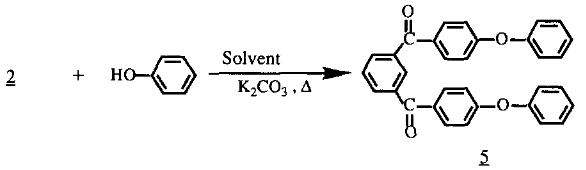
Results and discussion

The polymerization reaction of 1,3-CBB and hydroquinone in DMAc/DPS/toluene solvent system in the presence of excess anhydrous potassium carbonate proceeds by competing S_NAR and $S_{RN}1$ processes[8–12]. These reactions are shown in *Scheme 1*. The $S_{RN}1$ reactions terminate when the radical, **3**, formed in the second step, abstracts a hydrogen atom from the surrounding solvent molecules. This results in the formation of chain ends which are devoid of chlorine atoms. As a consequence, only oligomeric products are



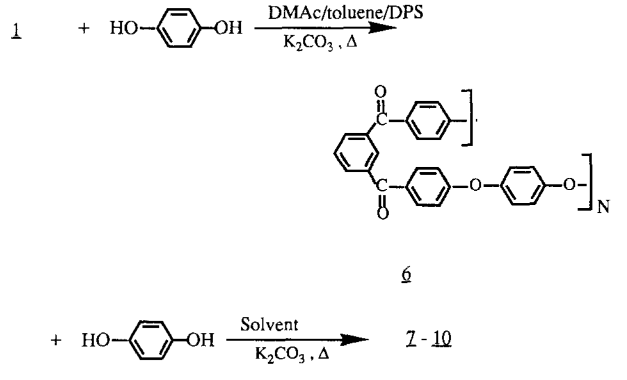
Scheme 1

formed[8]. It is possible to eliminate the $S_{RN}1$ pathways by the addition of a radical scavenger, TPH. Under these conditions, high molecular weight semicrystalline polymers can be obtained by S_NAR reactions only[8]. An examination of *Scheme 1* indicates that **3** can combine with the phenoxide in step 3 to form the radical anion **4** which can transfer an electron to the halogen-bearing nucleus, 1,3-CBB (step 4), and form the desired ether linkage. It therefore follows that in the absence of the termination step (*Scheme 1*), high molecular weight polymers can be formed even with the $S_{RN}1$ pathways. Since DMAc and/or toluene can serve as the source of a hydrogen atom in the termination step, model compound studies (*Scheme 2*) and polymerization reactions were carried out in the absence of these two solvents (*Scheme 3*). The reactions of two equivalents of phenol with one equivalent of 1,3-CBB in DPS resulted in the formation of **5** as the sole product (*Scheme 2*). Compound **5** was identical in all respects (melting point, n.m.r., etc.) with the bisether obtained from the reactions of phenol with 1,3-FBB in DMAc/toluene via S_NAR processes[8]. It was also possible to obtain high molecular weight polymer, **7**, by the reactions of hydroquinone and 1,3-CBB in DPS. Polymer **7** was fibrous in nature and exhibited a high intrinsic viscosity value ($\eta = 0.60\,\mathrm{dl\,g^{-1}}$) in concentrated aqueous sulfuric acid solution. Polymer **6**, obtained from the S_NAR reactions[8] between hydroquinone and 1,3-FBB in DMAc/DPS/toluene under the same reaction conditions, exhibited an intrinsic viscosity value of $1.0\,\mathrm{dl\,g^{-1}}$ (concentrated aqueous sulfuric acid). Furthermore, the ^{13}C n.m.r. (trifluoromethanesulfonic acid) of both polymers **6** and **7** (*Figure 1*) were identical in all respects. The thermal behaviours of **6** and **7** were also similar. Both polymers exhibited a glass transition temperature (T_g) at ~142°C and a melting point endotherm at ~282°C. The polymers did not crystallize upon slow cooling. Upon subsequent heating, only a well-defined T_g could be observed at 142°C. These behaviours of polymers **6** and **7** are significantly different from the low molecular weight oligomer that was obtained from the reactions of hydroquinone and 1,3-CBB in DMAc/DPS/toluene solvent system in the absence of TPH[8].



Solvent: DPS or DPS/toluene or DPS/1-DDM or DPS/toluene/1-DDM

Scheme 2



Solvent: DPS or DPS/toluene or DPS/1-DDM or DPS/toluene/1-DDM

Scheme 3

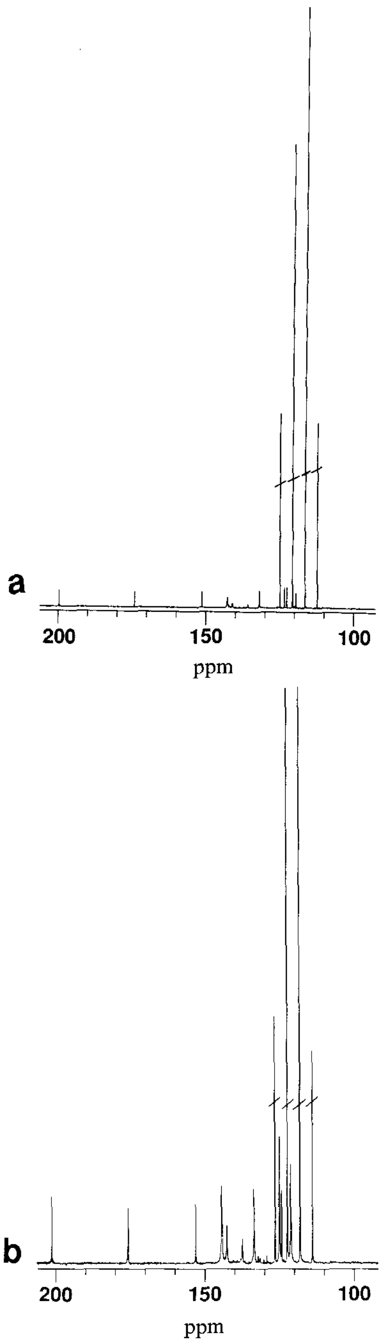


Figure 1 ^{13}C n.m.r. (trifluoromethanesulfonic acid) of (a) poly(aryl ether ketone) **6** and (b) **7**

Although toluene can be regarded as a source of hydrogen atom in the termination step (*Scheme 1*), it is conceivable that, owing to an exceedingly low concentration at a high reaction temperature of 230°C, toluene does not participate in the termination step. This is based on the tacit assumption that $S_{RN}1$ processes operate only at a higher temperature after most of the toluene has been removed from the system. To verify this, both model compound studies (*Scheme 2*) and polymerization reactions (*Scheme 3*) were carried out. Reactions of phenol with 1,3-CBB in DPS/toluene resulted in the formation of the desired bisether, **5**, as the only product. Further, high molecular weight polymer, **8**, could be obtained by the reactions between hydroquinone and 1,3-CBB in this

Table 1 Characteristics of polymers **6**–**10** derived from hydroquinone

Polymers	Solvent system	Additive	Bishalide	η^a (dl g^{-1})
6	DMAc/toluene/DPS	–	1,3-FBB	1.00
7	DPS	–	1,3-CBB	0.60
8	DPS/toluene	–	1,3-CBB	0.90
9	DPS	1-DDM	1,3-CBB	0.60
10	DPS/toluene	1-DDM	1,3-CBB	0.62

[a] Intrinsic viscosity measured in concentrated H_2SO_4 at 25°C

solvent combination also. The high molecular weight nature of polymer **8** was judged from the intrinsic viscosity value of 0.90 dl g^{-1} in aqueous concentrated sulfuric acid solution. In addition, the ^{13}C n.m.r. and the thermal behaviours of polymer **8** were identical with those of polymers **6** and **7**. These observations suggested that toluene does not take part in the termination step of the $S_{RN}1$ process. This implied that either $S_{RN}1$ process operates at a higher reaction temperature (after toluene has been removed from the system) or these reactions were taking place via S_NAR pathways only. To ascertain this, model compounds and polymers were prepared (DPS and DPS/toluene solvent systems) in the presence of a catalytic amount (0.02 mol% of phenolic hydroxyl groups) of a chain transfer agent[13], 1-dodecylmercaptan (1-DDM) (*Schemes 2* and *3*). This was done under the premise that if $S_{RN}1$ processes were operating alone or in combination with S_NAR reactions, then only oligomeric products would be formed in the presence of the chain transfer agent. Once again, the desired bisether was the only product when the model reactions were carried out in DPS or in DPS/toluene in the presence of a catalytic amount of 1-DDM (*Scheme 2*). The corresponding polymerizations (*Scheme 3*) yielded high molecular weight polymers, **9** and **10**, with intrinsic viscosity values of 0.60 and 0.62 dl g^{-1}, respectively, in concentrated aqueous sulfuric acid solution. The thermal behaviours and the ^{13}C n.m.r. of **9** and **10** were identical with those of polymers **6**–**8**. The model compound studies and the high molecular nature of the polymers (*Table 1*) suggest that in the absence of DMAc, reactions proceed by S_NAR pathways only.

Conclusions

It is possible to prepare high molecular weight semicrystalline polymer from hydroquinone and the less expensive monomer 1,3-CBB by using a suitable solvent system (DPS or DPS/toluene). In the absence of DMAc, only S_NAR processes operate for the formation of the ether linkages.

We are investigating the feasibility of preparing high molecular weight polymers from a series of chlorinated monomers and hydroquinone in the absence of DMAc. In particular, monomers which are known to undergo $S_{RN}1$ reactions in the presence of a weak nucleophile are being considered. These and related findings will be reported shortly.

Acknowledgements

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