Synthesis and Characterization of Novel Organosoluble Polychloro Substituted Aromatic Poly(ether ketone)s

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A novel monomer of tetrachloroterephthaloyl chloride (TCTPC) was prepared by the chlorination of terephthaloyl chloride catalyzed by ferric chloride at 175-180 °C for 10 h, and confirmed by FTIR, MS and elemental analysis. A series of new polychloro substituted poly(aryl ether ketone)s with inherent viscosities of 0.58-0.65 dL/g have been prepared from TCTPC with aromatic ether monomers by electrophilic Friedel-Crafts acylation in the presence of DMF with anhydrous AlCl₃ as a catalyst in 1,2-dichloro-ethane. Glass-transition temperatures of these polychlorinated polymers ranged from 267 to 280 °C by DSC. The degradation temperature at 5% weight loss by TGA in nitrogen for these polymers ranged from 486 to 534 °C, and the char yields at 700 °C were 54-65%. The polymers having a weight-average molecular weight in the range of 65,900-79,300 are all amorphous and readily soluble in polar solvents such as DMF, DMSO and NMP at room temperature. All the polymers formed transparent, strong, and flexible films, with tensile strengths of 86.1-99.7 MPa, Young's moduli of 2.32-3.35 GPa, and elongations at break of 10-15%.

Keywords: Poly(aryl ether ketone)s; Polychloro-substituted; Soluble; Synthesis; Characterization.

INTRODUCTION

Aromatic poly(ether ketone)s (PEKs), including poly (ether ether ketone) (PEEK), poly(ether ketone ketone) (PEKK), and poly(ether ether ketone ketone) (PEEKK), are a family of high-performance engineering thermoplastics, and are currently receiving considerable attention for potential applications in aerospace, automobile production, electronics, and other high technology fields.^{1–5} PEKs are commonly prepared by two general methods: (1) a synthesis involving an aromatic electrophilic substitution that yields an aryl ketone linkage and (2) a route involving an aromatic nucleophilic substitution in which an aryl ether linkage is obtained.⁶ Although PEKs show good solvent resistance, excellent thermal, mechanical and electrical properties, their poor solubility in almost all known ordinary solvents except for concentrated sulfuric acid and high pro-

Scheme I

cessing temperature limit their extensive application. In view of this, a great deal of research on PEKs has been concentrated on the introduction of pendant groups to improve the solubility and processability, and to provide other desired properties. To meet various demands without thermal stability being sacrificed, PEKs with phenyl, methyl, butyl, halogen trifluoromethyl, ditrifluoromethylphenyl, bromomethyl and sulfonate side groups have been successfully prepared.⁷⁻¹⁵ However, to our knowledge, PEKs containing polychloro substituents have not been reported. As part of an ongoing research program we focused on the design and modification of PEKs with structure to improve their properties.¹⁶ Herein, we wish to report the synthesis and characterization of a novel aromatic diacid chloride monomer, tetrachloroterephthaloyl dichloride (TCTPC) (Scheme I), and a series of the corresponding PEKs with pendent polychloro groups (Scheme II) via the electrophilic aromatic



Scheme II



substitution polymerization. In this communication, the solubility, thermal and mechanical properties of these new polymers are investigated.

EXPERIMENTAL

Materials

Terephthaloyl chloride (TPC), N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), chloroform, carbon tetrachloride, dichloromethane, methanol, toluene, anhydrous aluminium chloride, anhydrous ferric chloride, iron powder, concentrated sulfuric acid 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 were refluxed with phosphorous pentoxide and distilled. Diphenyl ether (2a) was purified by vacuum distillation before use. 2-Methyldiphenylether (2b), 3-methyldiphenylether (2c), 4,4'-diphenoxybenzophenone (2d), 1,4-bis(4phenoxybenzoyl)benzene (2e) and 4,4'-bis(4-phenoxybenzoyl)biphenyl (2f) were prepared in our lab according to the standard procedure.

Synthesis of Tetrachloroterephthaloyl Dichloride (TCTPC)

A 100-mL three necked flask equipped with a reflux condenser, magnetic stirrer, thermometer, and Cl₂ inlet was

fitted with TPC (20.3 g, 0.10 mol), iron powder (0.28 g, 0.005 mol) and anhydrous FeCl₃. The reaction mixture was placed in an oil bath preheated to 120 °C, charged with dried Cl₂ maintained at 120 °C for 2 h, and the temperature was then raised to175-180 °C until the Cl₂ uptake ceased (generally 9-10 h). The hot reaction mixture was rapidly filtered, and the white precipitate which formed was collected and recrystallized from carbon tetrachloride twice to afford 27.25 g (80% yield) of white crystals, m.p. 144-145 °C; ¹³C NMR (CDCl₃): δ 162.9, 139.8, 128.3; EI-MS (70 eV): m/z = 340 (M⁺, 15.26), 342 (M⁺+2, 12.46), 305 (100.00), 277 (59.47), 249 (22.36), 214 (23.64), 177 (23.31), 142 (47.66), 107 (36.28), 95 (8.48), 71 (21.04), 47 (15.61); FT-IR: v_{max} 1776, 1377, 1354, 1242, 1164, 945, 893, 743, 697, 589, 482 cm⁻¹.

Polymer Synthesis

The general procedure in this study was performed as follows. 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 TCTPC **1** (6.8156 g, 0.02 mol) and aromatic ether 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 several times, extracting with boiling methanol for 20 h in a Soxhlet instrument, and drying at 120 °C overnight in vacuo to furnish pale yellow powder polymer in 95-97% yield.

Measurements

Infrared spectra (FT-IR) were determined on a Perkin-Elmer SP One FT-IR spectrophotometer. ¹H NMR spectra were recorded on a 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. Mass spectra (EI, 70 eV) were recorded on an HP 5989B mass spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with Perkin Elmer DSC 7 and TGA 7 analyzers, respectively. All of the samples were tested under nitrogen, at 10 °C/min for TGA and at 20 °C/min for DSC. Mechanical properties of the thin films (about 0.2 mm, cast from NMP solutions onto the glass plates, and followed by heating at 100-250 °C in vacuo) were evaluated at room temperature on an Instron 1121 instrument at a strain rate of 10 mm/min. The wideangle x-ray diffraction measurements were recorded at room temperature (approx. 25 °C) on power with a Rigaku Geiger Flex D-Max III x-ray diffractometer, using Ni-filtered CuK_{α} radiation (operating at 40 kV and 15 mA); the scanning rate was $2^{\circ}/\text{min}$ over a range of $2\theta = 2-40^{\circ}$). Inherent viscosities were measured with an automated Ubbelohde viscometer, with concentrated H₂SO₄ as a solvent for all polymers at a 0.5 g/dL concentration at 25.0 \pm 0.1 °C. Gel permeation chromatography experiments were carried out on a device consisting of a Waters 510 pump, a set of three PL columns of the nominal pore sizes $500, 10^3$, and 10⁴ Å, and a Phillips Pye Unicam PU 4025 ultraviolet detector. Chloroform was used as a solvent, and the analyses were carried out at room temperature at a flow rate of 1.0 mL/min. The molecular weights of the polymers were calculated with the aid of polystyrene standards. Polymer samples were dissolved in CHCl₃, filtered, precipitated in methanol and dried under vacuum at room temperature before performing GPC measurements. The solubility of the polymers was determined with 2 mg of a polymer in 3 mL of a solvent.

RESULTS AND DISCUSSION

Synthesis of TCTPC

The main aromatic diacid chloride monomer, TCTPC

was prepared by the chlorination of commercially available terephthaloyl chloride (TPC) at 175-180 °C for 10 h in the presence of ferric chloride outlined in Scheme I. To optimize crystallizing agents, several different solvents including *n*-hexane, petroleum ether, dichloromethane, benzene as well as carbon tetrachloride for purification of TCTPC were used. After a series of experiments, we found that carbon tetrachloride gave the best results. The structure of TCTPC was confirmed by mass spectrometry, FTIR, ¹³C NMR spectroscopy, and elemental analysis. In the IR spectroscopy (Fig. 1), TCTPC showed strong characteristic carbonyl absorption at 1776 cm⁻¹. Fig. 2 shows the ¹³C NMR spectrum of TCTPC, in which all the carbons were assigned as expected.

Polymer Synthesis

As depicted in Scheme II, a series of new polymers 3 were synthesized by reaction of TCTPC with selected aromatic ethers 2 using Friedel-Crafts acylation polymerization under mild conditions as described in one of our previous papers.^{16a} This technique was used in this work, with an initial reaction temperature between -20 and 0 °C, which was found to be the most effective. In the course of the re-







Fig. 2. ¹³C NMR spectrum of TCTPC.

Table 1. Preparation and characterization of polym	ers 3
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D - 1	$V_{1}^{2} = 1 + (0/1)$	Elemental analysis ^a		η_{inh}	$M_{\rm n}$	$M_{ m w}$	M/M
Polymer	Y leid (%)	C (%)	H (%)	$(dL/g)^{b}$	$(g/mol)^c$	(g/mol) ^c	$M_{\rm W}/M_{\rm n}$
3a	96	53.78 (54.83)	1.89 (1.84)	0.65	41,500	79,300	1.91
3b	95	54.88 (55.79)	2.29 (2.23)	0.60	36,500	69,400	1.90
3c	97	54.91 (55.79)	2.27 (2.23)	0.58	34,200	65,900	1.93
3d	96	62.34 (62.49)	2.62 (2.54)	0.64	37,100	72,600	1.96
3e	95	64.84 (65.06)	2.81 (2.73)	0.63	39,300	72,700	1.85
3f	97	66.78 (67.83)	3.15 (2.97)	0.62	d	_ <i>d</i>	d

^a Theoretical percentages are in parentheses.

^b Measured at a concentration of 0.5 g/dL in concentrated H₂SO₄ at 25 °C.

^c Determined by GPC, using CHCl₃ as the eluent and the polystyrene as the standard.

^d Not obtained.

action, a polymer/catalyst complex precipitated from the reaction media in the form of swollen, isolated particles. After completion of the reaction, the polymer particles formed were isolated from the reaction media in high yields (Table 1).

Gel permeation chromatography and solution viscosity results are given in Table 1. When a monomer concentration of 0.40-0.45 mol/L was adopted, the polymers with high inherent viscosity in the range of 0.58-0.65 dL/g were obtained. The GPC curves indicated that weight-average molecular weight (M_w 's) values of these new polymers except for polymer **3f** were in the range of 65,900-79,300, relative to standard polystyrene, and the polydispersity index [weight-average molecular weight/number-average molecular weight (Mw/Mn)] ranged from 1.85 to 1.96. There is no GPC data available because the obtained polymer **3f** was insoluble in chloroform presumably because of its rigid biphenyl structure.

Structural features of all the polymers were conformed by FTIR and NMR spectroscopy. All the polymers exhibit the characteristic absorption bands around 1220 cm⁻¹ due to aryl ether linkages and around 1660 cm⁻¹ corresponding to aryl carbonyl groups. As an example, the FTIR spectrum of polymer **3a** has been reproduced in Fig. 3. Fig. 4 shows a typical set of ¹H NMR and ¹³C NMR spectra for polymer **3a**. As can be seen, the spectra are in good agreement with the proposed structures.

The wide-angle X-ray diffraction (WAXD) patterns of some chlorinated PEKs are shown in Fig. 5. The results indicate that the polymers are amorphous in nature. The amorphous behavior of the polymers was mainly due to the presence of polychloro pendant groups, which disrupted the regularity of molecular chains and inhibited the close packing of the polymer chains.

Thermal Properties of Polymers

As anticipated, all of the polymers with pendent poly-



mer **3a**.

chloro groups showed high glass transition temperatures $(T_{\rm g}$'s) as listed in Table 2, as measured by a differential scanning calorimeter, and their corresponding DSC curves are shown in Fig. 6. The high $T_{\rm g}$'s for these polymers might mainly result from the pendent polychloro substituents of monomers inhibiting the polymer backones' free rotation. The incorporated, single, undersized methyl groups might act as self-lubricant groups, which lead to polymers 3b and 3c showing slightly lower T_g 's than non substituted polymer **3a**. As depicted in Table 2, the T_g values of the polymer 3f are higher than those of the other corresponding polymers. This is explained by the introduction of carbonyl and biphenyl groups that lead to an increase in the rigidity of the polymer chains, which would increase the T_{g} 's of the polymer. No melting endotherms were observed in the DSC traces, which further confirmed the amorphous nature



Fig. 5. WAXD patterns of the polymers 3.



Fig. 6. DSC curves of polymers 3a-3f.

Table 2. The thermal properties of polymers 3

Polymer	T_g (°C) ^{<i>a</i>}	$DT_5 (^{\circ}C)^{b}$	DT_{10} (°C) ^c	Yc (%) ^d
3a	270	525	572	61
3b	268	488	523	56
3c	267	486	521	54
3d	272	526	570	62
3e	274	520	568	63
3f	280	534	580	65

^a Measured by DSC at a heating rate of 20 °C in N₂.

^b 5% weight loss temperature measured by TGA at a heating rate of 10 °C/min in N₂.

 c 10% weight loss temperature measured by TGA at a heating rate of 10 °C/min in $N_{2}.$

^d Char residual at 700 °C in N₂.

of the polymers.

Dynamic thermogravimetry in nitrogen was used to study the thermal stability of the various polymers; the results of the study are given in Table 2. The polymers had excellent stabilities against thermal decomposition. The temperatures at a 5% weight loss (TD₅) are above 485 °C and the temperatures at a 10% weight loss (TD_{10}) are above 520 °C. However, it must be pointed out that the incorporation of polychloro substitents produced a decrease in $T_{\rm d}$ in every case, and that this effect also had to do with the nature of the substituents. For example, polymer 3a exhibited a 5% lower weight loss temperature ($T_d = 525$ °C) than did nonsubstituted polymer PEKK ($T_d = 554 \text{ °C}$).^{16a} Evidently, polymers **3b** and **3c** with methyl groups exhibited lower T_d values than others, which was attributable to the thermooxidatively weak C-H bonds in the -CH₃ group, which might scission before the decomposition of the polymer backbone. However, char yields at 700 °C in nitrogen atmosphere exceed 50% for all polymers, comparable to those of wholly aromatic PEKs.

Solubility of Polymers

The solubility behavior of the polymers in some solvents was examined and the results are shown in Table 3. All the polymers were found to be soluble in concentrated sulfuric acid like the conventional PEKK. It is well known that PEKK could not be dissolved in most known organic solvents. In sharp contrast, all the newly synthesized aromatic C-PEKs showed excellent solubility in aprotic polar organic solvents, such as NMP, DMF and DMSO. Except for polymer **3f**, other polymers could also dissolve in the less polar solvents such as chloroform and tetrahydrofuran (THF). The good solubility of the polymers could be attributed.

Table 3.	The solubility	of polymers	3
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Polymer	CHCl ₃	THF	DMF	DMSO	NMP	Conc.H ₂ SO ₄
3a	+ +	+ +	+ +	+ +	++	+ +
3b	+ +	+ +	+ +	+ +	+ +	+ +
3c	+ +	+ +	+ +	+ +	+ +	+ +
3d	+ +	++	+ +	+ +	+ +	+ +
3e	+ +	++	+ +	+ +	+ +	+ +
3f		+ _	+ +	+ +	+ +	+ +
PEKK						+ +

+ +, Soluble at room temperature; + -, soluble on heating; - -, insoluble.

Table 4. Mechanical properties of polymers 3

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
3a	87.4	2.45	13
3b	86.1	2.32	15
3c	86.2	2.34	14
3d	88.2	2.52	12
3e	89.4	2.64	11
3f	99.7	3.35	10

uted to the introduction of the polychloro substituents, which disturb the close packing of the polymer chains and lead to the increased free volume. Therefore, it will become easy for solvents to solubilize the polymer, which is necessary in industrial processing for the polymer. However, the solubility of polymer **3f** is relatively lower with the incorporation of the rigid carbonyl and biphenyl moieties. Polymer **3f** was insoluble in chloroform at room temperature, but could dissolve in THF with heating. Transparent and tough films could be made from all of these new polymers by film casting and solvent evaporation for polymer solutions in chloroform, except for polymer **3f**, which can be cast into films from NMP.

Mechanical Properties of Polymers

The mechanical properties of the polymer thin film cast from NMP are summarized in Table 4. All the films were transparent, strong, and flexible. The polymer films had tensile strengths of 86.1-99.7 MPa, Young's moduli of 2.32-3.35 GPa, and elongations at a break of 10–15%, indicating that they are strong materials.

CONCLUSION

A new monomer of tetrachloroterephthaloyl chloride

(TCTPC) has been successfully synthesized from terephthaloyl chloride. Several novel polychloro substituted poly(aryl ether ketone)s with high molecular weight, high glass transition temperatures, good thermal stability and mechanical properties have been prepared. The resulting C-PEKs have remarkably improved solubilities in common organic solvents over the unsubstituted PEKK. These polymers were well soluble in dipolar solvents such as DMF and NMP. The soluble polymers can be cast into transparent and tough films from solution.

ACKNOWLEDGEMENTS

The authors are grateful to the National Natural Science Foundation of China (No. 20264001), the Research Program of the Educational Bureau of Jiangxi Province of China (No. 2007-123) and the Natural Science Foundation of Jiangxi Province of China (No. 0520028) for financial support of this work.

Received October 3, 2007.

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