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Termination by Reductive Elimination in the Polyetherification of Bis(aryl chlorides), Activated by Carbonyl Groups, with Bisphenolates

Aromatic poly(ether ketone)s and poly(ether sulfone)s are synthesized by an aromatic nucleophilic substitution reaction in which a bis(aryl halide), which is activated by a carbonyl or sulfone group, is condensed with a bisphenolate.[1] It is generally accepted that this aromatic nucleophilic substitution reaction proceeds through the S$_N$Ar mechanism, which is shown in Figure 1.[2]

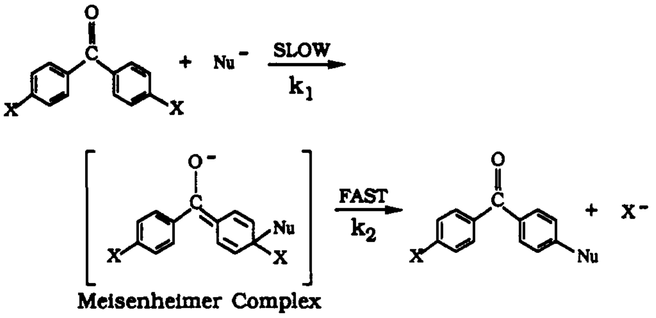

Figure 1. S$_N$Ar mechanism of aromatic nucleophilic substitution.

In general, bis(aryl halides) activated by the carbonyl group provide high molecular weight polymers when fluorine is the leaving group and low molecular weight polymers when chlorine is the leaving group. It is well established that, in S$_N$Ar reactions, the rate of substitution of fluorine is much greater than that of chlorine.[3] 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 obtain higher molecular weights with longer reaction times. This paper will demonstrate that high molecular weights are not obtainable by simply increasing the reaction time and that, in some polymerizations, the chain is terminated by reductive elimination of chlorine from the aryl chloride propagating chain, leading to a benzophenone unreactive chain end. A possible mechanism is proposed.

Polymerizations were conducted by conventional procedures.[4,5] The bis(aryl halides) employed were 4,4′-dichlorobenzophenone (DCB), 4,4′-difluorobenzophenone (DFB), 1,3-bis(4-chlorobenzoyl)benzene (1,3-CBB),[4a] and 1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB),[4a] and the bisphenols were Bisphenol A (BPA) and *tert*-butylhydroquinone (TBH). The polymerization solvents were *N*,*N*-dimethylacetamide and *N*-methyl-2-pyrrolidone. Polymer molecular weights were determined by gel permeation chromatography and are relative to polystyrene standards.[6] Polymerizations were carried out until no increase in M_n was seen.

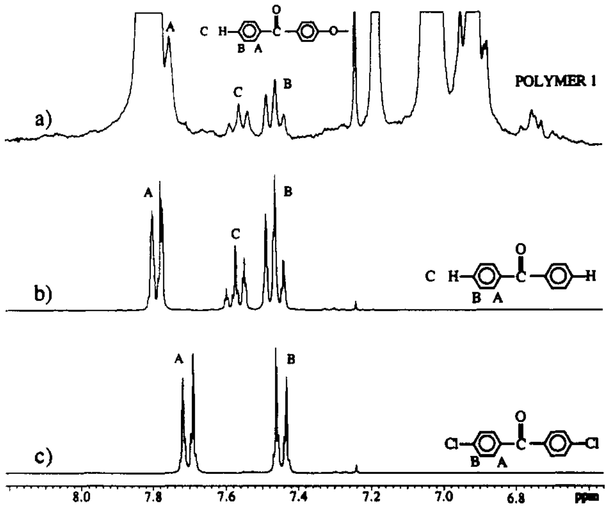

Figure 2. Comparison of the aromatic regions of the ^{1}H NMR spectra of (a) polymer 1 (see Table I) with (b) benzophenone and (c) 4,4′-dichlorobenzophenone indicating the absence of chlorobenzophenone chain ends and the presence of benzophenone chain ends. In a, the triplet at 7.46 (B), the triplet at 7.56 (C), and the partially overlapped doublet at 7.76 ppm (A) are due to the protons meta, para, and ortho to the carbonyl group. These resonances are due to the terminal phenyl ring in the benzophenone chain end. The resonances from 6.64 to 6.80 ppm are due to *tert*-butylhydroquinone chain ends. The peaks which are off scale are due to the polymer backbone and chloroform.

Table I gives the highest number-average molecular weight obtained during the course of the polymerization. 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) of identical structure except for the leaving group. The choice of bisphenolate 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 polymer 1 with 3 and 2 with 5. The solvent also affects the molecular weight. DCB and BPA polymerize in *N*,*N*-dimethylacetamide to yield a polymer whose M_n equals 25 000 (polymer 3), whereas the same monomers polymerized in *N*-methyl-2-pyrrolidone resulted in a polymer whose M_n equals 4000 (polymer 4). These two polymers did not appear to precipitate out of solution during the polymerization, and this is verified by the higher molecular weights obtained with the fluoro derivatives.

Table I
Summary of Polyetherification Results

polymer	bis-(aryl halide)[a]	bis-phenol[b]	solvent[c]	M_n[d]	benzo-phenone chain end[e]
1	DCB	TBH	DMAc	7 000	yes
2	1,3-CBB	TBH	DMAc	12 000	yes
3	DCB	BPA	DMAc	25 000	no
4	DCB	BPA	NMP	4 000	yes
5	1,3-CBB	BPA	DMAc	28 000	no
6	DFB	TBH	DMAc	107 000	no
7	1,3-FBB	TBH	DMAc	82 000	
8	DFB	BPA	DMAc	125 000	
9	DFB	BPA	NMP	66 000	
10	1,3-FBB	BPA	DMAc	46 000	

[a] DCB = 4,4′-dichlorobenzophenone, 1,3-CBB = 1,3-bis(4-chlorobenzoyl)benzene, DFB = 4,4′-difluorobenzophenone, 1,3-FBB = 1,3-bis(4-fluorobenzoyl)benzene. [b] TBH = *tert*-butylhydroquinone, BPA = bisphenol A. [c] DMAc = *N*,*N*-dimethylacetamide, NMP = *N*-methyl-2-pyrrolidone. [d] Determined by gel permeation chromatography. [e] Determined by ^{1}H NMR spectroscopy.

^{1}H NMR characterization of the polymers[7] revealed that polymers 1, 2, and 4 all contained benzophenone chain ends and no chlorobenzophenone chain ends. Figure 2 shows the aromatic regions of the spectra of polymer 1, benzophenone, and 4,4′-dichlorobenzophenone. 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. The 2D COSY spectrum,[8] Figure 3, of the polymer confirms the presence of the benzophenone chain end. The protons meta to the carbonyl are *J*-coupled to the protons ortho and para to the carbonyl group. Polymers 2 and 4 also contained phenol chain ends. The resonances attributed to the phenol chain end were assigned by ^{1}H NMR characterization of low molecular weight polymers which were end

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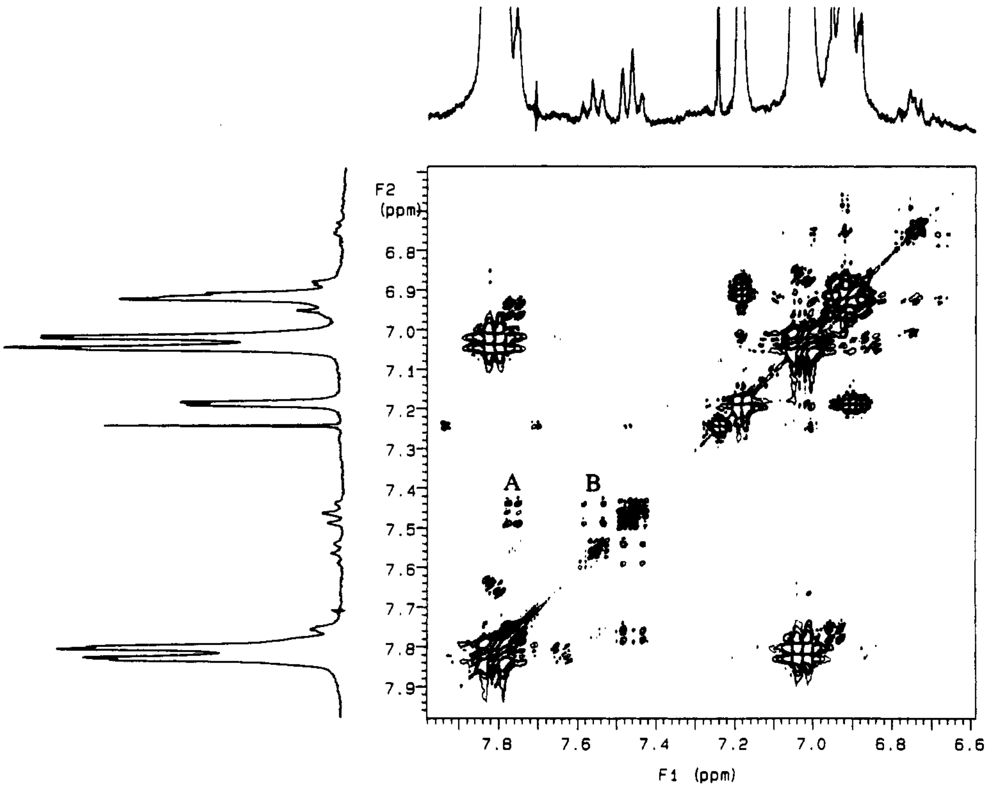

Figure 3. 2D COSY spectrum of polymer 1 confirming the presence of the benzophenone chain end. Crosspeaks A and B show that the protons resonating at 7.46 ppm are *J*-coupled to the protons resonating at 7.76 and 7.56 ppm, respectively. This is in accord with the assignment of the resonances at 7.46, 7.56, and 7.76 ppm to the protons meta, para, and ortho to the carbonyl group, respectively.

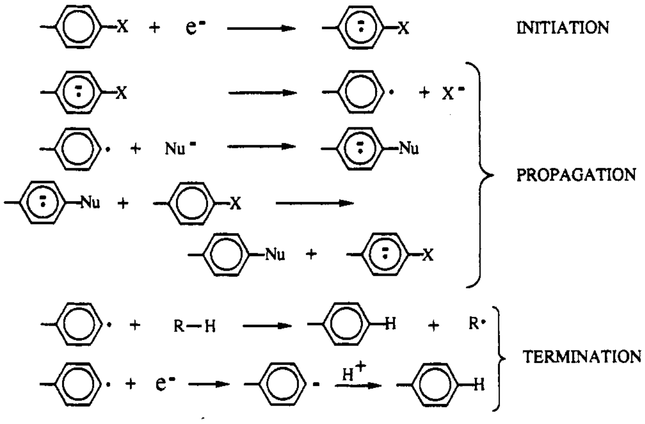

Figure 4. $S_{RN}1$ mechanism of aromatic nucleophilic substitution.

capped with the phenol. These polymers were synthesized by using the bisphenol monomer in excess. Chemical structures have not been assigned to a few, small resonances in the spectra of polymers 2 and 4. The identification of the chemical structures responsible for these resonances is in progress and will be reported elsewhere.

The presence of the benzophenone chain end correlates with very low molecular weights as can be seen in Table I. The polymers with the lowest molecular weights (polymers 1, 2, and 4) all contain the benzophenone chain end. Reductive elimination of chlorine from the chlorobenzophenone propagating chain results in the unreactive benzophenone chain end. This side reaction can be explained by a $S_{RN}1$ mechanism.[9]

The $S_{RN}1$ mechanism is presented in Figure 4.[10] The aryl halide accepts an electron to form a radical anion in the initiation step. The halide leaves with an electron, generating a phenyl radical. The phenyl radical can react with a nucleophile and eventually form the substitution product, or the phenyl radical can undergo a termination reaction. One of the most common termination steps involves hydrogen abstraction from a hydrogen donor. This termination step effectively results in the reductive elimination of the halide from the aryl halide.

Polymerization of BPA and TBH with the same bis(aryl chlorides) under the same reaction conditions yields very different results. Use of TBH results in low molecular weight polymers which have undergone reductive elimination of chlorine, whereas use of BPA results in moderate molecular weight polymers which have not undergone this side reaction. This observation coupled with the fact that the bisphenolate of TBH is more easily oxidized than the bisphenolate of BPA suggests that the phenolate serves as the electron donor in the initiation step of the $S_{RN}1$ mechanism.

In regards to aromatic nucleophilic substitution, the concept of the nucleophile acting as an electron donor and the electrophile as an electron acceptor in a single-electron-transfer (SET) step is not totally unfamiliar. Several reactions have been shown to involve formation of free radicals by ESR or radical trapping experiments.[11] Some of the authors of these studies have proposed the formation of the Meisenheimer complex proceeds via an SET pathway.[11a–e] The relationship between polar and SET pathways in organic chemistry has recently been addressed by Pross.[12] Application of these concepts to aromatic nucleophilic substitution is depicted in eq 1.

$$\underset{\text{reactant configuration}}{\mathrm{ArX} + \colon\!\overset{-}{\mathrm{Nu}}} \rightarrow \underset{\text{product configuration}}{(\mathrm{ArX})^{\overline{\cdot}}\cdot\mathrm{Nu}} \qquad (1)$$

All reactions which proceed through the S_NAr mechanism involve a single-electron shift from the nucleophile to the electrophile. If bond formation between the nucleophile and electrophile and the single-electron shift occur simultaneously, then the product configuration in eq 1 represents the Meisenheimer complex, and the reaction

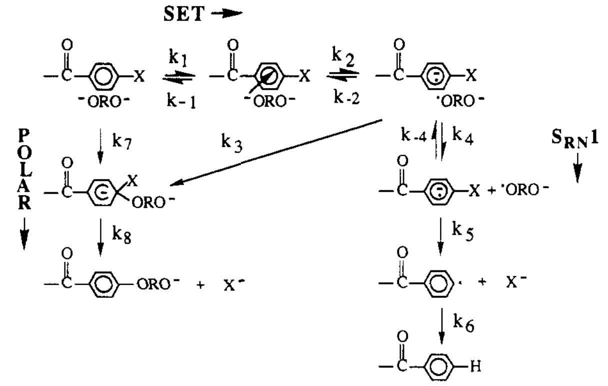

Figure 5. Proposed mechanism for the polymerization of bis(aryl chlorides), which are activated by the carbonyl group, with bisphenolates.

has proceeded via a polar pathway. Conversely, if bond formation does not occur simultaneously with the single-electron shift, then the product configuration represents a radical anion–radical pair. This pair can couple in a subsequent step to form the Meisenheimer complex via a SET pathway, or the pair can dissociate into a radical anion and a radical. This viewpoint is supported by the study of some aromatic nucleophilic substitution reactions by stopped-flow spectrometry.[13] In practice, a reaction is deemed polar or SET depending on our ability to detect free radicals. So a reaction is polar if bond formation occurs on a time scale too fast to allow detection of free radicals. This view of the polar pathway is in contrast to the commonly held belief that two spin-paired electrons of the nucleophile form the bond between the nucleophile and electrophile resulting in the formation of the Meisenheimer complex. Then the two spin-paired electrons in the carbon–halogen bond leave with the halogen, thus forming the substitution product and the halide.

The proposed mechanism is presented in Figure 5. The formation of the Meisenheimer complex can proceed through both polar and SET pathways. Intermediates along the SET pathway are a π-complex and a radical anion–radical pair (charge-transfer complex).[13] The halogen leaves the Meisenheimer complex as a halide ion, resulting in the creation of the substitution product. These steps constitute propagation of the polymer chain. Termination of the polymer chain by an unreactive benzophenone chain end involves only the SET pathway. The radical anion–radical pair dissociates into the radical anion and radical. The radical anion then undergoes $S_{RN}1$ type reactions. The halide leaves the radical anion, thus yielding a phenyl radical. The phenyl radical can abstract a hydrogen from a hydrogen donor, or it can accept an electron to form an anion which can be protonated.

The polymer molecular weight is determined by the rate of propagation relative to the rate of termination. One can speculate that the bis(aryl fluorides) afford higher molecular weight polymers than the bis(aryl chlorides) because the bis(aryl fluorides) have greater values for k_7 and k_3 and smaller values for k_5 relative to the bis(aryl chlorides). The rate constants k_7 and k_3 may be greater for the bis(aryl fluorides) due to the greater electrophilic character of the aromatic carbon bonded to the halogen. This greater electrophilic character is a direct consequence of the higher electronegativity of fluorine relative to chlorine. On the other hand, k_5 is much smaller for bis(aryl fluorides) since carbon–fluorine bond cleavage is much less facile than carbon–chlorine cleavage, owing to the greater bond strength of carbon–fluorine relative to carbon–chlorine.[14] The carbon–fluorine bond strength is approximately 30 kcal/mol greater than the carbon–chlorine bond strength.[15] Of course, verification of these concepts will require further experimental support for the proposed mechanism and determination of the rate-limiting step and its respective rate constant for each pathway.

In conclusion, reductive elimination of chlorine from the chlorobenzophenone chain end is responsible for termination of the polycondensation of bis(aryl chlorides), activated by the carbonyl group, with some bisphenolates. The amount of reductive elimination is determined by the structure of the bisphenol–bis(aryl chloride) pair and the solvent. We propose that a SET pathway may be involved in this termination step. However, the available results cannot discriminate between propagation by way of a polar or SET pathway.

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(5) A typical polymerization procedure is as follows. A mixture of 3.75 mmol of bis(aryl halide), 3.75 mmol of bisphenol, 9.23 mmol of potassium carbonate, 7.5 mL of *N*,*N*-dimethylacetamide, and 3.7 mL of toluene was heated to reflux. Argon was sparged through the reaction mixture. Water formed during the reaction was removed as an azeotrope with toluene. The temperature of the reaction mixture was slowly raised over a 3-h period to 160 °C. The reaction mixture was maintained at 157–160 °C during the remainder of the reaction. Samples were withdrawn during the reaction in order to monitor the polymer molecular weight. Polymerizations were also carried out in *N*-methyl-2-pyrrolidone using a similar procedure except the amount of potassium carbonate was 5.25 mmol and the reaction temperature was 180 °C.[4b]

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(7) The polymers were fractionated in either methanol or acetone, depending on their molecular weights, and the insoluble (higher molecular weight) fraction was analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR spectra were acquired at 299.95 MHz on a Varian VXR-300 NMR spectrometer equipped with a 5-mm indirect detection probe. 1D spectra were obtained with a 5600-Hz spectral width, 2.926-s acquisition time, 6-μs 40° pulse, and 0-s relaxation delay. The number of transients varied with the sample. $CDCl_3$ was used as the solvent.

(8) (a) The 2D COSY spectrum was acquired at 299.95 MHz on a Varian VXR-300 NMR spectrometer equipped with a 5-mm indirect detection probe. Phase-sensitive data were collected at ambient temperature without sample spinning using the method of States et. al.[8b] A total of 512 free induction decays (fid's) was acquired with a 13-μs 90° pulse, 0.233-s acquisition time (512 points), 1-s relaxation delay, and 1100-Hz spectral width in f1 and f2. Each fid was acquired with 16 transients and 4 dummy pulses for establishing the steady state. Data were processed on a Sun SPARCstation using VNMR software with zero filling (4× in f_2 and 4× in f_1) and shifted sinebell

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V. Percec* and R. S. Clough

Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

P. L. Rinaldi and V. E. Litman

Department of Chemistry, University of Akron
Akron, Ohio 44325

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