Synthesis and Properties of Aromatic Poly(Ether Sulfone)s and Poly(Etherketone)s Containing Naphthalene or Quinoline Units, and Methyl-Substituted Biphenyl-4,4'-Diols

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SYNTHESIS AND PROPERTIES OF AROMATIC POLY(ETHER SULFONE)S AND POLY(ETHER KETONE)S CONTAINING NAPHTHALENE OR QUINOLINE UNITS, AND METHYL-SUBSTITUTED BIPHENYL-4,4′-DIOLS

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ABSTRACT

A series of poly(ether sulfone)s and poly(ether ketone)s were synthesized from combinations of 1,5- and 2,6-bis(4-fluorosulfonyl)naphthalene, 2,6-bis(4-fluorobenzoyl)naphthalene, and 2,6-bis(4-fluorobenzoyl)quinoline with 3,3′,5,5′-tetramethylbiphenyl-4,4′-diol and 2,2′,3,3′,5,5′-hexamethylbiphenyl-4,4′-diol. The polycondensations proceeded quantitatively in diphenylsulfone in the presence of anhydrous potassium carbonate to afford polymers with inherent viscosities between 0.40 and 1.28 dL/g measured in N-methyl-2-pyrrolidone or concentrated sulfuric acid. The tetramethyl- and hexamethyl-substituted aromatic polyethers exhibited good thermal stability, did not decompose below 330°C in both air and nitrogen atmospheres, and had higher glass transition temperatures than the corresponding unsubstituted polymers. The methyl-substituted poly(ether sulfone)s and poly(ether ketone)s showed good solubility in such common organic solvents as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, tetrahydrofuran, chloroform, and 1,4-dioxane.

INTRODUCTION

Poly(aryl ether sulfone)s and poly(aryl ether ketone)s are known as high-performance engineering thermoplastics [1]. They show desirable characteristics such as exceptional thermooxidative stability, glass transition temperature (T_g) ranging from 150 to 220°C, and excellent mechanical properties [2]. The presence of ether linkages in the polymer backbone renders hydrolytic stability to the polymer, improved solubility, and processability but lower T_g [3]. Therefore, attempts have been made to raise the T_g of the polymers while maintaining the desirable attributes of the ether functionalities. One approach used to get this result could consist of the introduction of substituents on the phenyl ring of the ether moiety. The presence of one or more substitution groups often results in reduction of the intermolecular reaction of connecting cyclic units with respect to each other; consequently, substituted polymers show greater solubility but lower glass and melt transition temperatures and reduced thermal stability than the corresponding unsubstituted polymers [4]. Interestingly, McGrath [5] and Cummings [6] reported that the poly(ether sulfone)s and poly(ether ketone)s synthesized from 3,3′,5,5′-tetramethyl-substituted 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) had about 40°C higher T_g than those of the corresponding polymers derived from unsubstituted bisphenol A, and were more soluble in organic solvents. These results indicate that polysubstitution on a ring unit could undergo high rigidity to the polymer chain.

The 4,4′-biphenyl unit is known as a rigid-rod core structure in various liquid crystalline polymers [7–9]; the polyarylates derived from biphenyl 4,4′-diol have high melting temperatures with high crystallinity, and are insoluble in organic solvents, but, as Keitoku [10] reported for tetramethyl- and hexamethyl-substituted aromatic polyethers, when methyl groups are introduced into the 4,4′-biphenyl unit, the solubility of the polymers improves with increased T_g. Moreover, recent works [11, 12] have demonstrated certain advantages in terms of thermal stability, higher T_g, and excellent T_g/T_m ratio as a consequence of incorporation of naphthalene or quinoline units in the polymer backbone of poly(arylene ether)s. The aim of the present work was to study the effects of methyl substituents introduced into the 4,4′-biphenyl unit on the solubility and thermal behavior of poly(ether sulfone)s and poly(ether ketone)s containing naphthalene or quinoline units. We report the synthesis and characterization of polymers derived from bis-sulfone and bis-ketone functional monomers containing 1,5- or 2,6-naphthalene moieties and from bis-ketone containing 2,6-quinoline units by reaction with different methyl-substituted biphenols.

EXPERIMENTAL

Materials

Biphenyl-4,4′-diol (**a**) (Aldrich Co.) was crystallized twice from aqueous ethanol after decolorizing with charcoal. 3,3′,5,5′-Tetramethylbiphenyl-4,4′-diol (**b**) and 2,2′,3,3′,5,5′-hexamethylbiphenyl-4,4′-diol (**c**) were synthesized according to literature procedures [13, 14] and crystallized from benzene and toluene, respectively. Bis-fluorobenzoyl monomers were synthesized as described elsewhere [11].

1,5- and 2,6-(4-Fluorosulfonyl)naphthalene were synthesized by reaction of the corresponding disulfonyl chlorides with anhydrous powdered aluminum chloride and fluorobenzene; the monomers were crystallized from acetic acid (yield 87%, mp 218–219°C; yield 70%, mp 270–271°C, respectively) [15]. Diphenyl sulfone (DPS) was crystallized from toluene. Potassium carbonate, anhydrous grade (Aldrich Co.), particle size less than 325 mesh, was heated at 100°C under reduced pressure before use. All reactions were performed under an inert atmosphere of N_2.

Polymerizations

A typical polymerization procedure is as follows: Bis-fluoro compound (0.005 m) and bis-hydroxy compound (0.005 m) in 15 g DPS were heated to 180°C under mechanical stirring until the slurry was clear. Then 1.035 g (0.0075 m) of potassium carbonate were added, and the temperature was raised until the flask contents reached 240°C. This temperature was maintained for 2 hours before the addition of a further quantity of bis-fluoro compound (0.00025 m). After a further 30 minutes the product was poured onto an aluminum sheet, crushed, and boiled several times for 2 hours in methanol to remove DPS and in water to remove any trapped inorganic salt, filtered, and dried in a vacuum oven at 80°C for at least 12 hours.

Measurements

Inherent viscosities ($\eta_{inh} = \ln \eta_{rel}/c$ at a polymer concentration of $c = 0.5$ g/ dL) were determined for a solution of 1-methyl-2-pyrrolidinone (NMP) or 96% sulfuric acid at 30°C with an Ostwald viscometer. Thermogravimetric analyses (TG) were performed with a Mettler M3 thermobalance at a heating rate of 10°C/ min in N_2 (25 mL/min) or in static air. The temperature of 10% weight loss was taken as the decomposition temperature (T_d). Differential scanning calorimetry (DSC) measurements were made using a Mettler DSC 20 with aluminum pans at a heating rate of 20°C/min in N_2. Qualitative solubility was determined using about 0.2 g polymer in 2 mL solvent.

RESULTS AND DISCUSSION

Syntheses of aromatic poly(ether sulfone)s **1a–2c** and poly(ether ketone)s **3a–4c** were carried out using DPS as solvent at high temperature (240°C) (Scheme 1).

Polymerizations were carried out using a monomers/carbonate ratio of 1/1.5 as described in the literature [12]. The results of polymer synthesis are summarized in Table 1. The yields of the polymers were quantitative, and the inherent viscosities of the methyl-substituted polymers were between 0.40 and 1.28 dL/g as measured in NMP or concentrated sulfuric acid. In our first approach we attempted to synthesize high molecular weight polymers by reaction of fluorine monomers with substituted tetra- and hexamethyl phenols in dipolar aprotic solvents like NMP at 180°C. The results were unsatisfactory, probably due to a nonquantitative replacement of the fluorine atoms by the sterically hindered phenoxide ions. Others authors had observed the same behavior using dichloro monomers with hindered bisphenols [6]; generally the substitution of Cl-monomers with F-monomers avoids this problem.

F-Ar-X-Ar-F
1-4
+
HO-Y-OH
a-c

$$\xrightarrow[K_2CO_3]{DPS} \text{-Ar-X-Ar-O-Y-O-}$$
1a-4c

X=

1 ; 2 ; 3 ; 4

Y=

a ; b ; c
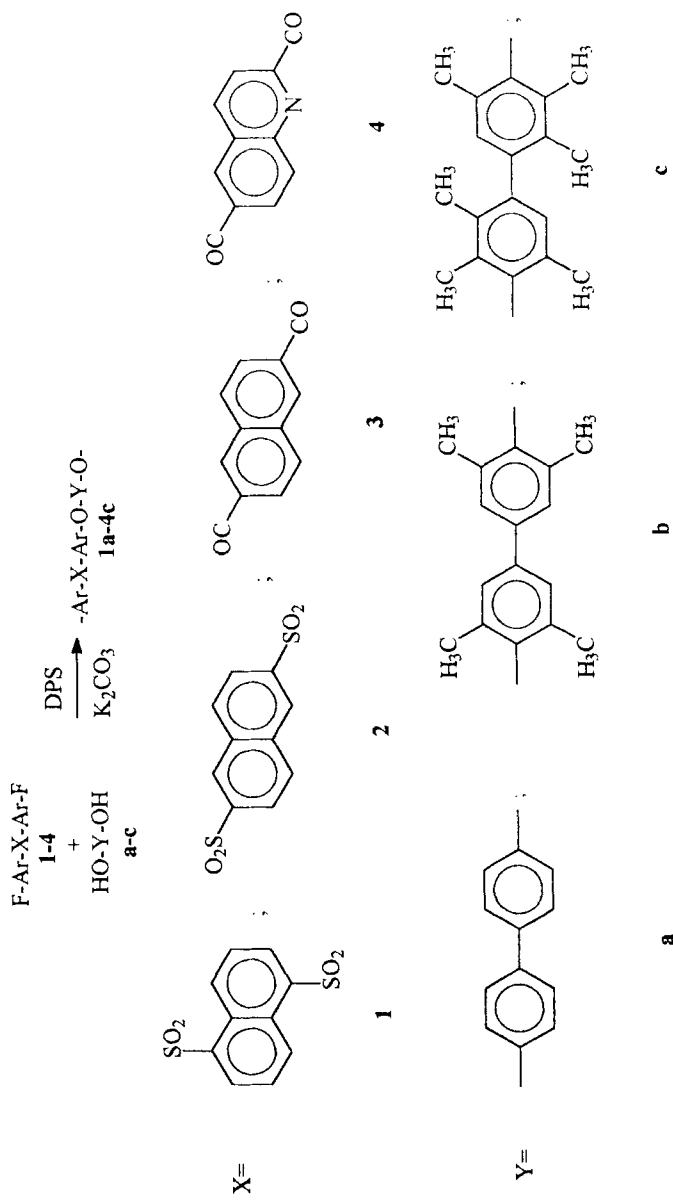
SCHEME 1.

TABLE 1.   Solution Viscosities and Thermal
Characterization of Polymers **1a–4c**

Polymer	η_{inh}, dL/g	T_d, °C[a]	T_d, °C[b]	T_g, °C
1a	0.42[c]	475	450	248
1b	0.52[c]	425	390	262
1c	0.49[c]	350	330	—
2a	0.48[c]	530	510	255
2b	0.56[c]	425	400	280
2c	0.56[c]	415	390	300
3a	0.88[d]	540	490	195[e]
3b	0.93[d]	465	380	270
3c	1.28[d]	350	330	—
4a	0.57[d]	565	460	155[e]
4b	0.85[c]	425	415	180
4c	0.40[c]	370	360	250

[a]Temperature of 10% weight loss determined in nitrogen atmosphere.

[b]Temperature of 10% weight loss determined in static air.

[c]In NMP.

[d]In concentrated sulfuric acid.

[e]Determined on quenched sample.

In our case also the F-monomers were unable to undergo high molecular weight polymerization. For this reason we carried out the polymerization in DPS medium at 240°C. The results were satisfactory for all polymers. Because endgroups could affect the thermal stability of the polymers, in order to ensure that most of the chains were fluorine terminated, an excess of 5 mol% F-monomer was added 30 minutes before stopping the polymerization. Moreover, the cleanup was done carefully to ensure that all the solvent and the inorganic salts were removed. Because the presence of any residual DPS can be revealed by TG analysis, the purification was checked in this way.

The thermal data are summarized in Table 1. All the aromatic polyethers were stable up to 350 and 330°C, respectively, in nitrogen and air atmosphere. The T_d values for the **1a–c** and **2a–c** series show relevant differences. It is evident from the data that in both N_2 and air, the polymers of series **2** (2,6 derivatives) possess higher thermal stability compared to the polymers of series **1** (1,5 derivatives) because of the comparative more rigid and symmetrical structure of 2,6 derivatives. The thermal stability is clearly affected by the increase of methyl group substituents. Interestingly, the loss of stability with this increase is more marked in series **1** (425→350°C) than series **2** (425→415°C) in N_2 (Fig. 1). The same behavior is shown in an air atmosphere. The T_d of **2a** polymer is comparable with that of polyether sulfone biphenyl [10], showing that in this case the bis-sulfones system containing the naphthalene unit doesn't affect the thermal stability appreciably. Also for poly(ether ketone) of the **3** and **4** series (Fig. 2), the methyl-substituted
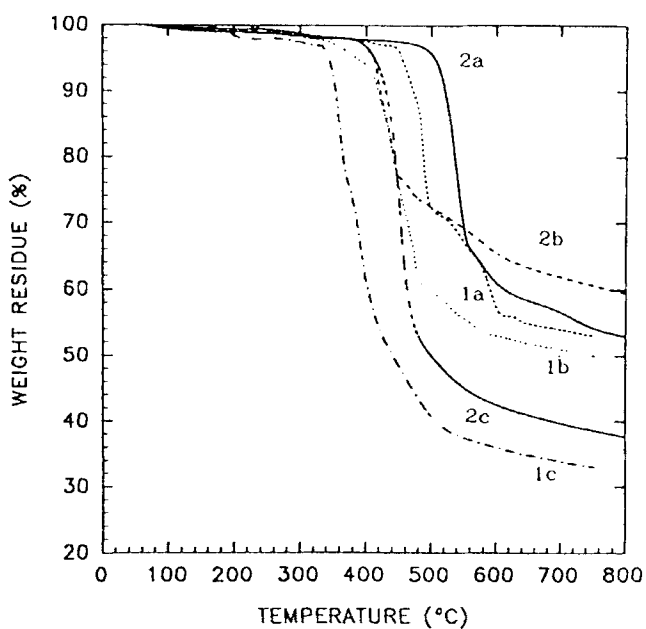
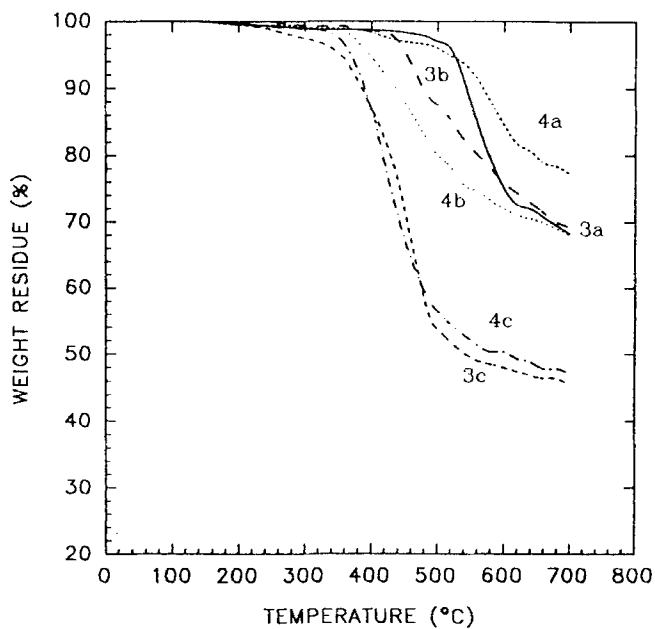FIG. 1.   Thermogravimetric curves of poly(ether sulfone)s (1a-c) and 2(a-c).

FIG. 2.   Thermogravimetric curves of poly(ether ketone)s 3(a-c) and 4(a-c).

polymers begin to decompose at a lower temperature in comparison with the unsubstituted ones. The T_d decreasing values depend strictly on the increase of methyl substitution.

The T_gs show a remarkable behavior. For all series the T_g values increase in moving from **a** to **c**. This increase is lower for the **1** and **2** series (20–45°C) and higher for poly(ether ketone)naphthalene derivatives (75°C) and the quinoline series (35–70°C). No T_gs were detected for the **1c** and **3c** polymers. It is interesting to compare the T_g values of polymers **3a** and **4a** with the analogous poly(ether ketone)s containing a phenyl ring instead of naphthalene or quinoline units (**5a** and **5b**). The comparison shows that polymers **3a** and **4a** have, respectively, a T_g 13 and 53°C higher than polymer **5a** (T_g = 142°C) [16], while the T_g of polymer **3b** was 90°C higher than that of polymer **5b** (T_g = 180°C) [17].
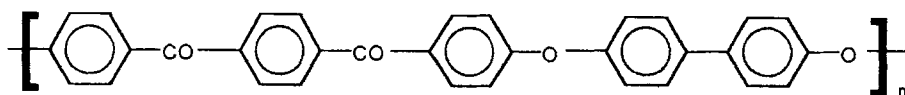
5a
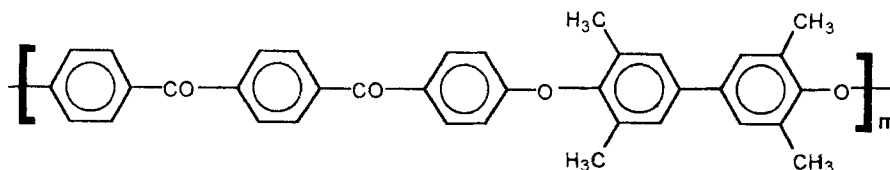
5b

Therefore, the introduction of a naphthalene or quinoline ring into the polymer main chain leads to an increase in thermal properties, such as a higher T_g, in comparison with the benzene ring, probably because of the contribution from the more rigid structure of the first two.

As shown in Table 2, all the methyl-substituted polymers were soluble in aprotic solvents such as DMAc and NMP, and partially soluble even in less polar solvents such as THF and chloroform. The unsubstituted bis-sulfone polymers **1a** and **2a** already show some solubility on heating in a polar aprotic solvent and, in particular for series **1**, also in solvents as THF, chloroform, etc. Methyl substitution has a small influence on solubility in NMP and DMAc, but we observed a large influence on solubility in the other solvents; in fact, hexamethyl-substituted polymers **1c** and **2c** show increased solubility with respect to polymers **1a–b** and **2a–b**, respectively. More remarkably, the solubility of polymers of the **3** and **4** series was greatly improved by the introduction of methyl substituents. The poly(ether ketone)s **3b–c** and **4b–c** were soluble on heating in NMP and DMAc and partially soluble in THF, chloroform, and 1,4-dioxane, while the unsubstituted polymers **3a** and **4a** were quite insoluble in all these solvents.

TABLE 2. Solubility of Aromatic Polyethers[a]

Polymer	Solvent				
	NMP	DMAc	THF	Chloroform	1,4-Dioxane
1a	+	+	+ −	+ −	+ −
1b	+	+	+ −	+ −	+ −
1c	+ +	+ +	+	+	+
2a	+	+	−	−	−
2b	+ +	+ +	−	−	−
2c	+ +	+ +	+ −	+ −	+ −
3a	−	−	−	−	−
3b	+	+	+ −	+ −	−
3c	+	+	+ −	+ −	+ −
4a	−	−	−	−	−
4b	+	+	+ −	+ −	+ −
4c	+ +	+ +	+	+	+

[a]Solubility: + + soluble, + soluble on heating, + − partially soluble on heating, − insoluble.

CONCLUSION

The introduction of methyl-substituted aromatic rings in the studied poly-(ether sulfone)s and poly(ether ketone)s creates polymers in which hindered chain rotation results compared with the methyl-unsubstituted analogues, and in noticeable increases of the T_g and solubility in common organic solvents. These effects are more marked for poly(ether ketone)s than for poly(ether-sulfone)s.

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