

Synthesis and Characterization of Novel Soluble Poly(ether ketone sulfone)s with Pendant Polychloro Groups

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ABSTRACT: 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. Five new polychloro substituted poly(aryl ether ketone sulfone)s (PEKs) with inherent viscosities of 0.68–0.75 dL/g have been prepared from 4,4'-diphenoxydiphenylsulfone, 4,4'-bis(2-methylphenoxy)diphenylsulfone, 4,4'-bis(3-methylphenoxy)diphenylsulfone, 4,4'-bis(2,6-dimethylphenoxy)diphenylsulfone, and 4,4'-bis(1-naphthoxy)-diphenylsulfone with TCTPC 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 molec-

ular weight in the range of 76,600–83,900 are all amorphous and show high glass transition temperatures ranging from 213 to 250°C, the 5% weight loss temperature over 450°C, high char yields of 60–67% at 700°C in nitrogen and good solubility in CHCl₃ and polar solvents such as DMF, DMSO, and NMP at room temperature. All the polymers formed transparent, strong, and flexible films, with tensile strengths of 85.1–90.8 MPa, Young's moduli of 2.52–3.24 GPa, and elongations at break of 21.2–27.2%. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1049–1054, 2008

Key words: poly(aryl ether ketone sulfone)s; polychloro-substituted; synthesis; characterization

INTRODUCTION

Aromatic poly(ether ketone)s (PEKs), including poly(ether ether ketone) (PEEK) and poly(ether ketone ketone) (PEKK) are a family of high-performance engineering thermoplastics and are currently receiving considerable attention for potential applications in aerospace, automobile, electronics, and other high technology fields.^{1–5} PEKs can be prepared via electrophilic or nucleophilic polycondensation.⁶ However, their poor solubility in almost all known ordinary solvents except for concentrated sulfuric acid and high processing temperature limit their extensive application. To overcome these limitations, a great deal of research on PEKs has been concentrated on the introduction of pendant groups such

as phenyl, methyl, butyl, halogen trifluoromethyl, ditrifluoromethylphenyl, bromomethyl, and sulfonate^{7–17} to improve the solubility and processability. Also, incorporation of the ether or sulfone flexibilizing linkages^{18,19} and molecular asymmetric structures^{20,21} into the main chain generally leads to their solubilities improvement. However, it is usually difficult to improve solubility or processability of PEKs without losing their original excellent thermal stability. Therefore, it would be still very interesting to develop novel PEKs with a combined advantage of excellent processability, thermal stability, and other desired properties. To the best of our knowledge, PEKs containing sulfone groups and pendant polychloro groups within the polymeric chain have not been reported. As part of an ongoing research program focused on the design and modifications of PEKs with structure to improve their properties.^{22–31}

Herein, we report the synthesis and characterization of a novel aromatic diacid chloride monomer, tetrachloroterephthaloyl dichloride (TCTPC) (Scheme 1), and a series of the corresponding poly(ether ketone sulfone)s (PEKs) with pendant polychloro groups (Scheme 2) via the electrophilic aromatic substitution polymerization. The solubility, thermal, and mechanical properties of these new polymers were investigated.

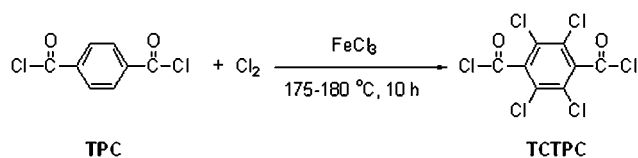
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Scheme 1 Synthesis of TCTPC.

EXPERIMENTAL

Materials

Phenol, *o*-cresol, *m*-cresol, 2,6-dimethylphenol, 1-naphthol, 4,4'-dichlorodiphenylsulfone (DCPS), *N*-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), chloroform, carbon tetrachloride dichloromethane, acetone, methanol, tetrahydrofuran, toluene, anhydrous aluminium chloride, anhydrous ferric chloride, iron powder, concentrated sulfuric acid, and calcium hydride were used as received. Terephthaloyl chloride (TPC) was purified by vacuum distillation before use. *N,N*-Dimethylformamide (DMF) was refluxed with calcium hydride, distilled under reduced pressure, and then dried over molecular sieves 4 Å before use. 1,2-Dichloroethane was refluxed with phosphorous pentoxide and distilled.

Monomer synthesis

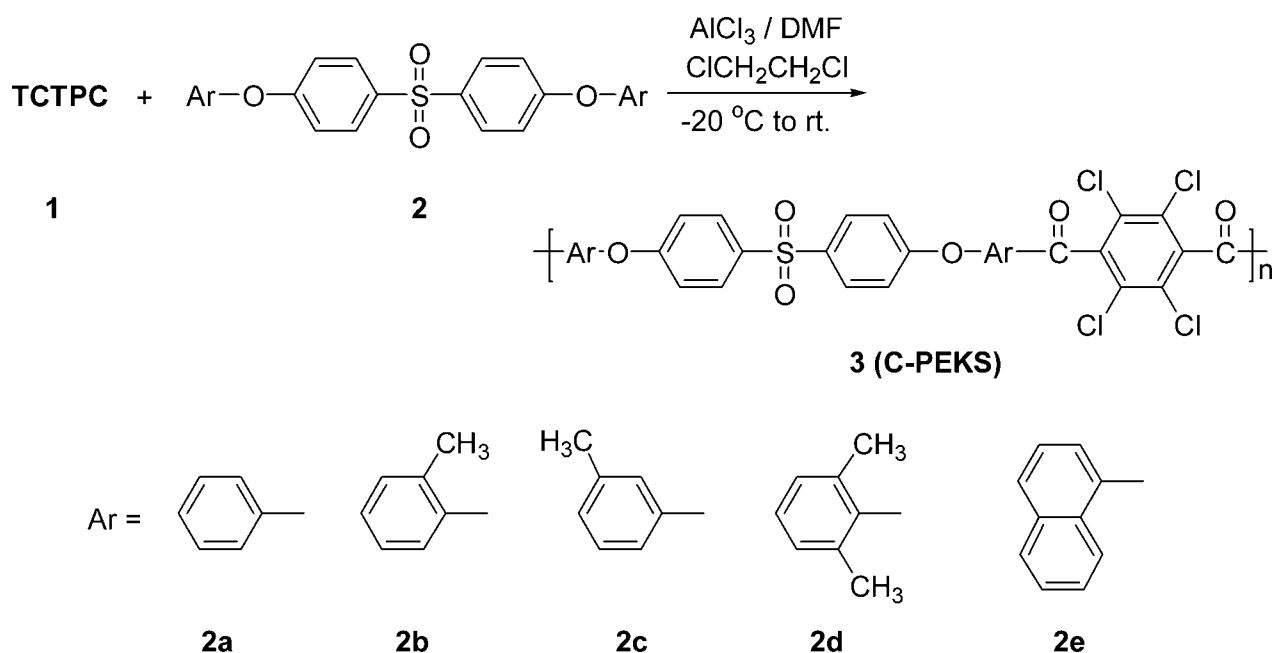
4,4'-Diphenoxydiphenylsulfone (**2a**), 4,4'-bis(2-methylphenoxy)diphenylsulfone (**2b**), 4,4'-bis(3-methylphenoxy)diphenylsulfone (**2c**), 4,4'-bis(2,6-dimethylphenoxy)diphenylsulfone (**2d**), and 4,4'-bis(1-naphthoxy)diphenylsulfone (**2e**) were prepared from DCPS with

phenol, *o*-cresol, *m*-cresol, 2,6-dimethylphenol, and 1-naphthol in our laboratory according to the literature,³² respectively.

TCTPC was prepared as follows: in 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 to 175–180°C until the Cl₂ uptake ceased (generally 9–10 h). The hot reaction mixture was rapidly filtered, and the white precipitate that 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); FTIR: ν_{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 N₂ atmosphere, DMF (5.0 mL, 4.76 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 monomer **2** (0.02 mol) were then added with stirring for 1 h. The mixture was allowed to warm to room



Scheme 2 Preparation of PEKs with pendant polychloro groups.

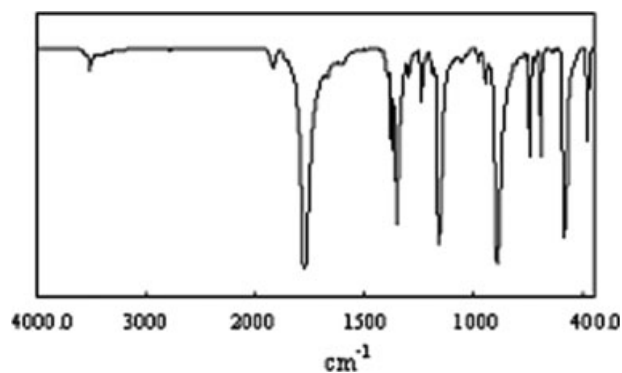


Figure 1 FTIR spectrum of TCTPC.

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 97% yield.

Measurements

Infrared spectra (FTIR) were determined on a PerkinElmer SP One FTIR 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 PerkinElmer C, H, N 2400 elemental analyzer. Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were recorded on a PerkinElmer 7 series thermal analysis system under nitrogen at a heating rate of 10°C/min. The wide-angle X-ray diffraction measurements were recorded at room temperature (~25°C) on power with a Rigaku Geiger Flex D-Max III X-ray diffractometer, using Ni-filtered Cu K α radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min over a range of 2 θ = 10–40°. Inherent viscosities were measured with an automated Ubbelohde viscometer, with chloroform as a solvent for all polymers at a 0.5 g/dL concentration at 30.0°C \pm 0.1°C. Molecular weights were determined by a gel permeation chromatography (GPC)

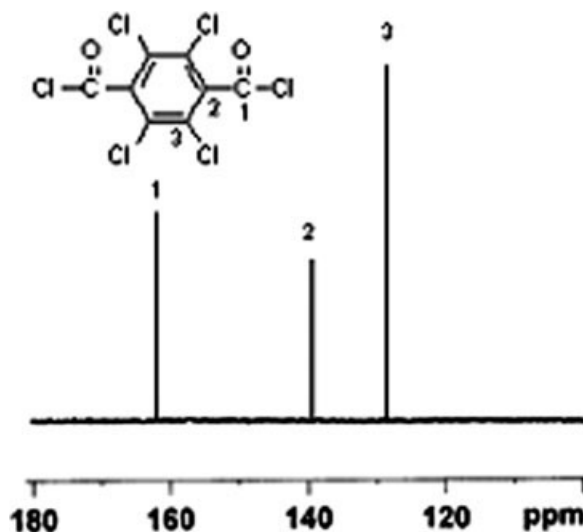


Figure 2 ¹³C NMR spectrum of TCTPC.

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

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 1. 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

TABLE I
Preparation and Characterization of the Polymers 3

Polymer	Yield (%)	Elemental analysis ^a		η_{inh} (dL/g) ^b	M_n (g/mol) ^c	M_w (g/mol) ^c	M_w/M_n
		C (%)	H (%)				
3a	97	57.39 (57.34)	2.50 (2.41)	0.75	40,500	82,400	2.03
3b	95	58.53 (58.47)	2.97 (2.89)	0.71	37,100	77,400	2.09
3c	96	58.55 (58.47)	2.97 (2.85)	0.72	37,300	78,300	2.10
3d	95	59.58 (59.52)	3.40 (3.33)	0.68	37,200	76,600	2.06
3e	97	62.44 (62.36)	2.71 (2.62)	0.74	39,800	83,900	2.11

^a Theoretical percentages are in parentheses.

^b Measured at a concentration of 0.5 g/dL in chloroform at 30°C.

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

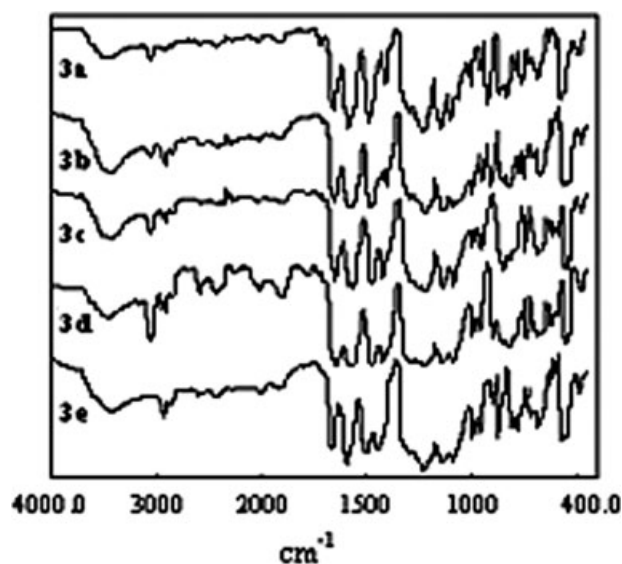


Figure 3 FTIR spectra of the polymers 3.

the FTIR spectroscopy (Fig. 1), TCTPC showed strong characteristic carbonyl absorption at 1776 cm^{-1} . Figure 2 shows the ^{13}C NMR spectrum of TCTPC, in which all the carbons were assigned as expected.

Polymer synthesis

As depicted in Scheme 2, five new polymers 3 were synthesized by reaction of TCTPC with various aromatic sulfone ether monomers 2 using Friedel-Crafts acylation polymerization under mild conditions as described in our previous work.²² 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 reaction, when a monomer concentration of $0.35\text{--}0.40\text{ mol/L}$

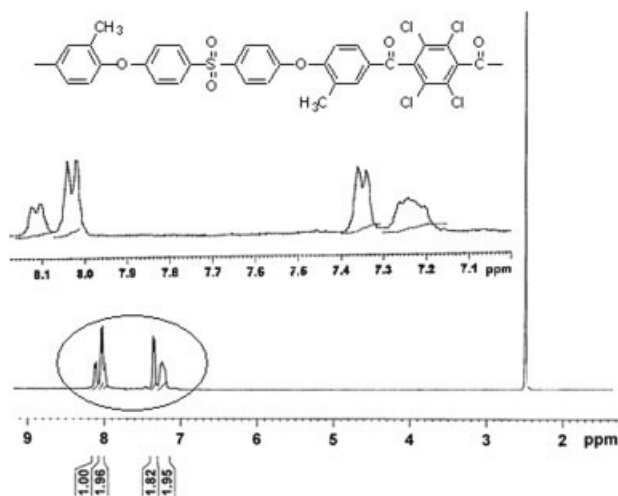


Figure 4 ^1H NMR spectrum of the polymer 3b in CDCl_3 .

TABLE II
The Thermal Properties of the Polymers 3

Polymer	T_g ($^\circ\text{C}$) ^a	DT_5 ($^\circ\text{C}$) ^b	DT_{10} ($^\circ\text{C}$) ^c	Y_c (%) ^d
3a	236	525	552	64
3b	232	478	525	60
3c	231	468	521	61
3d	245	453	507	62
3e	250	530	561	67

^a Measured by DSC at a heating rate of 10°C in N_2 .

^b 5% weight loss temperature measured by TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 .

^c 10% weight loss temperature measured by TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 .

^d Char residual at 700°C in N_2 .

was adopted, the polymers with high inherent viscosity in the range of $0.68\text{--}0.75\text{ dL/g}$ in chloroform and high yields ($95\text{--}97\%$) were obtained (Table I). The GPC curves indicated that weight-average molecular weight (M_w) values of the polymers 3 were in the range of $76,600\text{--}83,900$, relative to standard polystyrene, and the polydispersity index ranged from 2.03 to 2.11. The molecular weights of these polymers are sufficiently high to permit casting flexible and tough films.

Figure 3 compares the FTIR spectra of all the resulting polymers, which exhibited the characteristic absorption bands around 1660 cm^{-1} corresponding to aryl carbonyl groups, around 1150 cm^{-1} corresponding to sulfone groups and around 1220 cm^{-1} due to aryl ether linkages. Additionally, FTIR spectra of polymers 3b, 3c, and 3d with a weak absorption bands around 2925 cm^{-1} , and a moderate strong absorptions around 1375 cm^{-1} are attributed to the stretching vibrations of the methyl groups. Figure 4 shows a typical set of ^1H NMR spectrum for polymer 3b in CDCl_3 . As can be seen, the peak that appeared at 2.48 ppm was assigned to methyl pendent protons,

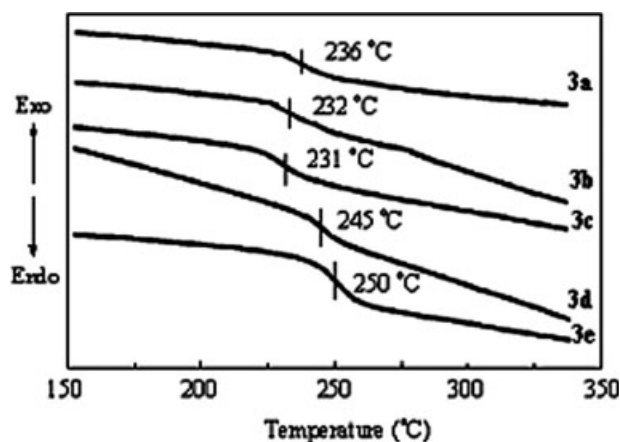


Figure 5 DSC curves of the polymers 3.

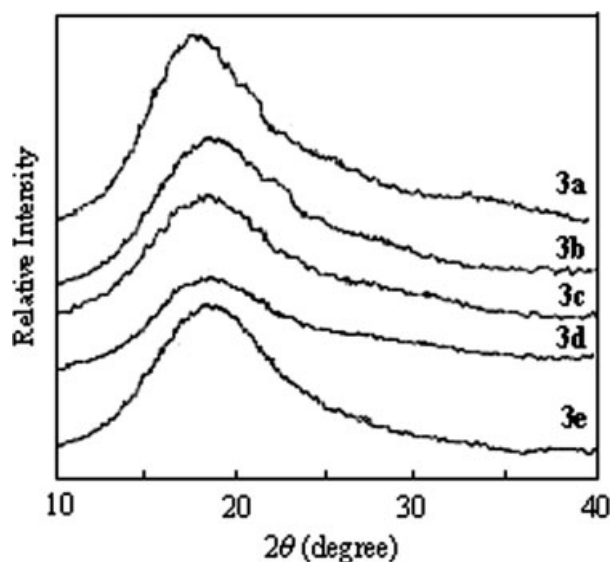


Figure 6 WAXD patterns of the polymers 3.

and the remaining aromatic protons were detected as multiplets at 8.01–8.12 ppm, which are in good agreement with the proposed structures. These results further demonstrated that the polychlorinated PEKs have the expected chemical structures.

Thermal stability

As anticipated, all of the polychloro-containing polymers showed the high glass transition temperatures (T_g 's) ranged from 231 to 250°C as listed in Table II, as measured by a differential scanning calorimeter, and their corresponding DSC curves are shown in Figure 5. Figure 5 indicated that all samples were amorphous, and only a single T_g was discernible on each curve. The high T_g 's for these polymers might mainly result from the pendent polychloro substituents of monomers inhibiting the polymer backbone's free rotation. The incorporated, single, undersized methyl groups might act as self-lubricant groups, which lead to polymers **3b** and **3c** showing little lower T_g 's than unsubstituted polymer **3a**. When double methyl groups are introduced, however, the motion of molecular segments is much harder; thus,

polymer **3d** showed higher T_g . On the other hand, the polymer **3e** exhibited higher than that of the other corresponding polymers, which is due to the incorporation of the rigid naphthalene moieties to the main chain.

Table II summarizes the decomposition temperatures of polymers **3a–3e** as determined by TGA. The temperatures at a 5% weight loss (TD_5) are above 453°C, and the temperatures at a 10% weight loss (TD_{10}) are above 507°C. Especially, it is noteworthy that the decomposition temperatures of methyl-containing polymers **3b–3d** in the range of 453–478°C is significantly lower than that of polymer **3a** without methyl group (>525°C). Evidently, this instability was attributable to the thermo-oxidatively weak C–H bonds in the –CH₃ group, which might scission before the decomposition of the polymer backbone. As a matter of fact, polymer **3d** with double methyl groups exhibited lower T_d values than their counterparts **3b** and **3c** with single methyl groups. However, all these polymers displayed char yields above 60% at 700°C in nitrogen, which shows their good thermal stabilities.

X-ray analysis

The wide-angle X-ray diffraction (WAXD) curves (Fig. 6) failed to show any sharp peak for the characteristically crystalline polymers, whereas an essentially Gaussian distribution appeared, signifying that these polymers were amorphous, which was consistent with the results of DSC analysis with no melting temperatures. The amorphous behavior of the polymers was mainly due to the presence of polychloro and/or methyl pendant groups, which disrupted the regularity of molecular chains and inhibited the close packing of the polymer chains.

Solubility

The solubility behavior of the polymers in some solvents was examined, and the results are shown in Table III. All the polymers could not dissolve in

TABLE III
The Solubility of the Polymers 3

Polymer	CHCl ₃	DMF	DMSO	NMP	THF	MeOH	Acetone	Toluene	Conc. H ₂ SO ₄
3a	++	++	++	++	+–	--	--	--	++
3b	++	++	++	++	++	--	--	--	++
3c	++	++	++	++	++	--	--	--	++
3d	++	++	++	++	++	--	--	--	++
3e	+	++	++	++	--	--	--	--	++
PEKK	--	--	--	--	--	--	--	--	++

+ +, fully soluble at room temperature; +, soluble; + –, partially soluble; – –, insoluble.

TABLE IV
Mechanical Properties of the Polymers 3

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
3a	86.8	2.70	27.2
3b	85.1	2.58	26.1
3c	85.4	2.63	26.2
3d	87.2	2.52	26.8
3e	90.8	3.24	21.2

methanol, acetone, and toluene, but were well soluble in concentrated sulfuric acid like the conventional PEKK. In sharp contrast, all the newly synthesized polychloro substituted PEKs showed excellent solubility in aprotic polar solvents such as NMP, DMSO, and DMF as well as in the less polar solvent chloroform. Apparently, the good solubility of the polymers could be attributed to the introduction of the polychloro substituents and polar bulky sulfone group, which disturb the close packing of the polymer chains and lead to the increased free volume. Therefore, introducing polar bulky sulfone group and polychloro pendant into PEKs would improve their solubility, which is necessary and useful in industrial processing for the polymer. All of these polymers could be cast into films by spin coating or casting processes from both chloroform and NMP solutions. In addition, the pendant methyl groups also have effects on the solubility of these polymers with the variation of the conformation of the polymer backbone. Actually, polymers **3b–3d** are soluble in THF, while their counterparts **3a** and **3e** without methyl groups are insoluble.

Mechanical properties

The mechanical properties of the polymer thin film cast from NMP are summarized in Table IV. All the films were transparent, strong, and flexible. The polymer films had tensile strengths of 85.1–90.8 MPa, Young's moduli of 2.52–3.24 GPa, and elongations at break of 21.2–27.2%, indicating that they are strong materials.

CONCLUSIONS

In conclusion, a new monomer of TCTPC has been successfully synthesized and characterized. Several novel polychloro substituted poly(aryl ether ketone sulfone)s with high molecular weight, high glass transition temperatures, good thermal stability, and mechanical properties have been prepared. These polymers were well soluble in CHCl_3 and polar solvents such as DMF, DMSO, and so on, and afforded

transparent, flexible, and amorphous films by solution casting.

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