5970 *Macromolecules* **1995,** *28,* 5970−5972

Enhanced Reactivity of Dihalobenzonaphthones in S_NAr Polycondensation

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Received March 14, 1995
Revised Manuscript Received June 6, 1995

The most popular method of synthesizing poly(aryl ether ketone)s (PAEKs) is by nucleophilic displacement of bisphenoxides and "activated" dihaloaryl ketones.[1] It is generally believed that these polycondensations proceed through the S_NAr mechanism involving an intermediate Meisenheimer complex.[2] Among several factors which govern the success of polycondensation between bisphenols and dihaloaryl ketone monomers, the reactivity and chemical specificity of the pair of monomers are of utmost importance.

It is well-known that the rates of S_NAr reactions are greater for difluoroaryl ketones than their chloride analogues.[2] Consequently, it is not difficult to displace fluorine from difluoroaryl ketones to form PAEKs. In fact, Victrex PEEK[3] is made by step-growth polymerization of 1,4-hydroquinone (HQ) with 4,4′-difluorobenzophenone instead of with less expensive 4,4′-dichlorobenzophenone.[4] In general, the displacement of chlorine from dichloroaryl ketones with bisphenoxides to form high molecular weight PAEKs is difficult. However, it has been shown that relatively high molecular weight polymer can be obtained with 4,4′-dichlorobenzophenone and 4,4′-isopropylidenediphenol.[5] Exceptions also include the use of (a) a diketo monomer having a 1:1 ketone/chlorine ratio as opposed to one with a 1:2 ketone/chlorine ratio,[6] (b) a small amount of potassium fluoride in the presence of a phase-transfer catalyst,[7] (c) "reactive" bisphenols, i.e., 9,9-bis(4-hydroxyphenyl)fluorene (HPF)[6a] and 2,2′-bis(4-hydroxyphenoxy)diphenol,[6b] or (d) reactive dichloroheteroaryl ketones such as bis(5-chlorothienyl-2) ketone.[8] The choice of bisphenol used can significantly affect polycondensations with all dihaloaryl ketone monomers. According to the hard−soft−acid−base theory, certain bisphenols (as bases) have stronger attractions to particular dihaloaryl ketones (as acids).[9] Thus, the pairing up of bisphenols with appropriate dihaloaryl ketones becomes an important factor.[6b] In cases of dichloroaryl ketones, a competitive reductive dehalogenation reaction can occur via a $S_{RN}1$ SET mechanism, which accounts for the formation of low molecular weight PAEKs.[5c,10] This reaction pathway has been effectively suppressed using a radical scavenger.[11]

The resonance stabilization of the Meisenheimer intermediate should also be considered. Generally speaking, the activation energy for halogen displacement can be lowered by stabilizing the intermediate.[2] The more stabilized the Meisenheimer complex is, the more reactive the monomer is. For many known monomers containing 4-halophenyl end groups (e.g., 4,4′-dihalobenzophenone), the Meisenheimer intermediate has only two principal resonance structures (Figure 1). The possibility of a different benzenoid moiety which could impart further resonance stability to the Meisenheimer complex became the focus of our work. The naphthyl group seemed the natural choice, since it can provide greater stabilization through many possible resonance forms to the Meisenheimer intermediate (Figure 1). Therefore, four dihalobenzonaphthones (**1a**−**d**, Figure 2) were designed to investigate their polymerizability and the relative reactivities of chloronaphthyl and chlorophenyl moieties that are both activated by a carbonyl group. The calculations of charge densities at the carbons bearing chlorine for all monomers **1a**−**d** using a Hückel molecular orbital program suggest that the chloronaphthyl unit is indeed more reactive than the chlorophenyl unit toward nucleophilic displacement.[12] The structures of these unsymmetric ketone monomers are also unique for studying the effects of symmetry and sequential order of the properties of the PEEK-like polymers.

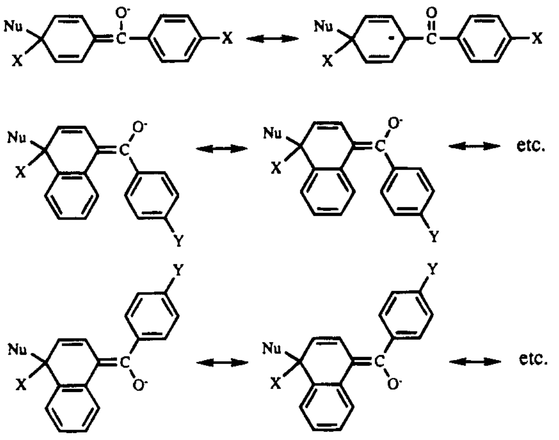

Figure 1. Resonance structures of phenyl- and naphthyl-containing Meisenheimer complexes.

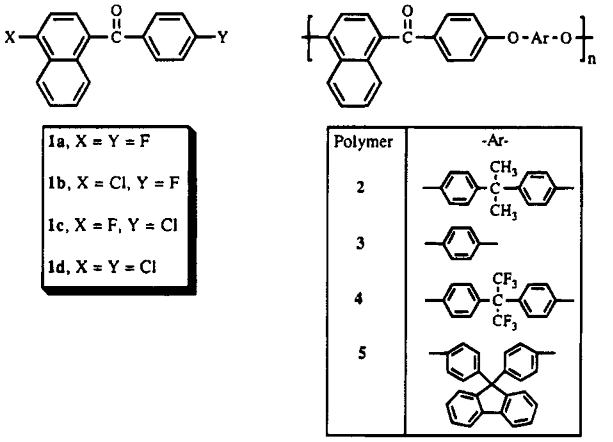

Figure 2. Poly(aryl ether ketone)s **2**−**5** derived from dihalobenzonaphthones **1a**−**d**.

Dihalobenzonaphthones **1a**−**d** (Figure 2) were synthesized by the Friedel−Crafts reactions of 4-chloro- and 4-fluorobenzoyl chlorides with 1-chloro- and 1-fluoronaphthalenes.[13] These monomers were polymerized with various bisphenols [4,4′-isopropylidenediphenol (BPA), 4,4′-hexafluoroisopropylidenediphenol (6F-BPA), HQ, and HPF] under the same reaction conditions to give PAEKs **2**−**5** (Figure 2).[14] Molecular weights and inherent viscosities are shown in Table 1. Polymer **3** derived from HQ represents the more PEEK-like polymer.

In the BPA polymer series (entries 1−4, Table 1), the difluoro monomer **1a** had no problems in forming a high molecular weight polymer (M_w = 159 900, η_{inh} = 0.90 dL/g). Monomers **1c** and **1d**, which both contain chlorophenyl end groups, could not be polymerized to high

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Table 1. Polymerizations of Dihalides 1a–d with Various Bisphenols

entry	polymer	dihalide	bisphenol	$M_w{}^a \times 10^{-4}$	$M_n{}^a \times 10^{-4}$	M_w/M_n	$\eta_{inh}{}^b$ (dL/g)
1	**2**	**1a**	BPA	15.99	5.70	2.80	0.90
2	**2**	**1b**	BPA	10.86	4.12	2.64	0.58
3	**2**	**1c**	BPA	3.67	1.88	1.95	0.28
4	**2**	**1d**	BPA	3.98	2.23	1.76	0.27
5	**3**	**1a**	HQ	7.20	2.26	3.19	0.61
6	**3**	**1b**	HQ	6.05	2.30	2.63	0.60
7	**3**	**1c**	HQ	6.73	2.66	2.53	0.56
8	**3**	**1d**	HQ	6.03	2.25	2.68	0.55
9	**4**	**1a**	6F-BPA	16.92	9.10	1.86	0.84
10	**4**	**1b**	6F-BPA	11.64	4.95	2.35	0.73
11	**4**	**1c**	6F-BPA	5.98	1.96	3.05	0.43
12	**4**	**1d**	6F-BPA	12.38	6.26	1.98	0.65
13	**5**	**1a**	HPF	18.83	10.02	1.88	0.76
14	**5**	**1b**	HPF	20.23	9.89	2.05	0.86
15	**5**	**1c**	HPF	11.85	5.15	2.30	0.55
16	**5**	**1d**	HPF	13.37	3.72	3.59	0.66

[a] Taken by GPC using polystyrene standards for the calibration curve. [b] Inherent viscosity taken of a 0.5% (g/dL) chloroform solution at 25.0 °C.

molecular weights (M_w = 36 700 and 39 800, respectively) despite several attempts. It is well-known the difficulty in displacing chlorine on keto-activated phenyl rings with bisphenoxides, especially with BPA.[5] In contrast, **1b** combines the undoubtedly reactive fluorophenyl part and the chloronaphthyl group which, by HMO calculation,[12] could be equally reactive. Indeed, a high polymer **2** (M_w = 108 600, η_{inh} = 0.58 dL/g, entry 2, Table 1) was obtained from **1b** and BPA. Under the preferred polyetherification conditions ($TMSO_2$, 210 °C),[15] the naphthyl ring appears to promote chlorine displacement with bisphenoxides relative to the phenyl ring. This can be attributed to the increased conjugation and stability imparted to the Meisenheimer complex by the naphthyl ring (Figure 1).

In comparison, the rest of the polymers **3**, **4**, and **5** made with HQ, 6F-BPA, and HPF showed higher molecular weights ($M_w > 59\,000$, $\eta_{inh} > 0.4$ dL/g) (entries 5–16, Table 1). It was felt that these bisphenols are simply more reactive and/or experienced less side reactions than BPA; i.e., they are chemically specific. Therefore, the "unreactivity" of the chlorophenyl part of monomers **1c** and **1d** was less pronounced. Still, a general decrease in molecular weight was seen from **1a** through to **1d** with an exception of **1c** with 6F-BPA and HPF. The polymers derived from **1c** (entries 11 and 15) had lower molecular weights than the corresponding polymers derived from **1d** (entries 12 and 16). This is likely due to the ether cleavage by a fluoride ion, which has been encountered in other PAEK systems.[16]

Finally, it is interesting to note that the replacement of the methyl groups in BPA by the trifluoromethyl groups in 6F-BPA resulted in significantly higher molecular weight polymers **4** (entries 11 and 12). Unfortunately, overlapping of peaks in the ^{1}H NMR spectra blocks the determination of chain ends, thus preventing the investigation of possible reductive dechlorination facilitated by the methyl groups as a hydrogen source. Nevertheless, the methyl groups must contribute somehow to the inability or "sensitivity" that BPA displays in polycondensations with monomers **1c** and **1d** (entries 3 and 4). Although readily available, BPA is not always an ideal candidate when establishing the propensity of a chloroaryl ketone monomer to form a high polymer.

Polymers **2**–**5** are soluble in chloroform and appear to be amorphous, with the T_gs ranging from 186 to 272 °C by differential scanning calorimetry (DSC) studies. DSC results also showed that polymer **3** derived from HQ had a T_g of 190 °C, about 45 °C higher than that of PEEK. Due to the unsymmetric structure of monomers **1** and the difference in the relative reactivity at both (head and tail) ends, the chemical microstructure of these polymers is likely to consist of a random distribution of the head-to-tail, head-to-head, and tail-to-tail diads. Therefore, in contrast to PEEK, the structural irregularity along the chain in polymer **3** inhibits the close packing of the polymer chain and consequently suppresses crystallization.

In summary, the facile displacement of chlorine from the naphthyl moiety in polycondensation of unsymmetric dihalobenzonaphthones with biphenols as opposed to the phenyl ring has been demonstrated. It follows that new dichloride monomers containing other types of fused benzenoids for poly(aryl ether)s can be realized. The success of the polymerizations of the monomers containing the chlorophenyl moiety (**1c** and **1d**) depended on the appropriate pairing between the dihalides with bisphenols. BPA proved to be more discriminating than other bisphenols when pairing with dihalobenzonaphthones in successful polycondensation. Preliminary results show that the random replacement of a benzoyl moiety with a naphthoyl group in PEEK's repeat unit increases the T_g yet reduces crystallinity. Thermal and mechanical properties of these PAEKs are under investigation.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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(12) Hückel molecular orbital program is available from the Molecular Modeling System, Cambridge Scientific Computing Inc., 875 Massachusetts Ave., Suite 61, Cambridge, MA. The greater the net charge at the carbon where the halogen is bonded, the more reactive it is with a phenoxide in nucleophilic displacement polycondensation. 4,4′-Dichlorobenzophenone has a net charge of +0.025 at C-4 and generally cannot polymerize to high molecular weight, whereas, 4,4′-difluorobenzophenone can (net charge = +0.050 at C-4). Calculations for monomers **1b** and **1d** showed that the carbon on the naphthyl ring to which chlorine is attached has a net charge of +0.044 and +0.045, respectively. These calculations, although not always accurate, indicate the increased aptitude the naphthyl ring has to displace chlorine over the phenyl ring.

(13) The following is a typical procedure for the synthesis of monomers **1a**–**d**: To a 100-mL, three-necked, round-bottomed flask containing a magnetic stirring bar were added 4-fluorobenzoyl chloride (5.060 g, 31.83 mmol), 1-fluoronaphthalene (5.120 g, 31.83 mmol), and dry CH_2Cl_2 (30 mL). The reaction flask was then cooled in an ice bath (5 °C) before anhydrous $AlCl_3$ (35.10 g, 38.50 mmol) was added slowly. The solution turned yellow and then a dark red/brown color. After an hour the solution was quenched with iced water and turned yellow. The organic layer was washed with aqueous HCl (5%), aqueous NaOH (5%), brine (23%), and water. The organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give **1a** as white crystals (crude yield 69%). Highly pure monomer **1a** was obtained after recrystallization twice from hexane: 4.71 g (55%); mp 84–86 °C; IR (KBr) 1657 cm^{-1} (C=O); MS (EI, *m/e*, relative intensity %) 173 ($M^{\bullet +} - {}^{\bullet}PhF$, 100), 268 ($M^{\bullet +}$, 87.6), 123 ($COPhF^{+}$, 68.9), 145 ($M^{\bullet +} - {}^{\bullet}COPhF$, 63.3), 95 ($PhF^{+}$, 54.4); ^1H NMR (400 MHz, $CDCl_3$) 8.16 (d, 1H), 8.21 (d, 1 H), 7.85–7.91 (m, 2 H), 7.54–7.64 (m, 3 H), 7.12–7.21 (m, 3 H). The syntheses of monomers **1b** and **1c** offered modest yields (63–67%) after recrystallization twice. Isomers were observed but removed satisfactorily during recrystallization. The dark orange/brown crude **1d** was more difficult to purify. It came in only 45% crude yield. After many attempts, it was found that the observed isomers were best removed by initial recrystallization with cyclohexane, then stirred in methanol, filtered, and recrystallized in ethanol to produce pure **1d** as white, prismatic needles (14%). The structures of all four monomers were confirmed by MS, IR, and ^1H NMR.

(14) All the polymerizations were done as follows: Bisphenol and dihalo monomer (3.0 mmol each) were dissolved in tetramethylene sulfone ($TMSO_2$) in 40% (w/v) solid content. An equivalent volume of chlorobenzene was added as the azeotroping solvent. Anhydrous potassium carbonate (5.4 mmol) was used, and the reaction mixture was heated under nitrogen from room temperature to 210 °C in 30 min. The polymerization was monitored by GPC and stopped when the molecular weight failed to increase. If the reaction mixture became too viscous to stir, it was diluted with $TMSO_2$ (1–2 mL). The polymer was isolated by precipitating in methanol. The low molecular weight fractions could be removed by reverse precipitation. All polymers were purified by dissolving in chloroform, filtering through Celite, and reprecipitating in methanol.

(15) Presumably, this polymerization system can sufficiently suppress the SET pathway and favors the S_NAr pathway. For comparison, polymerizations of **1b** and BPA in NMP or DMAc at 170–190 °C afforded relatively lower molecular weight polymers **2** (M_w = 36 400 or 49 200, respectively). Percec et al. found no reductive dehalogenation occurring in the $TMSO_2$/toluene system when polymerizing HQ with 1,3-bis(4-chlorobenzoyl)-5-*tert*-butylbenzene at 160 °C but did observe some at 220 °C and higher.[5c] It has also been shown by Strukelj, Hedrick, and co-workers that $TMSO_2$ is a better solvent than NMP for making poly(arylene ether ketone)s. Strukelj, M.; Hedrick, J. C.; Hedrick, J. L.; Twieg, R. J. *Macromolecules* **1994**, *27*, 6277.

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