

Synthesis and characterization of new poly(arylene ether)s based on dihydroxynaphthalene isomers

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A series of new poly(arylene ether ketone)s and poly(arylene ether sulfone)s, obtained starting from dihydroxynaphthalene isomers, have been prepared by solution condensation polymerization. The polymers, having inherent viscosities from 0.20 to 0.77 dl g⁻¹, have been obtained in quantitative yields, had excellent thermal stability as shown by 10% weight loss temperatures in nitrogen and air (above 460 and 430°C, respectively) and high glass transition temperatures (in the range 151–278°C). X-ray diffraction patterns confirmed the semicrystalline character of some polymers. The location of the naphthalene–ether bond appears to affect the polymer properties. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In recent years, high temperature resistant engineering thermoplastic resins have gained acceptance for use as matrices in advanced resin composites for aerospace structural applications, including military aircraft and missiles. To this class of engineering thermoplastics belong poly(aryl ether ketone)s and poly(aryl ether sulfone)s¹. Poly(aryl ether ketone)s have achieved a remarkable position among other thermoplastic polymers because of their unique combination of toughness, stiffness, thermo-oxidative stability, chemical and solvent resistance, electrical performance, flame retardancy, and retention of physical properties at high temperatures². In addition, the indefinite shelf life, along with suggested ease of fabrication, repairability and reprocessing capability, suggest that poly(ether)ketones have potential advantages over thermoset materials in their various applications^{3,4}. Poly(ether)ketones are usually crystalline and therefore resistant to solvents, which is a vital factor in an aerospace environment. They resemble poly(ether)sulfones in their high thermal stability^{5,6}; however, with few exceptions polysulfones are amorphous engineering thermoplastics having excellent heat resistance, oxidative stability, steam resistance and optical transparency, but they are subject to attack by solvents like dichloromethane, isopropanol, hydraulic fluid, kerosine and others, occurring commonly in and around aircraft. These characteristics arise from the structural irregularity along the chain due to introduction of the aryl sulfonyl linkage having a tetrahedral configuration⁷, which inhibits close packing of the polymer chain and consequently suppresses crystallization.

Recent works involving incorporation of rigid groups or heterocyclic units within the backbone of poly(arylene)-ethers demonstrated certain advantages over those without

these units, such as higher glass transition temperatures (T_g), tensile strengths and moduli. They incorporated units such as biphenyl⁸, naphthalene or quinoline^{9,10}, phenylquin-oxaline^{11,12}, benzimidazoles¹³ and isoquinolinediyl¹⁴.

In an effort to obtain semicrystalline poly(arylene ether)s with high thermal stabilities and high glass transition temperatures, we have designed the incorporation of naphthalene or pyridine units in the polymer backbone, taking into account that these units would introduce enhanced chain stiffness. The purpose of this research is to synthesize new poly(arylene ether ketone)s and poly(arylene ether sulfone)s in an attempt to produce polymers with high thermal stability, and to understand how the naphthalene unit and its isomers affect polymer properties. The synthesis and characterization of polymers are discussed and the thermal properties of the polymers obtained have been compared with those of polymers containing phenyl or biphenyl units.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP) and toluene, used as azeotropic solvents, were purified by distillation over calcium hydride, in a nitrogen atmosphere. Potassium carbonate [anhydrous grade (Aldrich Co.), particle size less than 325 mesh] was heated at 100°C under reduced pressure before use. Bis-fluorobenzoyl and bis-fluorosulfonyl monomers were synthesized as described elsewhere^{9,15}. 1,5-Dihydroxynaphthalene (Aldrich Co.) was crystallized from 1,4-dioxane; 2,7- and 1,4-dihydroxynaphthalene (Aldrich Co.) were crystallized from toluene. Other reagents were commercial materials. All reactions were performed under an inert atmosphere of N₂.

Instrumental methods

Inherent viscosities ($\eta_{inh} = \ln \eta_r / C$ at polymer concentration

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$C = 0.5 \text{ g dl}^{-1}$) were measured with an Ubbelohde suspended-level viscometer at 30°C using NMP or conc. H_2SO_4 as solvent. Elemental analyses were conducted on a Carlo Erba Elemental Analyzer 1106 and are in accordance with the proposed structures. Thermogravimetric analyses (t.g.a.) were performed with a Mettler M3 thermobalance at a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 flow (25 ml min^{-1}) or in static air. The temperature of 10% weight loss was taken as the decomposition temperature (T_d). Differential scanning calorimetry (d.s.c.) measurements were made using a Mettler DSC 30 with aluminium pans at a heating rate of $20^\circ\text{C min}^{-1}$ in N_2 . Char yields (C_y) were calculated as the percentage of solid residue after heating from room temperature to 700°C in N_2 . Infrared (i.r.) spectra were measured with a Perkin Elmer FT-1725-X spectrophotometer on a pressed mixture with KBr. X-ray scattering data were obtained on pellets of the polymers with an X-ray diffractometer operating at 50 kV and 25 mA, using copper radiation. The data were recorded at room temperature over the 2θ angular range of $10\text{--}40^\circ$.

Polymerizations

A typical polymerization procedure is as follows.

Poly(ether ketone) 1a from **1** and **a** (Scheme 1). In a 100-ml three-necked round-bottomed flask fitted with a Dean–Stark trap, a condenser, a nitrogen inlet and a thermometer, 2.11 g (5.7 mmol) of 2,6-bis-fluorobenzoylnaphthalene (**1**), 0.91 g (5.7 mmol) of 1,5-dihydroxynaphthalene (**a**) and 0.802 g (5.8 mmol) of potassium carbonate were dissolved in a mixture of 15 ml of NMP and 20 ml of toluene. The entire operation was conducted under a constant purge of nitrogen. The reaction mixture was heated under reflux at 150°C until water was essentially removed from the reaction mixture by azeotropic distillation. After the water was removed, the temperature was slowly raised to 180°C and kept at that temperature overnight. The resulting reaction mixture was then cooled to 80°C and slowly poured into 150 ml of acetic acid solution. The precipitate was washed with water and boiled in methanol, to remove any trapped inorganic salt and solvent (NMP). Finally, the polymer was dried under vacuum at 100°C for 12 h. The yield was 2.64 g

(95%). The inherent viscosity of the polymer was 0.77 dl g^{-1} in conc. H_2SO_4 .

The i.r. spectrum exhibited absorptions at 1650 (CO) and $1240 \text{ cm}^{-1} \text{ (COC)}$. Calc. for $(\text{C}_{34}\text{H}_{20}\text{O}_4)_n$: C, 82.91%; H, 4.09%. Found: C, 82.71%; H, 4.20%.

When 2,7-dihydroxynaphthalene was used as monomer, the temperature of the polycondensation reaction was maintained at 160°C because this monomer melts with decomposition at 183°C .

RESULTS AND DISCUSSION

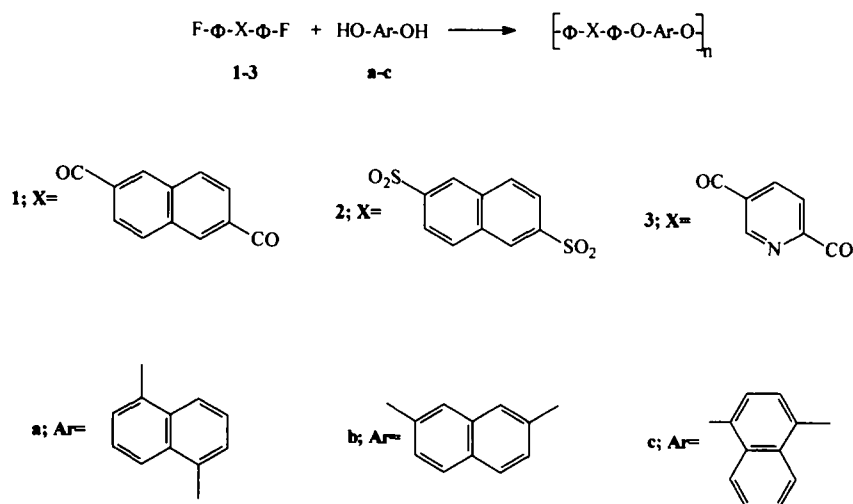
Aromatic poly(ether)ketones and poly(ether)sulfones **1a–3c** were synthesized by the aromatic nucleophilic substitution polycondensation of activated aromatic dihalides **1–3** with bis-phenols **a–c** in a mixed solvent system of NMP and toluene in the presence of anhydrous potassium carbonate (Scheme 1). The clean-up of the polymers was carefully done to ensure that all the solvent and the inorganic salts were removed. The yields of the polymers were always higher than 90% and the η_{inh} values were between 0.20 and 0.77 dl g^{-1} as measured in NMP or concentrated sulfuric acid (Table 1). The elemental analysis values for carbon, hydrogen, sulfur and nitrogen were in close agreement with the calculated values for all polymers. I.r. spectra showed absorptions at $\sim 1650 \text{ (CO)}$ and $\sim 1240 \text{ cm}^{-1} \text{ (COC)}$ for

Table 1 Inherent viscosities of polymers **1a–3c**

Polymer	η_{inh}
1a	0.77 ^a
1b	0.20 ^a
1c	0.59 ^a
	0.55 ^b
2a	0.30 ^b
2b	0.33 ^b
2c	0.25 ^b
3a	—
3b	—
3c	0.64 ^a
	0.55 ^b

^aDetermined in conc. H_2SO_4

^bDetermined in NMP



Scheme 1

polymers **1a–c**, at ~ 1320 (asymmetric SO_2 stretch), ~ 1245 (COC) and $\sim 1150 \text{ cm}^{-1}$ (symmetric SO_2 stretch) for polymers **2a–c**, and at ~ 1650 (CO) and $\sim 1230 \text{ cm}^{-1}$ (COC) for polymers **3a–c**.

The determination of the inherent viscosities was affected by the influence of the structure of polymers on the solubility. In general, it is known¹⁶ that the presence in the chain of benzene-sulfonyl groups promotes the solubility, and in fact it was possible to determine the inherent viscosities of polymers **2a–c** in NMP. The substitution of the sulfonyl with a ketone group causes a drop in solubility and then the poly(ether)ketones were less soluble. In

particular, polymers **3a** and **3b** were insoluble in all solvents and it was not possible to determine their inherent viscosity, while polymers **1a** and **1b** were soluble in conc. H_2SO_4 . The presence of the 1,4-dihydroxynaphthalene unit introduces a pendant group in the chain, with the consequence of increasing the solubility. In fact, polymer **1c** was also soluble in NMP, while polymer **3c** was soluble in conc. H_2SO_4 . The solubility also influences the molecular weight. The low η_{inh} registered for polymer **1b** was probably caused by the early precipitation of the polymer from the reaction medium, which hindered further polycondensation.

The thermal behaviour of the polymers was investigated

Table 2 Thermal characterization of polymers **1a–3c**

Polymer	T_g^a (°C)	T_g^b (°C)	T_g^c (°C)	T_m (°C)	C_c^d (%)
1a	525	490	230 ^d	260	77
1b	540	510	151 ^d	332	70
1c	510	480	207 ^e	—	70
2a	490	485	270 ^e	285	57
2b	500	490	261 ^e	—	56
2c	460	450	278 ^e	—	55
3a	510	460	222 ^d	—	73
3b	520	460	185	—	72
3c	460	430	197	—	69

^aTemperature of 10% weight loss determined in nitrogen atmosphere

^bTemperature of 10% loss weight determined in static air

^cChar yield

^dDetermined on quenched sample

^eDetermined on annealed sample

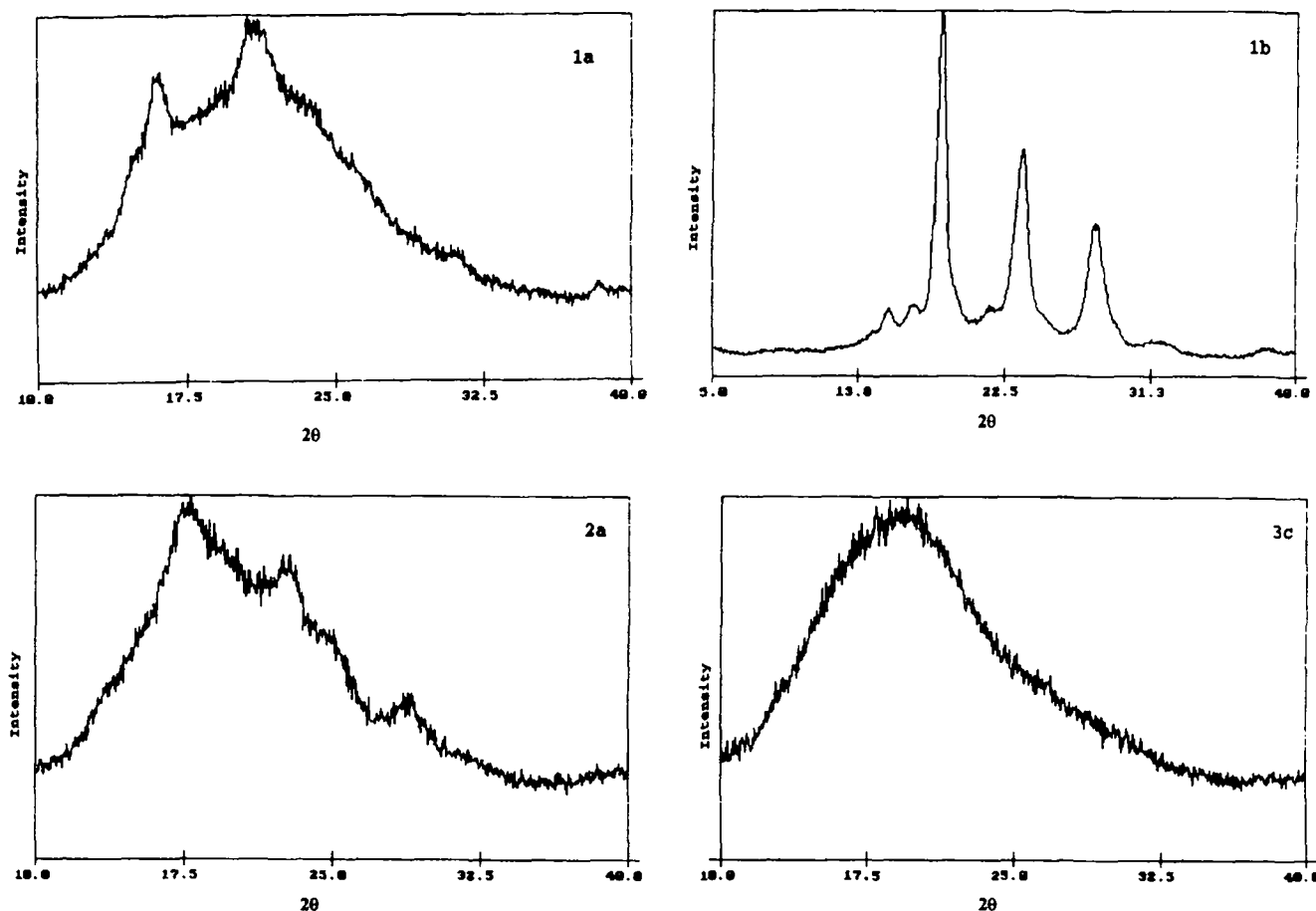


Figure 1 X-ray diffraction patterns of poly(arylene ether)s **1a**, **1b**, **2a** and **3c**

Table 3 Thermal data for poly(arylene ether)s

Polymer	T_g (°C)	T_m (°C)	Reference
$[-\text{FCO}(2,6\text{-naphthalene})\text{CO}\text{F}\text{O}\text{F}\text{O}-]_n$ (4)	150	325	10
$[-\text{FCO}(2,6\text{-naphthalene})\text{CO}\text{F}\text{O}\text{F}\text{O}\text{F}\text{O}-]_n$ (5)	195	—	10
$[-\text{FCO}\text{F}\text{CO}\text{F}\text{CO}\text{F}\text{CO}\text{F}\text{CO}-]_n$ (6)	183	431	19
$[-\text{FCO}\text{F}\text{CO}\text{F}\text{CO}\text{F}\text{CO}\text{F}\text{CO}\text{F}\text{CO}-]_n$ (7)	209	462	19
$[-\text{FO}_2\text{S}\text{F}\text{SO}_2\text{FO}\text{F}\text{O}-]_n$ (8)	241	480	8
$[-\text{FO}_2\text{S}\text{F}\text{SO}_2\text{FO}\text{F}\text{CO}-]_n$ (9)	262	485	8

by t.g.a. and d.s.c. As predicted, the T_d values determined in nitrogen were all higher than those determined in static air (Table 2). All the polymers were stable up to 460 and 430°C in nitrogen and air atmospheres respectively. The data reported in Table 2 show that the T_d values determined in N_2 flow were in the 510–540°C range for polymers **1a–c**, in the 460–500°C range for polymers **2a–c** and 460–520°C for polymers **3a–c**: poly(ether)ketones **1a–c** show a higher thermal stability than the corresponding poly(ether)sulfones **2a–c**^{5,6} and also higher thermal stability than polymers **3a–c** containing the 2,5-pyridine unit. The excellent thermal stabilities were confirmed by the char yield (C_y), as defined in the Experimental section. For all the poly(arylene ether ketone)s, C_y stays in the 69–77% range, while lower values of C_y resulted for poly(arylene ether sulfone)s (55–57%).

Glass transition temperatures determined by d.s.c. were in the 151–278°C range. T_g is known to depend on the rigidity of the polymer main chain: the increase of the rigidity of the polymer backbones increases the energy barrier for segmental motion, and hence T_g increases¹⁷. Polymers obtained by reaction with monomer **a** reveal the highest T_g , because the 1,5-naphthalene linkage seems to hinder mobility more effectively than the other two isomers. The decrease in T_g for polymers containing the bulky unsymmetric 2,7-oriented naphthalene ring in the polymer backbone can be attributed to the greater flexibility of the polymer chain due to the kink structure of the diol¹⁸. Polymers **1a** and **1b** showed, as made, T_m values at 260 and 332°C respectively, characteristic of a crystalline structure: after quenching they showed T_g values at about 230 and 151°C respectively. In the case of polymer **1c**, d.s.c. indicated that the material was amorphous, with a T_g at about 207°C. As expected¹⁷, the poly(arylene ether sulfone)s **2a–c** had higher T_g values (between 261 and 278°C) than corresponding poly(arylene ether ketone)s (151–230°C range). Polysulfones are generally amorphous, but very interestingly, a T_m at 285°C was observed for 'as made' polymer **2a**, and only after annealing was a T_g at 270°C obtained: the semicrystalline character of this polymer can be attributed to the rigid 1,5-naphthalene unit. Polymers containing pyridine moieties in the polymer backbone (**3a–c**) had high T_g values, between 185 and 222°C. All the polymers containing the 1,4-naphthalene units did not show a T_m : it could be supposed that the presence in this monomer of a pendant group inhibits the close packing of polymer chain and consequently suppresses crystallization.

The data obtained for the presence of crystalline domains in samples **1a–3c** detected by the onset of T_m were confirmed by wide angle X-ray diffraction. The sharp and diffuse patterns for poly(arylene ether ketone)s **1a** and **1b** (Figure 1) were characteristic of semicrystalline polymers. Although the presence of the 1,5-naphthalene unit could induce a more efficient packing of polymer chains, polymer

1a exhibited lower crystallinity than polymer **1b**. This result could be due to the low molecular weight of polymer **1b** ($\eta_{inh} = 0.2$), and also to a possible kinetic effect of the easier reorientation and packing of the slightly less rigid polymer **1b**. Polymer **2a** showed a pattern characteristic of the presence of semicrystalline domains, while all the other polymers were amorphous.

The influence of the presence of naphthalene moieties in the polymer backbone could be evaluated by comparison of the thermal properties of the obtained polymers **1a–3c** with analogues containing phenyl and/or biphenyl rings. The thermal data for these poly(arylene ether)s are reported in Table 3. Interestingly, the introduction of another naphthalene unit in the main chain with respect to a phenyl (polymer **4**)¹⁰ or biphenyl (polymer **5**)¹⁰ ring seems to considerably increase the T_g of polymers **1a** and **1c**. The exception of polymer **1b** is probably due to the presence of the unsymmetric 2,7-naphthalene unit. The T_g values of polymers **1a** and **1c** were also higher than those of polymers **6** and **7**¹⁹, where naphthalene units have been substituted with another rigid structure as the biphenyl unit. Poly(arylene ether sulfone)s of series **2** show T_g values similar or higher than those polymers where one naphthalene unit has been substituted with a biphenyl ring and the other with a phenyl or biphenyl unit (polymers **8** and **9** respectively)⁸.

In conclusion, the polymers obtained showed excellent thermal properties, such as high glass transition temperatures, comparable to some of the highest T_g values known for poly(aryl)ethers. These properties seem to be modulated as a function of the location of the naphthalene–ether bond present in the chain. The 1,5-dihydroxy isomer seems to be the most efficient in promoting high T_g values and development of crystallinity. In fact, some crystallinity was also observed in the case of a poly(arylene ether sulfone)s.

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