

Synthesis and Properties of Novel Phosphorus-Containing Poly(ether Ether Ketone Ketone)s

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ABSTRACT: A novel monomer, bis[4-(4-fluorobenzoyl)phenyl]phenylphosphine oxide, was synthesized through the reaction of bis(4-chloroformylphenyl) phenyl phosphine oxide with fluorobenzene. Three poly(ether ether ketone ketone)s derived from bis[4-(4-fluorobenzoyl) phenyl]phenylphosphine oxide and different aromatic bisphenols were prepared by aromatic nucleophilic substitution reactions. The resulting polymers had inherent viscosities in the range of 0.55–0.73 dL/g. The structures of the poly(ether ether ketone ketone)s were characterized with Fourier transform infrared and ¹H-NMR. Thermal analysis indicated that the glass-transition temperatures of the poly(ether ether ketone ketone)s were higher than 200°C, and

the 5% weight loss temperatures in nitrogen were higher than 463°C. All the polymers showed excellent solubility in polar solvents such as *N*-methyl-2-pyrrolidone, dimethylformamide, and dimethylacetamide and could also be dissolved in chlorinated methane. The polymers afforded transparent and flexible films by solvent casting. Organic phosphorous moieties also imparted good flame-retardancy to the polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1304–1309, 2008

Key words: poly(ether ether ketone)s; nucleophilic substitution reaction; bis[4-(4-fluorobenzoyl)phenyl]phenylphosphine oxide

INTRODUCTION

Aromatic poly(ether ketone)s have been used in many areas, such as the aerospace, electronics, and nuclear industries, because of their good thermal stability and excellent mechanical and dielectrical properties. Victrex poly(ether ether ketone), for example, has achieved commercial success.¹ However, because of their aromatic structure and semicrystallinity, poly(ether ketone)s generally are insoluble in common organic solvents. Their insolubility and high melting temperatures make these polymers difficult to process and fabricate. Therefore, many efforts have been directed toward synthesizing soluble poly(ether ketone)s without scarification of their desired properties. Several approaches have been investigated to improve their solubility, such as the insertion of flexible linkages, the introduction of bulky pendent groups, and the incorporation of a noncoplanar structure into the polymer backbone.^{2–8}

This study describes the synthesis of a new monomer, bis[4-(4-fluorobenzoyl)phenyl]phenylphosphine oxide (*p*-FPPPO), and its derived poly(ether ether ketone ketone)s (PEEKKs). For this purpose, bis(4-carboxyphenyl)phenyl phosphine oxide (*p*-BCPPO) was synthesized according to a reported procedure.⁹ The

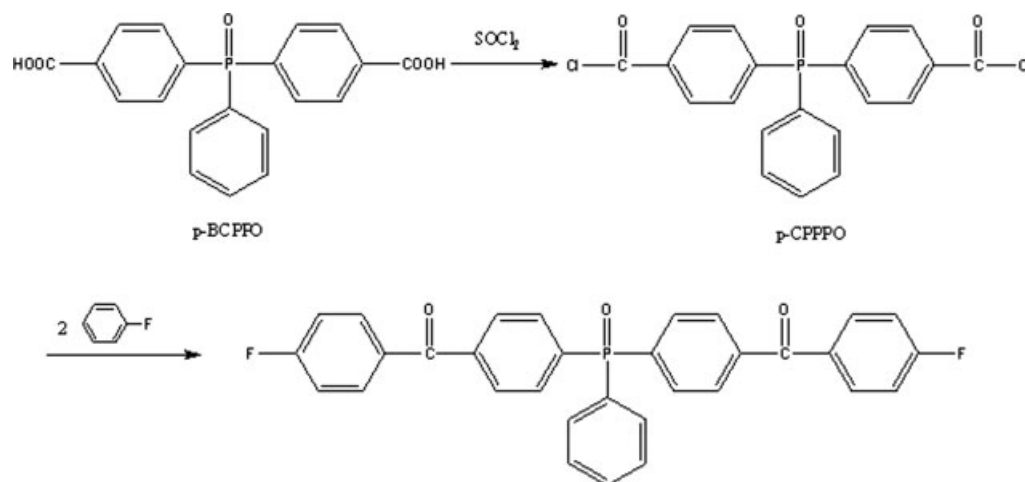
treatment of *p*-BCPPO with thionyl chloride in the presence of dimethylformamide gave the corresponding acid chloride (*p*-CPPPO). A reaction with fluorobenzene afforded *p*-FPPPO (Scheme 1). The obtained monomer was reacted with aromatic bisphenols via nucleophilic substitution reactions to synthesize novel soluble PEEKKs (Scheme 2). The tetrahedral geometry of the phosphine oxide group may have disrupted the crystal packing, reducing intermolecular interactions and enhancing the solubility of the polymers. The incorporation of phenylphosphine oxide moieties also could increase the adhesion, resistance to atomic oxygen, and flame resistance of the polymers.^{10–20} The attachment of phenyl pendent groups may have increased the glass-transition temperature by restricting segment mobility.

EXPERIMENTAL

Materials

p-BCPPO was prepared in our laboratory according to ref. ⁹, and the melting point was 334°C. Fluorobenzene (Wujin Chemistry Co., Jiangsu, China), bisphenol A (Damao Chemical Reagent Factory, Tianjin, China), bisphenol S (Aolunda High-Tech Industry Co., Jiangsu, China), and hydroquinone (Jiangtian Chemical Technology Co., Tianjin, China) were recrystallized before use. Tetramethylene sulfone, anhydrous K₂CO₃, and other solvents were analytical-grade reagents and were used as received.

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Scheme 1 Synthesis of *p*-FPPPO.

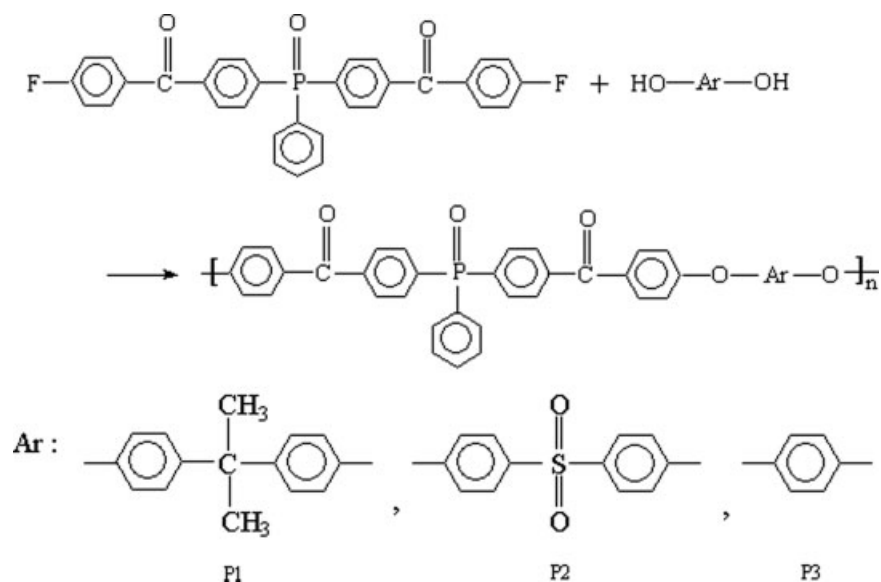
Characterization

The Fourier transform infrared (FTIR) spectra were recorded on a Bruker (Germany) Vector 22 spectrometer. $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$ spectra were recorded with a Bruker AMX-400 NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane and H_3PO_4 as the internal references. The inherent viscosities of the PEEKKs were measured at a concentration of 0.5 g/dL in CH_2Cl_2 with an Ubbelohde capillary viscometer at 25°C . Differential scanning calorimetry (DSC) analysis was conducted on a Setaram (France) DSC141 instrument under a nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. Glass-transition temperatures were read at the middle of the baseline shift. Thermogravimetric analysis (TGA) was performed with a TGA-Q50 (TA Instruments, USA) in a nitrogen atmosphere (40 mL/min)

at a heating rate of $20^\circ\text{C}/\text{min}$; the decomposition temperature was determined when 5% weight loss occurred. Solubility was determined by the dissolution of 0.1 g of the polymer in 10 mL of the solvent. An RGT-5 (China) universal tester was used to measure the tensile properties of the PEEKK films (10 mm wide, 120 mm long, 0.06 mm thick), and the crosshead speed was 5 mm/min. Limiting oxygen indices (LOIs) were tested according to the GB/T2406-93 procedure.

Synthesis of *p*-FPPPO

Into a 250-mL, round-bottom flask equipped with a magnetic stirrer, a reflux condenser, and a thermometer, 22.0 g (0.06 mol) of *p*-BCPPO and 100 mL of thionyl chloride were charged, and several drops of



Scheme 2 Synthesis of PEEKKs.

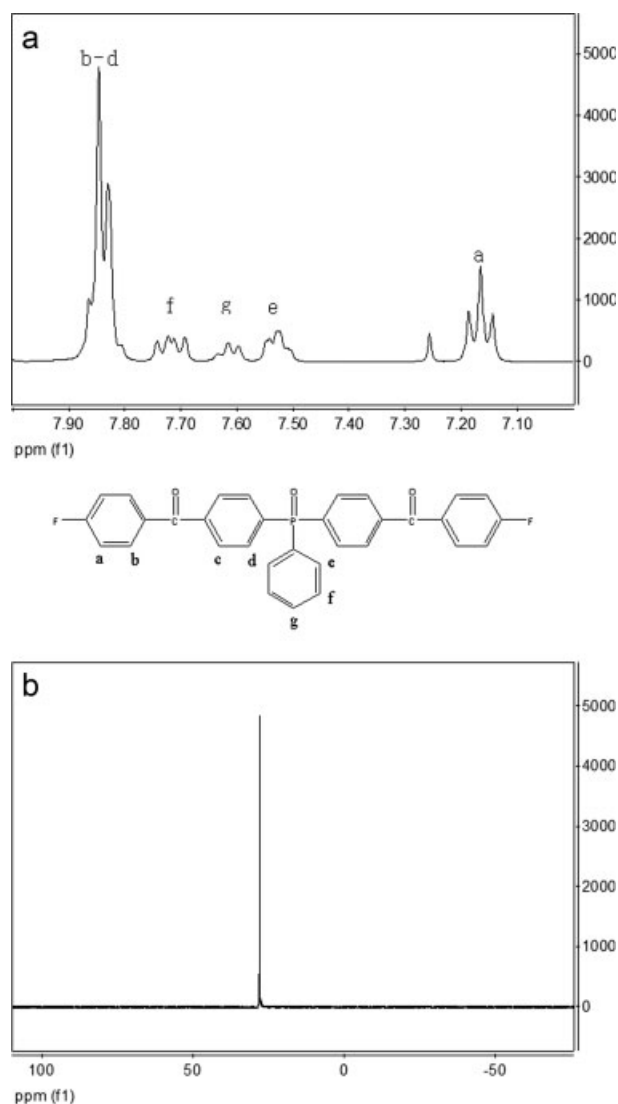


Figure 1 (a) ¹H-NMR and (b) ³¹P-NMR spectra of *p*-FPPPO.

dimethylformamide were added as a catalyst. The mixture was refluxed for 6 h, and a transparent solution was obtained. Excess thionyl chloride was removed by distillation *in vacuo*. The product was purified by recrystallization from hexane and then dried *in vacuo* at 50°C. A pale yellow powder was obtained, and the yield was 94%.

The obtained *p*-CPPPO (24.5 g, 0.06 mol), AlCl₃ (24.0 g, 0.18 mol), and 60 mL of dichloromethane were mixed in a 250-mL, round-bottom flask. The reaction flask was heated to 40°C, and fluorobenzene (15 mL, 0.16 mol) was added dropwise via an addition funnel in 1 h. The solution was then kept at this temperature for 5 h. The resulting solution was poured into 200 mL of a 10% sodium hydroxide solution. The precipitated pale yellow powder was collected by filtration and washed with water to neutrality. The crude product was recrystallized from dimethylformamide/ethanol (3 : 10 v/v), and

22.6 g of a white, crystalline powder was obtained. The melting point of *p*-FPPPO was 202°C. The FTIR spectrum exhibited absorption bands at 1155 and 1229 (Ar—F), 1660 (C=O), 1437 (P—Ar), and 1196 cm⁻¹ (P=O). The ¹H-NMR and ³¹P-NMR spectra of *p*-FPPPO are shown in Figure 1.

¹H-NMR (CDCl₃, δ): 7.12–7.22 (4H, ArH_a), 7.46–7.56 (2H, ArH_e), 7.56–7.65 (1H, ArH_g), 7.65–7.75 (2H, ArH_f), 7.78–7.89 (12H, ArH_{b-d}). ³¹P-NMR (CDCl₃, δ): 28.18.

Polymerization

The synthesis procedure of P1 was described as follows. *p*-FPPPO (3.132 g, 6 mmol), bisphenol A (1.368 g, 6 mmol), K₂CO₃ (1.98 g, 14.4 mmol), and 12 mL of tetramethylene sulfone were placed in a 100-mL, round-bottom flask equipped with a stirrer, a Dean–Stark trap, a condenser, and a nitrogen inlet. Toluene (30 mL) was added as an azeotrope. The mixture was stirred under a nitrogen atmosphere and heated to 125°C; it was kept at this temperature for 3 h to separate the water that formed during the reaction. Then, the temperature was elevated to 190°C and reacted for 1 h. As polycondensation proceeded, the solution gradually became very viscous. After polymerization, the viscous solution was poured into 400 mL of ethanol. The pale yellow, fibrous precipitate was filtered and washed with hot water and then was dried at 100°C *in vacuo* for 24 h. The yield was almost quantitative.

Other PEEKKS were prepared via analogous procedures.

Film Preparation

PEEKK (1 g) was dissolved in 10 mL of CH₂Cl₂, and then the solution was poured onto a glass plate, which was placed in a 60°C oven overnight for the removal of the solvent. The semidried film was stripped off from the glass substrate and further dried in a vacuum oven at about 100°C for 12 h. The obtained films were used for tensile tests and flame-retardancy measurements.

RESULTS AND DISCUSSION

Polymerization and structure

Three PEEKKS were synthesized by nucleophilic aromatic substitution from *p*-FPPPO and different

TABLE I
Polymerization Data of PEEKKS

Polymer	Reaction time (h)	Reaction temperature (°C)	Inherent viscosity (dL/g)	Yield (%)
P1	4	190	0.72	94
P2	10	180	0.55	96
P3	7	210	0.63	95

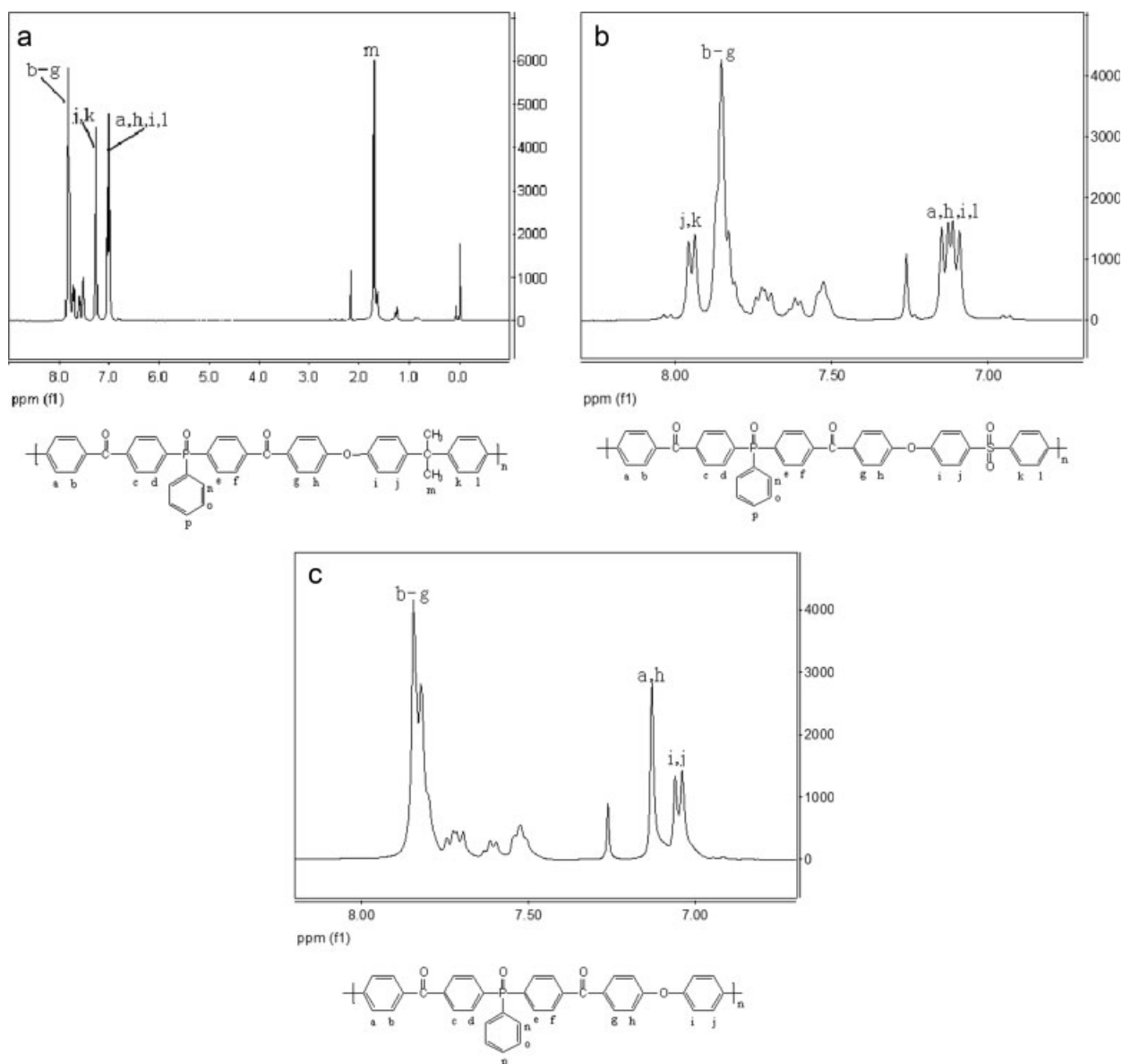


Figure 2 $^1\text{H-NMR}$ spectra of PEEKKs: (a) phosphorus-containing PEEKK with a bisphenol A moiety, (b) phosphorus-containing PEEKK with a bisphenol S moiety, and (c) phosphorus-containing PEEKK with a hydroquinone moiety.

bisphenols. Reactions were conducted in tetramethylene sulfone with monomers in 1 : 1 molar ratios. Table I summarizes the polymerization results for the polymers. The inherent viscosities of PEEKKs were in the range of 0.55–0.72 dL/g, which indicated that *p*-FPPPO was active enough to polymerize with bisphenols.

The structures of the polymers were characterized with FTIR, $^1\text{H-NMR}$, and $^{31}\text{P-NMR}$. In the FTIR spectra, the peaks around 1230 cm^{-1} indicate the Ar–O–Ar stretching vibration, the peak at 1657 cm^{-1} is derived from C=O, and Ar–F absorption peaks at 1155 and 1229 cm^{-1} have disappeared. The $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$ spectra of the polymers corresponded with their structures. The $^1\text{H-NMR}$ spectra of PEEKKs are shown in Figure 2.

P1

$^1\text{H-NMR}$ (CDCl_3 , δ): 1.68–1.76 (6H, RH_m), 6.98–7.06 (8H, $\text{ArH}_{a,h,i,l}$), 7.24–7.31 (4H, $\text{ArH}_{j,k}$), 7.46–7.56 (2H, ArH_n), 7.56–7.64 (1H, ArH_p), 7.66–7.76 (2H,

TABLE II
Thermal Properties of PEEKKs

Polymer	T_g ($^{\circ}\text{C}$) ^a	T_d ($^{\circ}\text{C}$) ^b	Residue (wt %) ^c	LOI
P1	205	475	41.6%	40
P2	235	463	48.7%	45
P3	213	476	48.5%	44

^a Glass-transition temperature from the second heating at $20^{\circ}\text{C}/\text{min}$ in N_2 .

^b Decomposition temperature (5 wt % loss) by TGA.

^c By TGA at 800°C in N_2 .

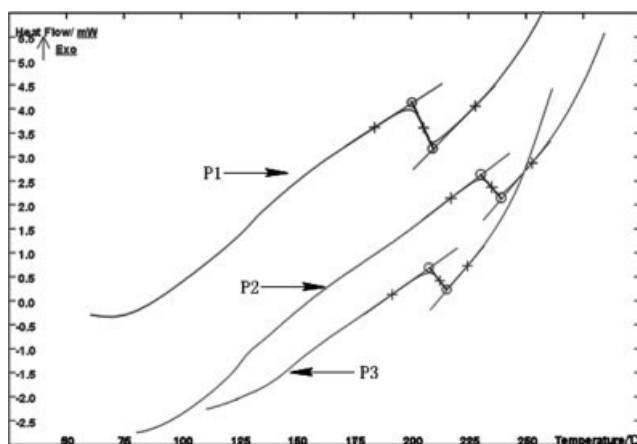


Figure 3 DSC curves of PEEKKs.

ArH_o), 7.76–7.88 (12H, ArH_{b–g}). ³¹P-NMR (CDCl₃, δ): 28.18.

P2

¹H-NMR (CDCl₃, δ): 7.06–7.18 (8H, ArH_{a,h,i,l}), 7.48–7.57 (2H, ArH_n), 7.57–7.67 (1H, ArH_p), 7.67–7.77 (2H, ArH_o), 7.77–7.91 (12H, ArH_{b–g}), 7.91–7.98 (4H, ArH_{j,k}). ³¹P-NMR (CDCl₃, δ): 28.18.

P3

¹H-NMR (CDCl₃, δ): 6.98–7.08 (4H, ArH_{i,j}), 7.10–7.16 (4H, ArH_{a,h}), 7.46–7.56 (2H, ArH_n), 7.56–7.66 (1H, ArH_p), 7.66–7.76 (2H, ArH_o), 7.76–7.92 (12H, ArH_{b–g}). ³¹P-NMR (CDCl₃, δ): 28.18.

The characteristic peaks correlated well with the proposed structure.

Thermal properties

The glass-transition temperature and thermal stability data from DSC and TGA are listed in Table II, and DSC curves are shown in Figure 3. The high glass-transition temperatures of the PEEKKs can be attributed to the rigidity of the polymer backbone and phenyl substituent, which hindered the rotation of the main chain. Because the sulfonyl group has more rigidity, P2 had the highest glass-transition temperature of the three PEEKKs.

All the PEEKKs possessed excellent thermal stability. TGA curves are shown in Figure 4. The thermal

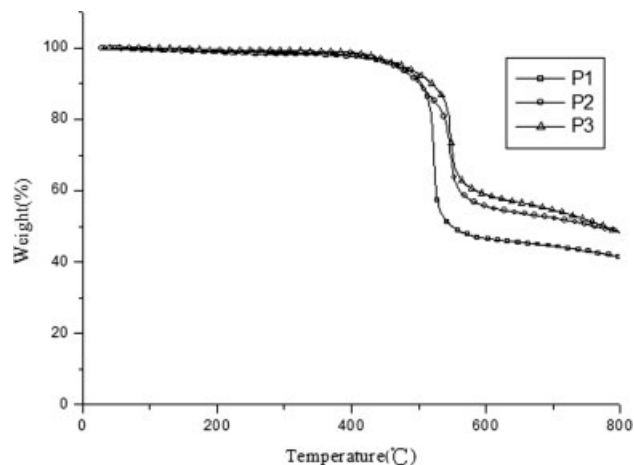


Figure 4 TGA curves of PEEKKs.

degradation procedure revealed one decomposition stage. The 5% decomposition temperatures of PEEKKs ranged from 465 to 476°C. Char yields at 800°C exceeded 40%. The amount of char that formed during thermal decomposition was linearly proportional to the LOI of the halogen-free polymer,²¹ so the high char yields indicated good flame retardancy of the PEEKKs. The LOIs of the PEEKKs were also measured, and the results are listed in Table II. LOIs of the phosphorus-containing PEEKKs were higher than that of commercial poly(ether ketone), and this indicated that the incorporation of phosphorus into the molecular chain increased the fire resistance of the polymers without a loss of their thermal stability.

The solubility of PEEKKs in common organic solvents was tested, and the results are reported in Table III. All the polymers were readily soluble at room temperature in polar, aprotic solvents, such as *N*-methyl-2-pyrrolidone, dimethylacetamide, dimethylformamide, and dimethyl sulfoxide. They were also soluble in chloroalkylenes. In addition, they were soluble in tetrahydrofuran at elevated temperatures. The good solubility can be attributed to the phosphine oxide moiety, which reduced the regularity of the main chain and led to the amorphous nature of the polymers. The excellent solubility makes the polymers potential candidates for practical applications in casting processes.

TABLE III
Solubility of PEEKKs

	DMF	NMP	DMAc	Sulfolane	DMSO	CHCl ₃	CH ₂ Cl ₂	C ₂ H ₄ Cl ₂	C ₂ H ₂ Cl ₄	THF	Benzene
P1	++	++	++	++	+	++	++	++	++	+	–
P2	++	++	++	++	+	++	++	++	++	+	–
P3	++	++	++	++	+	++	++	++	++	+	–

++ = soluble at room temperature; + = soluble at heating; – = insoluble; DMAc = dimethylacetamide; DMF = dimethylformamide; DMSO = dimethyl sulfoxide; NMP = *N*-methyl-2-pyrrolidone; THF = tetrahydrofuran.

TABLE IV
Mechanical Properties of PEEKKs

Polymer	Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)
P1	68.7	11	2.5
P2	71.5	12	3.3
P3	67.2	45	3.0

Ten percent CH₂Cl₂ solutions of the polymers were prepared and then cast onto clean plate glass. The clear, light yellow films that were obtained were tough and did not break after being folded a dozen times. Table IV presents the tensile properties of the films. The data indicate that the PEEKKs were strong and tough materials.

CONCLUSIONS

Three novel PEEKKs were synthesized from *p*-FPPPO by nucleophilic substitution polymerization. The polymers had high glass-transition temperatures (>200°C) and good thermal stability. They were readily soluble in aprotic, polar solvents and chloroalkylene. The cast films of PEEKKs exhibited good mechanical properties.

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