

Synthesis of Aromatic Poly(ether ketone)s in Phosphorus Pentoxide/Methanesulfonic Acid

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ABSTRACT: Aromatic poly(phenylene ether ether ketone)s were prepared by the direct self-polycondensation of 4-(4'-phenoxyphenoxy)benzoic acids using phosphorus pentoxide/methanesulfonic acid (PPMA) as a condensing agent and solvent. The polycondensations proceeded smoothly at 60—100°C and produced poly(phenylene ether ether ketone)s with inherent viscosities up to 1.5 dl g⁻¹. The synthesis of poly(phenylene ether ketone)s by the direct self-polycondensation of *ortho* substituted phenoxybenzoic acids in PPMA was also carried out, where the polycondensation of 4-(*o*-methoxyphenoxy)benzoic acid produced high molecular weight poly(phenylene ether ketone) at 80°C for 24 h. The thermogravimetry of the aromatic poly(ether ketone)s showed 10% weight loss both in air and in nitrogen around 500°C.

KEY WORDS Poly(phenylene ether ether ketone) / Poly(phenylene ether ketone) / Direct Self-Polycondensation / Phosphorus Pentoxide-Methanesulfonic Acid / Condensing Agent /

High performance thermoplastics are currently receiving considerable attention for their potential applications in aerospace, automotive, electronic, and related markets. In particular, poly(phenylene ether ether ketone)s have shown promise as excellent engineering plastics because of their good mechanical properties and thermooxidative stabilities.

A number of synthetic routes for producing poly(ether-ketone)s has been developed and reviewed in detail.¹ Quite recently, Colquhoun *et al.* developed a convenient method for the synthesis of certain aromatic poly(ether-ketone)s of high molecular weights in the super acid solvent, trifluoromethanesulfonic acid.²

Developing efficient and mild methods for the synthesis of condensation polymers continues to be a significant aspect of synthetic polymer chemistry. Our studies on the synthesis of condensation polymers by a direct procedure in phosphorus pentoxide/methanesulfonic acid (PPMA) in a weight ratio of

1:10 have revealed that PPMA is a suitable condensing agent and solvent for the preparation of poly(ketone)s,³ poly(ether-sulfone)s,⁴ and heterocyclic polymers.⁵

In the preceding paper,^{3b} we showed that certain aromatic poly(ether ketone)s of high molecular weights could be prepared readily by the direct polycondensation of dicarboxylic acids containing phenyl ether structures with diphenoxybenzene or by self-polycondensation of *m*-phenoxybenzoic acid in PPMA. In our continuing investigation of the versatility of this method, we now report a successful synthesis of poly(ether ketone)s by direct self-polycondensation of various benzoic acids containing phenyl ether structures in PPMA.

EXPERIMENTAL

Materials

The reagent PPMA was prepared according

to the reported procedure.⁶

4-(4'-Phenoxyphenoxy)benzoic Acid (2a). 4-(4-Phenoxyphenoxy)benzotrile (**1**) was prepared by the reaction of 4-phenoxyphenol with *p*-chlorobenzotrile in the presence of potassium carbonate in DMAc.

A mixture of **1** (4.6 g, 0.016 mol), ethanol (60 ml), and 10 *N*-aqueous potassium hydroxide (60 ml) was heated at reflux for 24 h. The solution was poured into hot water, filtered and the hot filtrate was acidified with concentrated hydrochloric acid. On cooling, the crude acid was filtered off and purified by reprecipitation with hydrochloric acid from a solution in sodium hydroxide. The yield was 4.86 g (99%). Recrystallization from methanol gave white plates, mp 187–188°C (lit.⁷ 183°C). IR (KBr) ν 1680 (C=O), 1240 cm⁻¹ (C–O–C). *Anal.* Calcd for C₁₉H₁₄O₄: C, 74.50%; H, 4.61%. Found: C, 74.25%; H, 4.68%.

3-(4'-Phenoxyphenoxy)benzoic Acid (2b). 1-Phenoxy-4-(*m*-tolylloxy)benzene (**3**) was prepared by the Ullmann reaction of *p*-bromodiphenyl ether with *m*-cresol.

To a mixture of **3** (11.7 g, 0.042 mol) in pyridine (132 ml) and water (22 ml) at 80–100°C was added potassium permanganate (18.7 g, 0.12 mol) in small amounts. The mixture was stirred vigorously for 4 h. The hot mixture was filtered by suction and the cake of manganese dioxide was washed with 10% aqueous potassium carbonate (150 ml). The combined filtrate was acidified with concentrated hydrochloric acid. This acid contained a trace amount of diphenoxybenzene, which was removed by dissolving the acid in alkaline solution and extracting with ethyl ether. The yield was 1.73 g (11%). Recrystallization from water–methanol afforded white crystals. mp 168–169°C. IR (KBr) ν 1690 (C=O), 1220 cm⁻¹ (C–O–C). *Anal.* Calcd for C₁₉H₁₄O₄: C, 74.50%; H, 4.61%. Found: C, 74.62%; H, 4.56%.

4-Phenoxybenzoic Acid (6a). This compound was prepared through the oxidation of 4-

phenoxytoluene. mp 167–168°C (lit.⁷ 160°C, from methanol).

4-(*o*-Phenylphenoxy)benzoic Acid (6b). 4-(*o*-Phenylphenoxy)benzotrile (**5b**) was prepared by the aromatic nucleophilic substitution reaction of *o*-phenylphenol with *p*-chlorobenzotrile in the presence of potassium carbonate in DMAc.

Compound **6b** was prepared by hydrolysis of compound **5b** as described in the synthesis of **2a**. The yield was 99%. Recrystallization from ethanol–water gave faint orange crystals. mp 160–161°C. IR (KBr) ν 1680 (C=O), 1230 cm⁻¹ (C–O–C). *Anal.* Calcd for C₁₉H₁₄O₃: C, 78.61%; H, 4.86%. Found: C, 78.39%; H, 4.86%.

4-(*o*-Methoxyphenoxy)benzoic Acid (6c). 4-(*o*-Methoxyphenoxy)benzotrile (**5c**) was prepared by the reaction of *o*-methoxyphenol with *p*-chlorobenzotrile.

Compound **6c** was synthesized by hydrolysis of the compound **5b** as described above. The yield was 97%. Recrystallization from methanol–water yielded faint orange crystals. mp 162–163°C. IR (KBr) ν 1680 (C=O), 1230 cm⁻¹ (C–O–C). *Anal.* Calcd for C₁₄H₁₂O₄: C, 68.85%; H, 4.95%. Found: 68.67%; H, 4.92%.

Polymer Synthesis

Two typical examples of the polymerization are as follows.

Polymer 4a from 2a. A solution of **2a** (0.306 g, 1 mmol) in PPMA (2 ml) was stirred at 60°C for 18 h. The resulting viscous solution was diluted with methanesulfonic acid. This solution was poured into water (500 ml) and neutralized with sodium carbonate. The polymer was collected, washed with water, and refluxed in water for 2 h. The polymer was dried *in vacuo* at 80°C for 2 d. The yield was 0.288 g (100%). The inherent viscosity of the polymer in concentrated sulfuric acid was 1.1 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C. The IR (KBr) ν 1630 (C=O), 1200 cm⁻¹ (C–O–C). *Anal.* Calcd for

(C₁₉H₁₂O₃)_n: C, 79.16%; H, 4.20%. Found: C, 79.97%; H, 4.24%.

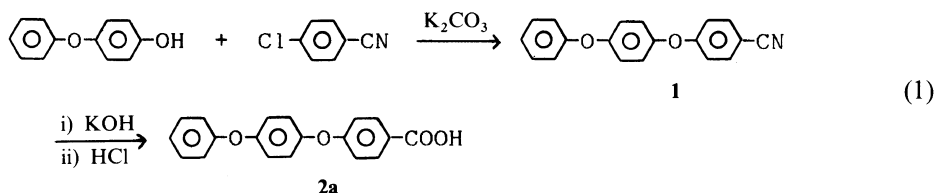
Polymer 4b from 2b. The polymer **4b** was prepared from **2b** at 100°C for 10 h as described above. The polymer, obtained in quantitative yield, had an inherent viscosity of 1.5 dl g⁻¹ in concentrated sulfuric acid (0.5 g dl⁻¹) at 30°C. The IR (film) ν 1660 (C=O), 1220 cm⁻¹ (C–O–C). *Anal.* Calcd for (C₁₉H₁₂O₃·H₂O): C, 74.50%; H, 4.61%. Found: C, 74.44%; H, 4.07%.

RESULTS AND DISCUSSION

Polymer Synthesis

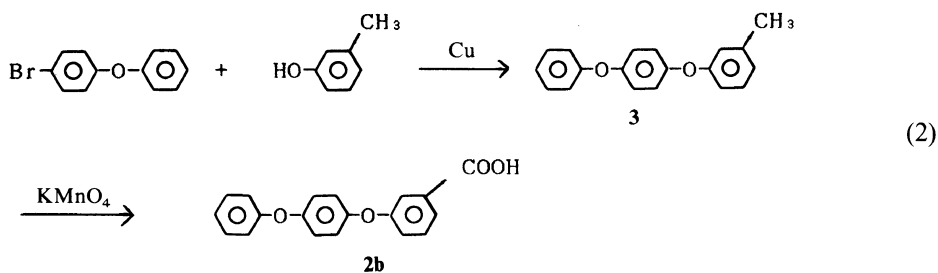
As described in the previous paper,^{3b} the reaction of aryl compound with benzoic acid in PPMA may proceed with the formation of a mixed anhydride, which then dissociates into an acylium ion under the influence of methanesulfonic acid. The acylium ion is markedly stabilized by resonance of electron-donating substituents.

On the basis of these structure–reactivity studies, we prepared two promising monomers for the poly(phenylene ether ether ketone) synthesis in PPMA as shown in eq 1. The



aromatic nucleophilic substitution reaction of 4-phenoxyphenol with *p*-chlorobenzonitrile gave 4-(4'-phenoxyphenoxy)benzonitrile (**1**), which was hydrolyzed in alkaline solution to yield 4-(4'-phenoxyphenoxy)benzoic acid (**2a**). On the other hand, 3-(4'-phenoxy-

phenoxy)benzoic acid (**2b**) was prepared through the oxidation of 1-phenoxy-4-(*m*-tolylloxy)benzene (**3**), which was obtained from the Ullmann reaction of *m*-cresol with *p*-bromodiphenylether (eq 2).



In order to determine the optimal conditions for the polycondensation, the polyconden-

sation of monomer **2a** was studied in PPMA (eq 3). The polycondensation was carried out

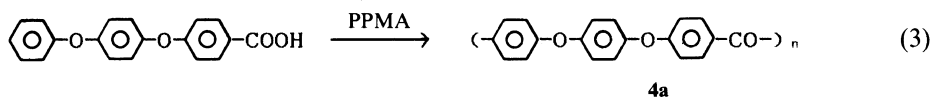


Table I. Effects of reaction temperature on polycondensation^a

Reaction conditions		Polymer	
Temp	Time	Yield	η_{inh}^b
°C	h	%	dl g ⁻¹
40	24	99	0.55
60	18	100	1.1
80	24	100	0.69
100	24	100	0.52
120	19	100	0.47

^a Polycondensation was carried out with 1 mmol of monomer in PPMA (2 ml).

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

Table II. Effects of the amount of PPMA on polycondensation at 60°C^a

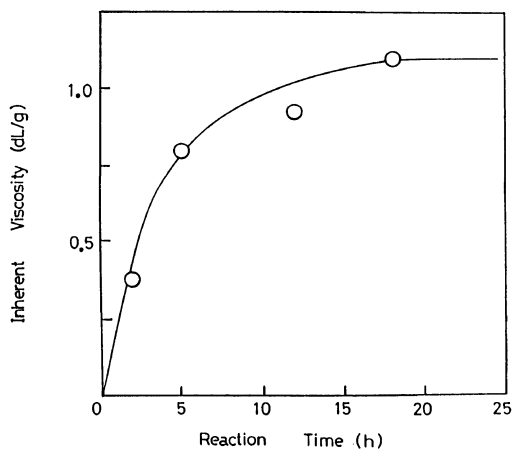
Reaction conditions		Polymer
Amount of PPMA	Time	η_{inh}^b
ml	h	dl g ⁻¹
1.5	18	1.1
2.0	18	1.1
2.5	24	1.0

^a Polycondensation was carried out with 1 mmol of monomer.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

simply by dissolving the monomer (1 mmol) in PPMA (2 ml). Table I lists the effects of the reaction temperature on the inherent viscosity of the resulting polymer. The polycondensation at 60°C gave a polymer with an inherent viscosity as high as 1.1 dl g⁻¹ in 18 h. The polymerization proceeded with the formation of a clear red solution at a temperature lower than 80°C, but at over 100°C the solution became dark red, possibly due to certain side reactions, such as decarboxylation of monomer.

The effect of the amount of PPMA on the polycondensation was studied at 60°C. No

**Figure 1.** Polycondensation of monomer **2a** in PPMA at 60°C.**Table III.** Synthesis of poly(ether ether ketone) **4b** in PPMA^a

Reaction conditions			Polymer
Amount of PPMA	Temp	Time	η_{inh}^b
ml	°C	h	dl g ⁻¹
2	80	48	0.40
1	100	10	1.5

^a Polycondensation was carried out with 1 mmol of monomer.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

appreciable effect has been observed in the concentration range studied (Table II).

Figure 1 shows the progress of the polycondensation at 60°C in terms of the inherent viscosity of the resulting polymer. The polymerization proceeded smoothly and gave a polymer with an inherent viscosity of 0.8 dl g⁻¹ in 5 h.

Next, the polycondensation of monomer **2b** in PPMA was performed with 1 mmol of **2b** as in the case of the polycondensation of **2a** described above except for the reaction temperature. The results are shown in Table III. The polymerization proceeded at 100°C and gave poly(phenylene ether ether ketone) **4b**

with inherent viscosities up to 1.5 dl g^{-1} . The difference of the effect of the reaction temperature for the polymerization between **2a** and **2b** is attributed to the monomer structures and explained as follows.

The acylium ion derived **2a** was easily formed compared to that for **2b** because the former acylium ion is stabilized by resonance with an electron-donating group.

The decarboxylation of aromatic carboxylic acids in a strong acid, known to take place, generally is accelerated by the presence of electron-donating groups on the ortho and para positions. Hence, monomer **2a** is decarboxylated more easily than monomer **2b**.

We attempted to synthesize of the poly(phenylene ether ketone) from 4-phenoxybenzoic acid (**6a**) in PPMA. The results are summarized in Table IV. As expected from the monomer structure, that is, low electrophilicity of the monomer due to the presence of deactivating group and low solubility of the resulting polymer in PPMA, only the low molecular weight polymer was obtained.

To circumvent these problems, we decided to modify the monomer structure of **6a**. The introduction of pendant phenyl groups along the polymer chains improved the solubility of polymers. Consequently, 4-(*o*-phenylphenoxy)benzoic acid (**6b**) was prepared by the aromatic nucleophilic substitution reaction of *o*-phenylphenol with *p*-chlorobenzonitrile, followed by hydrolysis in alkaline solution (eq 4). The direct polycondensation of monomer **6b** proceeded in homogeneous solution, but a high molecular weight of poly-

Table IV. Synthesis of poly(ether ketone) **7a** in PPMA^a

Reaction conditions			Polymer
Amount of PPMA	Temp	Time	η_{inh}^b
ml	°C	h	dl g^{-1}
2	40	24	0.07
1	60	24	0.16
2	60	24	0.25
6 ^c	100	24	0.32

^a Polycondensation was carried out with 1 mmol of monomer.

^b Measured at a concentration of 0.5 g dl^{-1} in concentrated sulfuric acid at 30°C .

^c 2.5 mmol of monomer was used.

Table V. Synthesis of poly(ether ketone) **7b** in PPMA^a

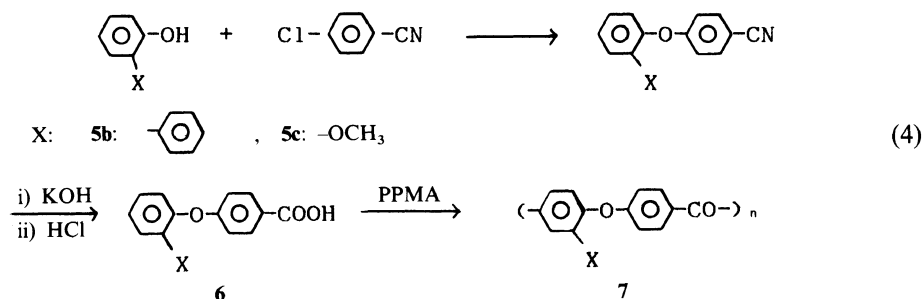
Reaction conditions			Polymer
Amount of PPMA	Temp	Time	η_{inh}^b
ml	°C	h	dl g^{-1}
1.5	60	24	0.07
1.0	100	24	0.24
1.5	100	24	0.21

^a Polycondensation was carried out with 1 mmol of monomer.

^b Measured at a concentration of 0.5 g dl^{-1} in concentrated sulfuric acid at 30°C .

mer **7b** was not obtained (Table V).

Then, to improve both the solubility of polymer and electrophilicity of the monomer, 4-(*o*-methoxyphenoxy)benzoic acid (**6c**) was prepared by a method similar to that above (eq 4). The direct self-polycondensation of



monomer (**6c**) was carried out under conditions similar to those for the preparation of polymers **4**. Table VI indicates that polymer **7c** was easily produced in quantitative yield

Table VI. Synthesis of poly(ether ketone) **7c** in PPMA^a

Reaction conditions			Polymer
Amount of PPMA	Temp	Time	η_{inh}^b
ml	°C	h	dl g ⁻¹
0.6	60	24	0.54
1	60	24	0.48
2.0	60	24	0.49
0.6	80	24	0.70
1.0	80	24	0.61
0.6	100	24	0.40
1.0	100	24	0.49

^a Polycondensation was carried out with 1 mmol of monomer.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

with an inherent viscosity of 0.7 dl g⁻¹.

Polymer Characterization

The polymers were defined as poly(ether-ketone)s with IR, ¹³C NMR spectroscopy and elemental analysis. The IR spectra exhibited characteristic absorptions at around 1640 and 1220 cm⁻¹ due to the C=O and C-O-C stretching. Elemental analyses also supported the formation of the expected polymers.

The most conclusive spectral evidence for the proposed poly(ether-ketone) structures, and especially for the selective para acylation rather than ortho acyl formation, was provided by ¹³C NMR. A typical ¹³C NMR spectrum of polymer **4b** is shown in Figure 2 together with assignments of the observed resonances. The calculated chemical shifts are all within ± 1 ppm of the observed values. No duplication of peak was found, clearly indicating the formation of para acylated linkages

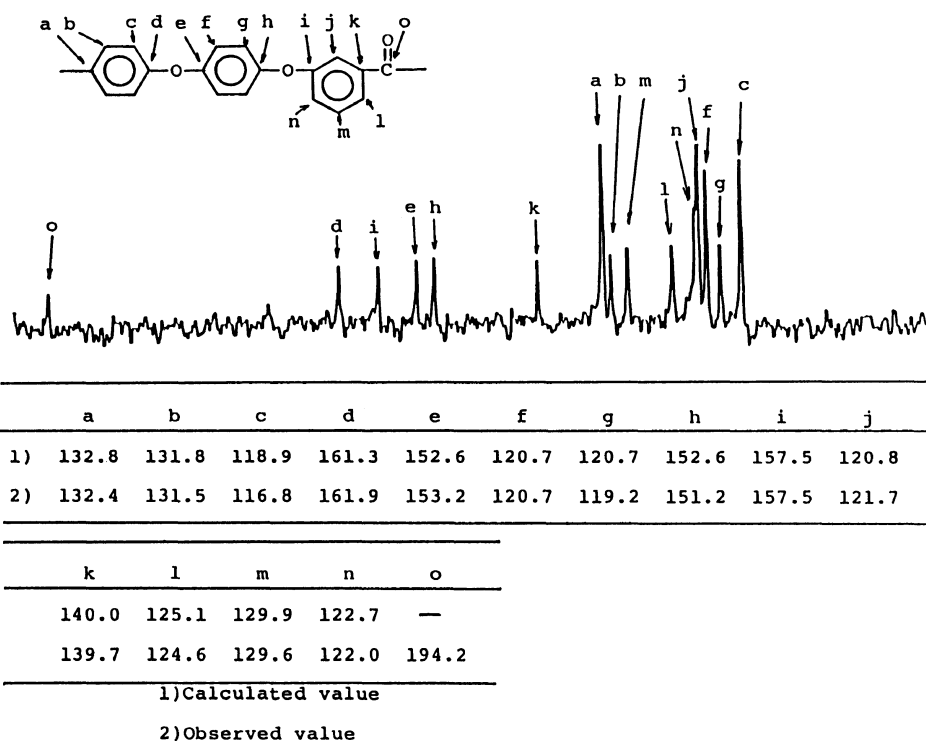


Figure 2. ¹³C NMR spectrum of polymer **4b** in CDCl₃ at 25°C.

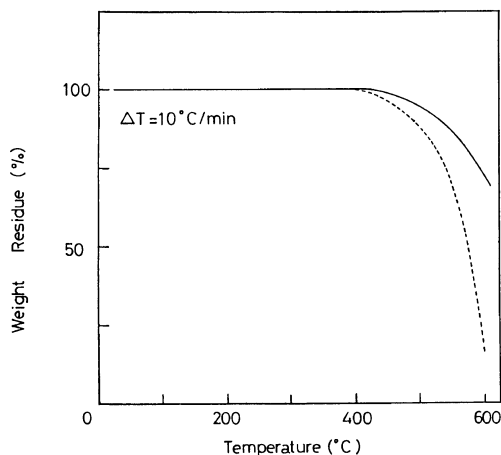


Figure 3. TG curves of polymer **4b**, (—) in nitrogen and (---) in air.

Table VII. Thermal behavior of poly(ether ketone)s **4, 7**

Polymer Type	T_g °C	T_m °C	Decomposition temp/°C ^a	
			In air	In nitrogen
4a	155	327	510	540
4b	118	—	490	520
7a	—	369	510	510
7b	185	280	520	520
7c	169	—	440	450

^a Temperature at which a weight loss of 10% was recorded by TG at a heating rate of 10°C min⁻¹.

during polymerization.

The poly(ether-ketone)s were white solids. Polymers **4a** and **7a** were soluble only in concentrated sulfuric acid and methanesulfonic acid. On the other hand, polymer **7c** was soluble in strong acids at room temperature and in polar aprotic solvents on heating. In

contrast, polymer **4b** was soluble in strong acids, aprotic solvents and haloalkanes at room temperature. Films, cast from a solution of polymer **4b** in chloroform, showed a high degree of toughness.

The thermal stability of the polymers was examined by thermogravimetry (TG). A typical trace of a polymer is shown in Figure 3. Polymer **4b** showed a 10% weight loss in air and nitrogen at 490 and 520°C, respectively. Differential scanning calorimetry on powders (**4b**) showed weak but reproducible endotherms at 118°C, which reflected the glass transition temperature. These data are presented in Table VII.

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