

## NOTE

# Synthesis and Properties of Novel Organosoluble Aromatic Poly(ether ketone)s Containing Pendant Methyl Groups and Sulfone Linkages

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**ABSTRACT:** Several novel aromatic poly(ether ketone)s containing pendant methyl groups and sulfone linkages with inherent viscosities of 0.62–0.65 dL/g were prepared from 2-methyldiphenylether and 3-methyldiphenylether with 4,4'-bis(4-chloroformylphenoxy)diphenylsulfone and 4,4'-bis(3-chloroformylphenoxy)diphenylsulfone by electrophilic Friedel–Crafts acylation in the presence of *N,N*-dimethylformamide with anhydrous AlCl<sub>3</sub> as a catalyst in 1,2-dichloroethane. These polymers, having weight-average molecular weights in the range of 57,000–71,000, were all amorphous and showed high glass-transition temperatures ranging

from 160.5 to 167°C, excellent thermal stability at temperatures over 450°C in air or nitrogen, high char yields of 52–57% in nitrogen, and good solubility in CHCl<sub>3</sub> and polar solvents such as *N,N*-dimethylformamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone at room temperature. All the polymers formed transparent, strong, and flexible films, with tensile strengths of 84.6–90.4 MPa, Young's moduli of 2.33–2.71 GPa, and elongations at break of 26.1–27.4%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 683–687, 2008

**Key words:** poly(ether ketone sulfone)s; methylated; soluble

## INTRODUCTION

Aromatic poly(ether ketone)s (PEKs) are classified as high-performance engineering thermoplastics and are widely used in the electronic, electric, aircraft, and aerospace industries.<sup>1</sup> Both aromatic electrophilic substitution (Friedel–Crafts acylation) and aromatic nucleophilic substitution reactions are versatile methods for synthesizing PEKs.<sup>2</sup> Although PEKs show excellent thermal, mechanical, and electrical properties, their poor solubility in ordinary organic solvents and high processing temperature limit their extensive applications. In view of this, considerable structural modifications have been carried out to improve the properties of PEK-type polymers by the incorporation of various moieties into or onto the polymer backbone.<sup>3</sup> However, it has been difficult to improve the solubility or processability of PEKs without the loss of

their original excellent thermal stability. Therefore, it would be very interesting to develop novel PEKs with the combined advantages of excellent processing properties and thermal stability. Our research group has been interested in the design and modifications of PEKs with structures to improve their properties.<sup>4</sup> In this article, we describe the synthesis of several novel soluble, methyl-substituted, aromatic poly(ether ketone ether sulfone ether ketone)s (PEKESEKs) prepared by electrophilic Friedel–Crafts acylation condensation of 2-methyldiphenylether (**1a**) and 3-methyldiphenylether (**1b**) with 4,4'-bis(4-chloroformylphenoxy)diphenylsulfone (**2a**) and 4,4'-bis(3-chloroformylphenoxy)diphenylsulfone (**2b**), respectively, as shown in Scheme 1. The purpose of this work was the preparation and evaluation of novel PEKESEKs with improved processability and properties through the introduction of methyl substituents and sulfone linkages.

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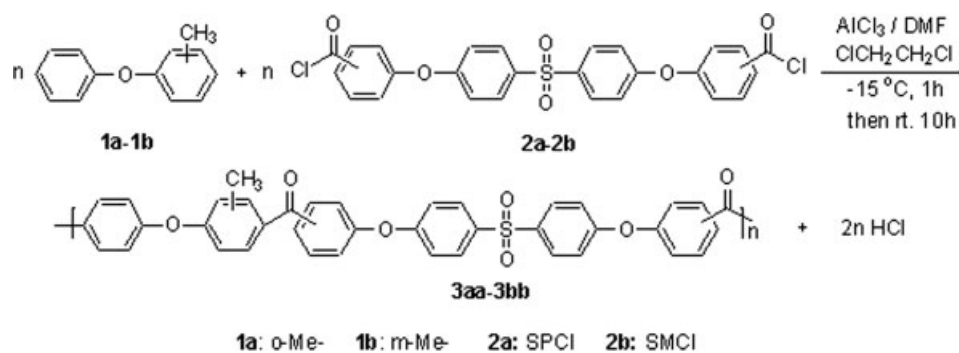
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## EXPERIMENTAL

### Materials

4,4'-Dichlorodiphenylsulfone, anhydrous aluminum chloride, concentrated sulfuric acid, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), chloroform, dichloromethane, acetone, methanol, chlorobenzene, bromobenzene, tetrahydrofuran (THF), and calcium hydride were used as received. *N,N*-Dimethylformamide (DMF) was refluxed with calcium hydride and distilled under reduced



**Scheme 1** Preparation of aromatic poly(ether ketone sulfone)s with pendant methyl groups.

pressure and then was dried over 4-Å molecular sieves before 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.

#### Monomer synthesis

**1a** and **1b** were prepared from bromobenzene with *o*-cresol and *m*-cresol according to the literature.<sup>5</sup> **2a** and **2b** were prepared with a procedure similar to that reported in another article.<sup>6</sup>

#### Polymer synthesis

Polymerizations were carried out in 1,2-dichloroethane from diaryl ether **1** with aromatic diacid chloride **2** in the presence of aluminum trichloride. The general method of synthesis was as follows. Under an N<sub>2</sub> atmosphere, DMF (5.0 mL, 4.75 g, 0.065 mol) was added with stirring and cooling to a mixture of aluminum chloride (20.0 g, 0.15 mol) in 1,2-dichloroethane (40 mL). The mixture was cooled to -15°C, and aromatic ether monomer **1** (3.6848 g, 0.02 mol) and aromatic diacid chloride monomer **2** (10.5478 g, 0.02 mol) were then added with stirring for 1 h. The mixture was allowed to warm to room temperature and stirred for about 9 h and then was worked up through blending with methanol in a Waring blender, filtering, washing with methanol, and drying at 120°C overnight *in vacuo* to furnish a white, powdery polymer.

#### Measurements

The Fourier transform infrared (FTIR) spectra of the polymers in KBr pellets were determined on a PerkinElmer (Waltham, MA) SP One FTIR spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on a Bruker (Kleve, Germany) Avance 400-MHz spectrometer with CDCl<sub>3</sub> as the solvent and with tetramethylsilane (TMS) as the internal standard. Differential scanning calorimetry (DSC) was conducted on a PerkinElmer Pyris 1 at a heating rate of 10°C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was recorded with a Shimadzu (Kyoto, Japan) TG 40 thermogravimetric analyzer at a heating rate of 10°C/min under a nitrogen or air atmosphere. The wide-angle X-ray diffraction measurements were recorded at room temperature (ca. 25°C) on power with a Rigaku (Kent, England) Geiger Flex D-Max III X-ray diffractometer using Ni-filtered Cu Kα radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min over a range of 2θ = 2–40°. The inherent viscosity data were obtained with concentrated H<sub>2</sub>SO<sub>4</sub> solutions with a concentration of 0.50 g/dL in an Ubbelohde (Shanghai, China) viscometer at 30°C. The mechanical properties of the thin films (ca. 0.2 mm, cast from CHCl<sub>3</sub> solutions onto the glass plates and followed by heating at 100–150°C *in vacuo*) were evaluated at room temperature on an Instron (UK) 1121 instrument at a strain rate of 10 mm/min. The molecular weights were determined by gel permeation chromatography (GPC) (Waters Associates Co., Ltd., USA) with polystyrene calibration with a Water ALC/GPC244 equipped with TSKGH9P, GMH6, Hitachi GL/A-120, and A-130 columns at 25°C

**TABLE I**  
Inherent Viscosities and Thermal Properties of Polymers 3aa–3bb

Polymer	Inherent viscosity (dL/g) <sup>a</sup>	T <sub>g</sub> (°C)	T <sub>d</sub> in N <sub>2</sub> (°C) <sup>b</sup>	T <sub>d</sub> in air (°C) <sup>b</sup>	Residue (wt %) <sup>c</sup>	M <sub>w</sub> × 10 <sup>-4</sup> <sup>d</sup>	M <sub>w</sub> /M <sub>n</sub>
<b>3aa</b>	0.63	167.0	470	462	57	6.8	1.9
<b>3ab</b>	0.62	164.1	465	450	56	5.7	1.7
<b>3ba</b>	0.61	163.3	475	459	54	6.2	1.8
<b>3bb</b>	0.65	160.5	472	462	52	7.1	1.8

<sup>a</sup> Measured at a concentration of 0.5 g/dL in concentrated H<sub>2</sub>SO<sub>4</sub> at 30°C.

<sup>b</sup> Measured at 10°C/min by TGA.

<sup>c</sup> Char residual at 700°C in N<sub>2</sub>.

<sup>d</sup> Determined by GPC with CHCl<sub>3</sub> as the eluent and polystyrene as the standard.

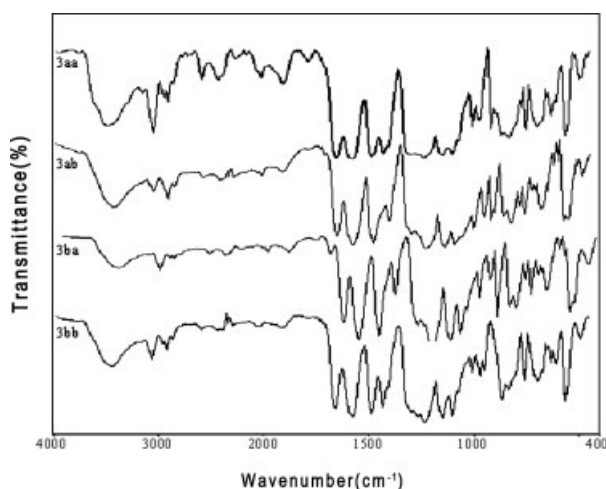


Figure 1 FTIR spectra of polymers 3ab–3bb.

with chloroform as an eluent. The polymer samples were dissolved in  $\text{CHCl}_3$ , filtered, precipitated in methanol, and dried *in vacuo* at room temperature before GPC measurements were performed.

## RESULTS AND DISCUSSION

### Polymer synthesis

As shown in Scheme 1, four novel polymers (3aa–3bb) were synthesized through the reaction of compounds 1 and 2 with Friedel–Crafts acylation polymerization as described in our previous article.<sup>7</sup> This technique was used in this work, with an initial reaction temperature between  $-15$  and  $0^\circ\text{C}$ , which was found to be the most effective. In the course of the reaction, when a monomer concentration of  $0.35$ – $0.40$  mol/L was adopted, polymers with high inherent viscosities in the range of  $0.62$ – $0.65$  dL/g and high yields ( $>95\%$  in all cases) were obtained (Table I). The GPC curves indicated that the weight-average molecular weight ( $M_w$ ) values of polymers 3aa–3bb were in the range of  $57,000$ – $71,000$ , with respect to standard polystyrene, and the polydispersity index [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] ranged from  $1.7$  to  $1.9$ . The molecular weights of these polymers were sufficiently high to permit the casting of flexi-

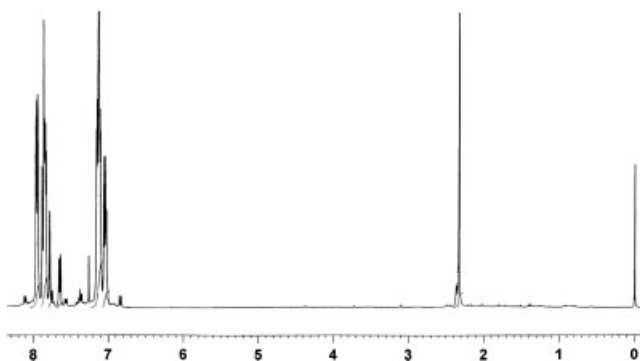


Figure 2  $^1\text{H-NMR}$  of polymer 3ab.

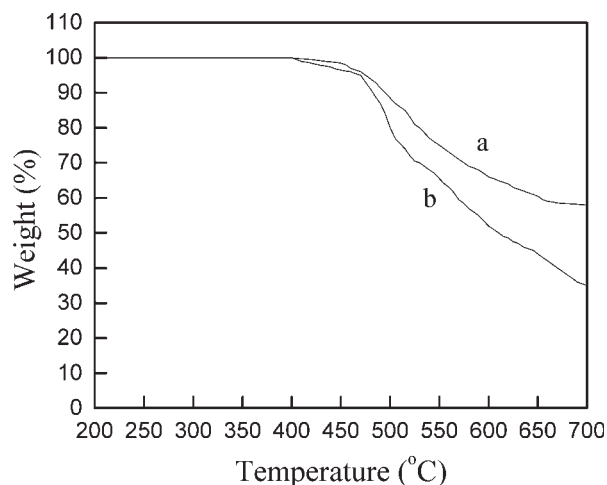


Figure 3 TGA curves of polymer 3aa (a) in  $\text{N}_2$  and (b) in air.

ble and tough films. Figure 1 compares the FTIR spectra of polymers 3aa–3bb. Characteristic absorptions of the polymers for carbonyl groups at  $1656$ – $1659$   $\text{cm}^{-1}$ , for  $-\text{SO}_2-$  at  $1147$ – $1151$   $\text{cm}^{-1}$ , for  $-\text{CH}_3$  at  $2925$  and  $1375$   $\text{cm}^{-1}$ , and for  $\text{C}-\text{O}-\text{C}$  near  $1250$   $\text{cm}^{-1}$  can all be observed. As an example, the  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of polymer 3ab has been reproduced in Figure 2. The peak that appears at  $2.33$  ppm has been assigned to six methyl pendent protons, and the remaining aromatic protons have been detected as multiplets at  $7.01$ – $7.96$  ppm. These results demonstrate that the aromatic poly(ether ketone sulfone)s with pendant methyl groups had the expected chemical structures.

### Thermal properties and X-ray analysis

The thermal behavior of the new polymers (3aa–3bb) was evaluated with DSC and TGA. The polymers exhibited

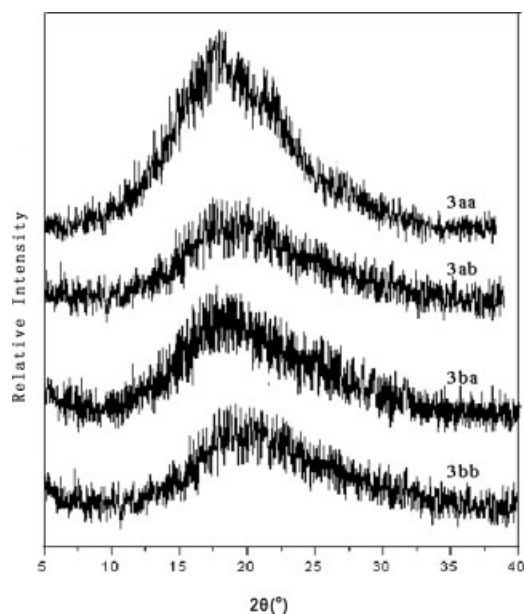


Figure 4 X-ray diffraction patterns of polymers 3aa–3bb.

TABLE II  
Solubility of Polymers 3aa–3bb

Polymer	DMF	DMSO	NMP	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	CH <sub>3</sub> OH	Acetone	THF	Concentrated H <sub>2</sub> SO <sub>4</sub>
3aa	++	++	++	++	++	+	–	–	–	++
3ab	++	++	++	++	++	+	–	–	–	++
3ba	++	++	++	++	++	+	–	–	–	++
3bb	++	++	++	++	++	+	–	–	–	++

+ + = soluble; + = soluble under heating; – = insoluble.

TABLE III  
Mechanical Properties of Polymers 3aa–3bb

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
3aa	90.4	2.71	27.4
3ab	85.2	2.58	26.5
3ba	86.4	2.66	26.8
3bb	84.6	2.33	26.1

good thermal stability. As summarized in Table I, the 5% weight loss temperature ( $T_d$ ) was over 450°C in both nitrogen and air. Furthermore, the  $T_d$  values of the polymers containing all *para*-phenylene linkages were higher than those of the corresponding polymers containing *meta*-phenylene linkages. The relatively low  $T_d$  values of the polymers were lower than those of most known wholly aromatic PEKs, such as ICI's poly(ether ether ketone) (PEEK) and Dupont's poly(ether ether ketone) (PEKK), and this is possibly because of the presence of less stable methyl groups. Representative thermogravimetric diagrams of polymer 3aa in air and nitrogen are shown in Figure 3. The initial decomposition temperature of polymer 3aa was lower in air than in nitrogen. In air, the rate of weight loss was relatively rapid above 480°C, and there was about 35% residue remaining at 700°C. All the other polymers showed similar thermal behavior. The char yields at 700°C in a nitrogen atmosphere exceeded 50% for all the polymers, and they were comparable to those of wholly aromatic PEKs. As depicted in Table I, the glass-transition temperatures ( $T_g$ 's) of the polymers were 160.5–167°C, and no melting endotherms were observed in the DSC traces. These observations further confirmed the amorphous nature of the polymers, which was consistent with the results of a wide-angle X-ray diffraction analysis showing amorphousness (Fig. 4). All the polymers exhibited higher  $T_g$ 's than PEEK ( $T_g = 143^\circ\text{C}$ ) and PEKK ( $T_g = 156^\circ\text{C}$ ), and this might have mainly resulted from the methyl side groups of the monomers inhibiting the polymer backbones' free rotation.

#### Solubility and mechanical properties

The solubility behavior of the polymers in some solvents is listed in Table II. Like PEEK and PEKK, all the polymers were found to be soluble in concentrated sulfuric acid. It is well known that conventional PEEK and PEKK cannot be dissolved in most known organic solvents. In sharp contrast, these polymers were soluble at room temperature in aprotic polar solvents such as NMP, DMSO, and DMF and

in less polar solvents such as chloroform. The good solubility of the polymers could be attributed to the introduction of the methyl substituents and polar bulky sulfone group, which disturbed the close packing of the polymer chains and led to the increased free volume. Therefore, it was easy for the solvents to solubilize the polymers, and this is necessary for the industrial processing of the polymers.

The mechanical properties of polymer thin films cast from chloroform are summarized in Table III. All the films were transparent, strong, and flexible. The polymer films had tensile strengths of 84.6–90.4 MPa, Young's moduli of 2.33–2.71 GPa, and elongations at break of 26.1–27.4%, which indicated that they were strong materials.

#### CONCLUSIONS

Four novel methyl-substituted poly(aryl ether ketone)s containing sulfone linkages with high-molecular-weights, high  $T_g$  values, and good thermal stability were successfully synthesized. All the polymers were amorphous and had remarkably improved solubility in common solvents, such as DMF, NMP, DMSO, and chloroform, over known and conventional wholly aromatic PEEK and PEKK. These polymers formed transparent, strong, and flexible films with tensile strengths of 84.6–90.4 MPa, Young's moduli of 2.33–2.71 GPa, and elongations at break of 26.1–27.4%.

#### References

- (a) Rose, J. B.; Staniland, P. A. U.S. Pat. 4,320,224 (1982); (b) Mullins, M. J.; Woo, E. P. *J Macromol Sci Rev Macromol Chem Phys* 1987, 27, 313.
- Kricheldorf, H. R. In *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; Chapter 9, p 545.
- (a) Elce, E.; Hay, A. S. *J Polym Sci Part A: Polym Chem* 1995, 33, 1143; (b) Klapper, M.; Wehrmeister, T.; Mullen, K. *Macromolecules* 1996, 29, 5805; (c) Taguchi, Y.; Uyama, H.; Kobaya-

- shi, S. *J Polym Sci Part A: Polym Chem* 1997, 35, 271; (d) Mercer, F. W.; Fone, M. M.; Mckenzie, M. T. *J Polym Sci Part A: Polym Chem* 1997, 35, 521; (e) Tunca, U; Hizal, G. *J Polym Sci Part A: Polym Chem* 1998, 36, 1227; (f) Fitch, J W.; Reddy, V. S.; Youngman, P. W.; Wohlfahrt, G. A.; Cassidy, P. E. *Polymer* 2000, 41, 2301; (g) Gao, Y; Jian, X.-G.; Xuan, Y.-N.; Xiang, S.; Liang, P.; Guiver, M. D. *J Polym Sci Part A: Polym Chem* 2002, 40, 3449; (h) Takeuchi, H; Kakimoto, M.-A.; Imai, Y. *J Polym Sci Part A: Polym Chem* 2003, 41, 1428; (i) Liu, B.-J.; Hu, W.; Chen, C.-H.; Jiang, Z.-H.; Zhang, W.-J.; Wu, Z.-W. *Polymer* 2004, 45, 3241; (j) Salunke, A K.; Sharma, M. Kute, V.; Banerjee, S. *J Appl Polym Sci* 2005, 96, 1292; (k) Shang, X.-Y.; Li, X.-H.; Xiao, M.; Meng, Y.-Z. *Polymer* 2006, 47, 3807.
4. (a) Sheng, S.-R.; Cai, M.-Z.; Song, C.-S. *Acta Polym Sinica* 1998, 616; (b) Sheng, S.-R.; Cai, M.-Z.; Song, C.-S. *Acta Polym Sinica* 1999, 490; (c) Qiu, Z.-B.; Chen, Q.-Y.; Sheng, S.-R.; Song, C.-S.; Mo, Z.-S. *Acta Polym Sinica* 2000, 499; (d) Qiu, Z.-B.; Wang, J.-K.; Sheng, S.-R.; Song, C.-S.; Zhou, E.-L.; Mo, Z.-S. *Chem J Chin Univ* 2000, 21, 1948; (e) Qiu, Z.-B.; Mo, Z.-S.; Zhang, H.-F.; Sheng, S.-R.; Song, C.-S. *J Macromol Sci Phys* 2000, 39, 373; (f) Qiu, Z.-B.; Mo, Z.-S.; Yu, Y.-N.; Zhang, H.-F.; Sheng, S.-R.; Song, C.-S. *J Appl Polym Sci* 2000, 77, 2865; (g) Qiu, Z.-B.; Mo, Z.-S.; Zhang, H.-F.; Sheng, S.-R.; Song, C.-S. *J Polym Sci Part B: Polym Phys* 2000, 38, 1992; (h) Qiu, Z.-B.; Mo, Z.-S.; Sheng, S.-R.; Song, C.-S. *Macromol Chem Phys* 2000, 201, 2756; (i) Gan, D.-J.; Cao, W.-J.; Song, C. S.; Wang, Z.-J. *Mater Lett* 2001, 51, 120; (j) Gan, D.-J.; Liu, S.-Q.; Song, C. S.; Wang, Z.-J. *Mater Lett* 2001, 51, 299; (k) Gan, D.-J.; Liu, S.-Q.; Song, C. S.; Wang, Z.-J. *Eur Polym J* 2001, 37, 1359; (l) Sheng, S.-R.; Kang, Y.-Q.; Huang, Z.-Z.; Chen, G.-H.; Song, C.-S. *Acta Polym Sinica* 2004, 773; (m) Wen, H.-L.; Song, C.-S.; Tong, Y.-F.; Chen, L.; Liu, X.-L. *J Appl Polym Sci* 2005, 96, 489.
5. Chen, L.; Xu, H.-H.; Yin, B.-L.; Xiao, C.; Hu, T.-S.; Wu, Y.-L. *Chin J Chem* 2004, 22, 984.
6. Idage, S. B.; Idage, B. B.; Vermekar, S. P. *J Appl Polym Sci* 1989, 33, 2057.
7. Song, C.-S.; Cai, M.-Z.; Zhou, L.-Y. *Acta Polym Sinica* 1995, 99.