Synthesis and Characterization of Novel Organosoluble Methyl Substituted Poly(aryl ether ketone)s Containing Sulfone Linkage

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Several new methyl substituted poly(aryl ether ketone)s containing sulfone linkage with inherent viscosities of 0.62-0.84 dL/g have been prepared from 4,4'-bis(2-methylphenoxy)diphenylsulfone and 4,4'-bis(3methylphenoxy)diphenylsulfone with terephthaloyl chloride and isophthaloyl chloride by electrophilic Friedel-Crafts acylation in the presence of DMF with anhydrous AlCl₃ as a catalyst in 1,2-dichloroethane, respectively. These polymers having weight-average molecular weight in the range of 71,000-49,000 are all amorphous and show high glass transition temperatures ranging from 167 °C to 191 °C, excellent thermal stability at temperatures over 400 °C in air or nitrogen, high char yields of 51-58% in nitrogen and good solubility in CHCl₃ and polar solvents such as DMF, DMSO and NMP at room temperature.

Keywords: Poly(aryl ether ketone)s; Sulfone linkage; Methyl-substituted; Synthesis; Characterization.

INTRODUCTION

Scheme I

Aromatic poly(aryl ether ketone)s (PEKs) are classified as high performance engineering thermoplastics and are widely used in the electronic, electric, aircraft and aerospace industries.¹ Friedel-Crafts acylation and nucleophilic displacement are synthetic routes for producing PEKs.² Although PEKs show excellent thermal, mechanical and electrical properties, their poor solubility in ordinary organic solvents and high processing temperature limit their extensive application. In view of this, considerable structural modifications have been carried out to improve the properties of PEK type polymers by incorporating the various moieties in or onto the polymer backbone.³ However, it has been difficult to be very interesting to develop novel PEKs with a combined advantage of excellent processing properties and thermal stability. Our research group has been interested in the design and modifications of PEKs with structure to improve their properties.⁴ In this paper we describe the synthesis of several novel soluble methyl substituted aromatic poly(ether sulfone ether ketone ketone)s prepared by electrophilic Friedel-Crafts acylation condensation of 4,4'-bis(2-methylphenoxy)diphenylsulfone and 4,4'-bis(3-methylphenoxy)diphenylsulfone with aromatic diacid chloride such as terephthaloyl chloride and isophthaloyl chloride, respectively, as shown in Scheme I. These novel PEKs are all amorphous and are

improve solubility or processability of PEKs without losing their original excellent thermal stability. Therefore, it would



readily soluble in common organic solvents at room temperature. They have excellent thermo-oxidative stabilities with high glass transition temperatures.

EXPERIMENTAL

Material

4,4'-Dichlorodiphenylsulfone (DCPS), anhydrous aluminium chloride, concentrated sulfuric acid, N-methyl-2pyrrolidone (NMP), dimethylsulfoxide (DMSO), chloroform, dichloromethane, acetone, methanol, chlorobenzene, tetrahydrofuran, toluene and calcium hydride were used as received. N,N-Dimethylformamide (DMF) was refluxed with calcium hydride and distilled under reduced pressure, then dried over molecular sieves 4 Å prior to use. 1,2-Dichloroethane and chloroform were refluxed with phosphorous pentoxide and distilled. *o*-Cresol and *m*-cresol were purified by distillation under reduced pressure. Terephthaloyl chloride and isophthaloyl chloride were prepared in our laboratory and purified by distillation under reduced pressure, m.p. 82-83 °C and 42-43 °C, respectively.

Monomer Synthesis

4,4'-Bis(3-methylphenoxy)diphenylsulfone (**1b**) were prepared from DCPS with *m*-cresol according to the literature.⁵ The ¹H NMR spectrum of **1b** was identical to that reported in the literature. 4,4'-Bis(2-methylphenoxy)diphenylsulfone (**1a**) was also prepared from DCPS with *o*-cresol using a procedure similar to that given in a paper.⁵ Yield 92%; FT-IR: v_{max} 2912, 1595, 1288, 1295, 1110, 1151, 1205, 965, 821, 700 cm⁻¹; ¹H NMR: δ 7.80 (d, *J* = 8.0 Hz, 4H), 6.88 (d, *J* = 8.0 Hz, 4H), 7.10-7.24 (m, 4H), 7.27-7.55 (m, 4H), 2.35 (s, 6H). Anal. calcd. for C₂₆H₂₂O₄S: C, 72.55%; H, 5.11%. Found: C, 72.45%; H, 5.18%.

Polymer Synthesis

The general procedure in this study was performed as follow. Under a N₂ atmosphere, DMF (5.0 mL, 47.6 g, 0.065 mol) was added with stirring and cooling to a mixture of aluminum chloride (18.0 g, 0.135 mol) in 1,2-dichloroethane (40 mL). The mixture was cooled to -20 °C and aromatic ether monomer **1** (0.02 mol) and aromatic diacid chloride monomer **2** (0.02 mol) were then added with stirring for 1 h. The mixture was allowed to warm to room temperature and stirred for about 8 h, then worked up by blending it with methanol in a Waring blender, filtering, washing with methanol, and drying at 140 °C for 4 h in vacuum to furnish a white powder

polymer.

Measurements

Infrared spectra (FT-IR) were determined on a Perkin-Elmer SP One FT-IR spectrophotometer. ¹H NMR spectra were recorded on Bruker Avance 400 MHz spectrometer using CDCl3 as the solvent and with TMS as internal standard. Elemental analyses were performed on a Perkin-Elmer C, H, N 2400 elemental analyzer. Differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer Pyris 1 at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was recorded with a Shimadzu TG 40 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere. The wide-angle X-ray diffraction measurements were recorded at room temperature (ca. 25 °C) on power with a Rigaku Geiger Flex D-Max III X-ray diffractometer, using Ni-filtered CuKa radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min over a range of $2\theta = 2-40^{\circ}$). The inherent viscosity data was obtained using conc. H₂SO₄ solutions with a concentration of 0.50 g/dL in an Ubbelohde viscometer at 30 °C. Molecular weights were determined by a gel permeation chromatography (GPC) with polystyrene calibration using a water ALC/GPC244 equipped with TSKGH9P, GMH6, Hitachi GL/A-120, A-130 columns at 25 °C using chloroform as eluent. Polymer samples were dissolved in CHCl₃, filtered, precipitated in methanol and dried under vacuum at room temperature before performing GPC measurements.

RESULTS AND DISCUSSION

As depicted in Scheme I, four new polymers (3aa-3bb) were synthesized by reaction of compounds 1 with selected aromatic diacid chloride 2 using Friedel-Crafts acylation polymerization as described in our previous paper.⁶ When a monomer concentration of 0.40-0.45 mol/L was adopted, the polymers with high inherent viscosity in the range of 0.62-0.84 dL/g and high yields (>95% in all cases) were obtained. The GPC curves indicated that \overline{Mw} values of the polymers **3** were in the range of 71,000-49,000, relative to standard polystyrene, and the polydispersity index Mw/Mn ranged from 1.7 to 1.9. The molecular weights of these polymers are sufficiently high to permit casting flexible and tough films. The FT-IR of polymers showing strong characteristic absorptions of carbonyl group at 1648 cm⁻¹, -SO₂- at 1148 cm⁻¹, -CH₃ at 2925, 1375 cm^{-1} and C-O-C at 1250 cm^{-1} demonstrated the performance of Friedel-Crafts acylation. In a typical ¹H NMR

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Polymer 3	$\eta_{inh}{}^a$ (dL/g)	<i>T_g</i> (°C)	T_d^{b} N ₂ (°C)	T_d^{b} air (°C)	Residue ^c (wt %)	$\overline{MW}^{d} \times 10^{-4}$	$\overline{Mw} / \overline{Mn}$
3aa	0.84	191.0	475	470	58	7.1	1.9
3ab	0.68	181.5	465	458	56	5.8	1.7
3ba	0.65	181.3	439	430	54	5.3	1.8
3bb	0.62	167.0	428	421	51	4.9	1.7

Table 1. Preparation of polymer 3

 a Measured at a concentration of 0.5 g/dL in conc. H_2SO_4 at 30 °C.

^b 5% Weight loss temperature measured at 10 °C/min by TGA.

^c Char residual at 700 °C in N₂.

 $^{\rm d}$ Determined by GPC, using CHCl_3 as the eluent and the polystyrene as the standard.

Table 2. The solubility of polymer 3 in various organic solvents at room temperature

Polymer 3	DMF	DMSO	NMP	CHCl ₃	CH_2Cl_2	ClC ₆ H ₅	CH ₃ OH	Acetone	THF	Toluene
3aa	++	++	++	++	++	+	-	-	-	-
3ab	++	++	++	++	++	+	-	-	-	-
3ba	++	++	++	++	++	+	-	-	-	-
3bb	++	++	++	++	++	+	-	-	-	-

++: soluble; +: soluble under heat; -: insoluble.

spectrum of polymer **3aa** in CDCl₃, the peak that appeared at 2.36 ppm was assigned to six methyl pendent protons, and the remaining aromatic protons were detected as multiplets at 7.12-7.86 ppm.

Polymers 3aa-3bb have excellent thermal stability according to dynamic TGA results (Table 1). Thermal stability as indicated by the temperature (T_d) at which 5% weight loss observed were over 420 °C both in nitrogen and air. Polymers 3aa and 3ab exhibited better thermal stability than polymers **3ba** and **3bb**. Furthermore, the T_d of polymers containing all para-phenylene linkages was higher than those of corresponding polymers containing meta-phenylene linkages. It should be noted that the relatively low T_d of the polymers are lower than those of most known wholly aromatic PEKs such as ICI' PEEK and Dupont' PEKK, which possibly arises from the presence of less stable methyl groups. The representative TG diagrams of polymer 3aa in air and nitrogen are shown in Fig. 1. The initial decomposition temperature of the polymer 3aa in air is lower than in nitrogen. In air, the rate of the weight loss was relatively rapid above 490 °C, and there was about 35% residue remaining at 700 °C. All other polymers showed similar thermal behavior. Char yields at 700 °C in nitrogen atmosphere exceed 50% for all polymers, comparable to those of wholly aromatic PEKs. All polymers exhibited higher glass transition temperatures than did PEEK (T_g = 143 °C) and PEKK ($T_g = 156$ °C), which might mainly result from the methyl side group of monomers inhibiting the polymer backones' free rotation. Especially, it is noteworthy that

the polymers **3aa**, **3ab** and **3ba** showed a high T_g over 180 °C. The WAXD analysis showed that all polymers were amorphous, which was consistent with the results of DSC analysis with no melting temperatures.

The solubility of the polymers in various solvents was examined and the results are shown in Table 2. These polymers could not dissolve in methanol, acetone, toluene or THF, but were well soluble in many kinds of organic solvents such as DMF, DMSO, NMP, CHCl₃, CH₂Cl₂ and chlorobenzene. Therefore, introducing polar bulky sulfone group and methyl pendant into PEKs would improve their solubility, which is necessary in industrial processing for the polymer. Strong, transparent, creasable films of the polymers are read-



Fig. 1. TGA curves of the polymer **3aa** in N_2 (a) and in air (b).

ily obtained by solution casting from chloroform.

In conclusion, four novel methyl substituted poly(aryl ether ketone)s containing sulfone linkage with high molecular weight, high glass transition temperatures and good thermal stability have been prepared. These polymers were well soluble in CHCl₃ and polar solvents such as DMF and DMSO, etc., and afforded transparent, flexible and amorphous films by solution-casting.

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