

Synthesis of Novel Poly(ether ketone diphenyl ketone ether ketone ketone)s by Electrophilic Friedel–Crafts Solution Polycondensation

Mingzhong Cai, Qin Xi, Nengwen Ding, Cai-Sheng Song

Department of Chemistry, Jiangxi Normal University, Nanchang 330022, People's Republic of China

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ABSTRACT: 4,4'-Bis(4-phenoxybenzoyl)diphenyl was prepared by the Friedel–Crafts reaction of 4-bromobenzoyl chloride and diphenyl followed by condensation with potassium phenoxide. Novel aromatic poly(ether ketone diphenyl ketone ether ketone ketone)s were obtained by the electrophilic Friedel–Crafts solution copolycondensation of 4,4'-bis(4-phenoxybenzoyl)diphenyl with a mixture of isophthaloyl chloride and terephthaloyl chloride over a wide range of isophthaloyl chloride/terephthaloyl chloride molar ratios in the presence of anhydrous aluminum chloride and *N*-methylpyrrolidone in 1,2-dichloroethane. The influence of the reaction conditions on the preparation of the copoly-

mers was examined. The copolymers were characterized with different physicochemical techniques. Because of the incorporation of diphenyl, the resulting copolymers exhibited outstanding thermal stability. The glass-transition temperatures were above 174°C, the melting temperatures were above 342°C, and the 5% weight loss temperatures were above 544°C in nitrogen. All these copolymers were semicrystalline and insoluble in organic solvents. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1543–1550, 2009

Key words: high performance polymers; poly(ether ketones); synthesis; thermal properties

INTRODUCTION

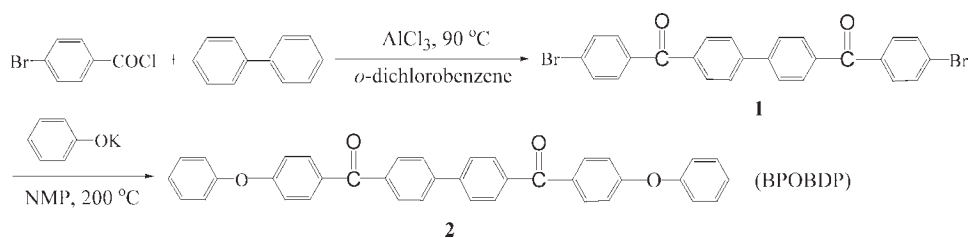
Aromatic poly(ether ketone)s are high-performance engineering thermoplastics possessing remarkable chemical stability, reasonably high glass-transition temperatures (T_g 's) and melting temperatures (T_m 's), and excellent mechanical and electrical properties. Most polymers of this type are semicrystalline, high-temperature, and solvent-resistant materials, and they are currently receiving considerable attention for potential applications in aerospace, automobiles, electronics, and other high-technology fields.^{1–3} Poly(aryl ether ketone)s (PAEKs) can be prepared in two ways.^{4–6} The first approach involves nucleophilic aromatic substitution in which a diaryl ether linkage is formed. The second approach involves Friedel–Crafts electrophilic substitution in which a diaryl ketone linkage is obtained. The electrophilic route has been the popular method for preparing various kinds of PAEKs because the monomers that are used in the electrophilic route have been more selective, cheaper, and readily available.^{7–12}

For many applications, however, modification of PAEK properties is desired. On the other hand, the

synthesis and investigation of novel PAEKs would be very useful for a more rigorous structure–property correlation of this very interesting class of polymers. One effective method of varying polymer properties involves the incorporation of a variety of groups in the main chains. Among these, stiff and bulky groups such as diphenyl or naphthalene are of considerable interest because they offer good advantages with respect to the stability and thermal resistance of the resulting polymer. Because PAEKs [e.g., poly(ether ether ketone)] suffer from poor creep behavior above their relatively low glass transitions, the synthesis of semicrystalline PAEKs with increased T_g value is of high interest. For example, it is well known that the incorporation of stiff and bulky groups into the main chain leads to an increase in T_g . Some articles have reported the synthesis of new PAEKs containing diphenyl or naphthalene moieties by nucleophilic aromatic substitution polycondensation.^{13–19} Zolotukhin et al.⁸ reported the synthesis of naphthalene-containing polyketones by precipitation electrophilic polycondensation. The obtained polymers possessed high T_g values (>180°C) and also too high T_m values (>380°C), and this is very difficult for melt processing. However, the synthesis of diphenyl-containing PAEKs by electrophilic polycondensation has received less attention.²⁰ In this study, we synthesized a new monomer containing diphenyl, 4,4'-bis(4-phenoxybenzoyl)diphenyl (BPOBDP or 2). A

Correspondence to: M. Cai (caimzhong@163.com).

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Scheme 1 Synthetic route of BPOBDP.

series of novel aromatic poly(ether ketone diphenyl ketone ether ketone ketone)s (PEKDKEKKs) were prepared by the electrophilic Friedel–Crafts solution copolycondensation of BPOBDP with a mixture of isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) over a wide range of IPC/TPC molar ratios in the presence of anhydrous aluminum chloride (AlCl_3) and *N*-methylpyrrolidone (NMP) in 1,2-dichloroethane (DCE). Their structure–property relationships were also examined.

EXPERIMENTAL

Materials

4-Bromobenzoyl chloride, TPC, and IPC (Shuanglin Chemical Co., China) were purified by distillation *in vacuo* before use. DCE (Aldrich, St. Louis, MO), NMP (Aldrich), *N,N*-dimethylformamide (DMF), and *o*-dichlorobenzene were purified by distillation and dried with a 0.5-nm molecular sieve. AlCl_3 was sublimed before use. Diphenyl and phenol were used as received.

Synthesis

Monomer synthesis

BPOBDP was synthesized by the Friedel–Crafts reaction of 4-bromobenzoyl chloride and diphenyl followed by condensation with potassium phenoxide, as shown in Scheme 1. The procedure for the synthesis of BPOBDP is described in detail hereafter.

Synthesis of 4,4'-bis(4-bromobenzoyl)diphenyl (1)

To a 100 mL, round-bottom flask were added 24.15 g (0.11 mol) of 4-bromobenzoyl chloride, 7.7 g (0.05 mol) of diphenyl, 20 g (0.15 mol) of anhydrous powdered AlCl_3 , and 60 mL of *o*-dichlorobenzene with stirring under nitrogen at 0°C. The suspension was stirred at room temperature for 1 h and at 90°C for 8 h. The reaction mixture was poured into cold aqueous hydrochloric acid, then the water was decanted off, and the residue was washed with water several times. Next, methanol was added to the oily residue to precipitate a solid. Finally, the crude product was recrystallized from DMF and dried *in vacuo* at 100°C to afford 21.5 g of white crystals.

Yield: 83%. mp: 338–339°C. ANAL. Calcd for $\text{C}_{26}\text{H}_{16}\text{O}_2\text{Br}_2$: C, 60.01%; H, 3.10%. Found: C, 59.73%; H, 2.88%. IR (KBr, ν , cm^{-1}): 1647, 1605, 1583, 852, 749. $^1\text{H-NMR}$ [hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$), δ , ppm]: 7.90 (d, $J = 8.4$ Hz, 4H), 7.77 (d, $J = 8.4$ Hz, 4H), 7.72 (d, $J = 8.4$ Hz, 4H), 7.66 (d, $J = 8.4$ Hz, 4H). MS (EI, 70 eV): m/z 522 (M^+ , ^{81}Br , 18), 520 (M^+ , 35), 518 (M^+ , ^{79}Br , 17), 363 (48), 185 (97), 183 (100), 152 (46), 76 (42).

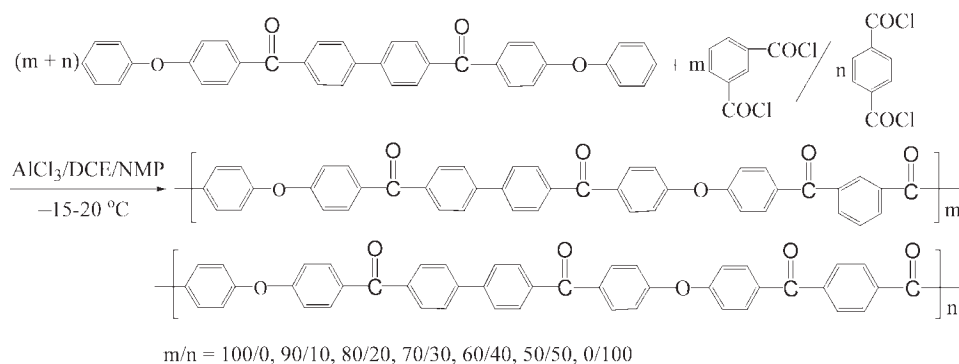
Synthesis of BPOBDP

A 100-mL, three-necked, round-bottom flask outfitted with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap outfitted with a condenser, and a nitrogen outlet was charged with a mixture of phenol (3.76 g, 0.04 mol), potassium hydroxide (1.91 g, 0.034 mol), potassium carbonate (0.83 g, 0.006 mol), toluene (30 mL), and NMP (50 mL). The reaction mixture was heated to 140°C until no further water was azeotropically distilled from the reaction mixture, and then the temperature was raised to 170°C to remove toluene. After it was cooled to 40°C, **1** (9.36 g, 0.018 mol) and copper powder (0.1 g) were added, and the reaction mixture was heated to 200°C and stirred at that temperature for 6 h. After cooling to room temperature, the product was precipitated from water. The solid product was washed with hot water several times, recrystallized from DMF, and dried *in vacuo* at 100°C to afford 8.25 g of white crystals.

Yield: 84%. mp: 280–281°C. ANAL. Calcd for $\text{C}_{38}\text{H}_{26}\text{O}_4$: C, 83.50%; H, 4.79%. Found: C, 83.23%; H, 4.61%. IR (KBr, ν , cm^{-1}): 3065, 1644, 1605, 1591, 1492, 1266, 853, 755. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ , ppm): 7.96 (d, $J = 8.0$ Hz, 4H), 7.87 (d, $J = 8.0$ Hz, 4H), 7.85 (d, $J = 8.4$ Hz, 4H), 7.49 (t, $J = 7.6$ Hz, 4H), 7.27 (t, $J = 7.6$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 4H), 7.13 (d, $J = 8.8$ Hz, 4H). $^{13}\text{C-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$, δ , ppm): 201.12, 163.99, 154.53, 144.95, 136.17, 133.81, 131.27, 130.08, 129.86, 127.44, 125.33, 120.52, 116.95. MS (EI, 70 eV): m/z 546 (M^+ , 33), 197 (100).

Polymer synthesis

PEKDKEKKs were prepared as shown in Scheme 2 by the electrophilic Friedel–Crafts solution copolycondensation of BPOBDP with a mixture of IPC and



Scheme 2 Synthetic route of the polymers.

TPC over a wide range of IPC/TPC molar ratios in the presence of anhydrous AlCl_3 and NMP in DCE. A typical preparative procedure for polymer III is described hereafter. Other polymers were also obtained in a similar manner.

To a 100-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, a thermometer, and nitrogen inlet and outlet tubes were added 5.34 g (40 mmol) of anhydrous AlCl_3 and 10 mL of DCE. The flask was cooled to 0°C with an ice-water bath, then a solution of 1.25 mL (13 mmol) of NMP in DCE (5 mL) was added dropwise with stirring over a period of 10 min, and the mixture was stirred for 30 min and then cooled to -15°C . Into the resulting suspension were added 2.730 g (5 mmol) of BPOBDP, 0.812 g (4 mmol) of IPC, and 0.203 g (1 mmol) of TPC with stirring; the reaction mixture was warmed to 20°C over 2 h, and the reaction was continued at this temperature for 6 h. The reaction mixture was quenched with methanol (50 mL) at 0°C , and the precipitate was crushed, washed with methanol and extracted with boiling methanol for 24 h, and allowed to dry in air. The air-dried product was heated at 100°C overnight *in vacuo* to yield polymer III.

Measurements

Elemental analysis was performed with a Perkin-Elmer (Waltham, MA) model 2400 CHN analyzer. The Fourier transform infrared (FTIR) spectra of the monomers and polymers in KBr pellets (2%) were recorded with a Nicolet (Midland, Canada) 510P FTIR spectrophotometer. $^1\text{H-NMR}$ (400 MHz) and $^{13}\text{C-NMR}$ (100 MHz) spectra were obtained with a Bruker (Fallanden, Switzerland) PC-A400 (400 MHz) spectrometer at an operating temperature of 25°C with $\text{DMSO-}d_6$ or $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ as a solvent. Mass spectra were obtained on a Finnigan (Waltham, MA) 4510 mass spectrometer. Inherent viscosities were obtained with a concentration of 0.2 g/dL in 95% H_2SO_4 at 25°C with an Ubbelohde suspended-level viscometer. Differential scanning calorimetry (DSC) measurements were performed on a

Mettler-Toledo (Zurich, Switzerland) DSC 821e instrument at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. T_g was taken from the DSC curve as the center of the step transition in the second heating run. Thermogravimetric analysis (TGA) was performed on a Netzsch (Burlington, MA) Sta 449c thermal analyzer system at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen. The mechanical properties were measured at 25°C with a Shimadzu (Tokyo, Japan) AG-2000A tester at a crosshead speed of 50 mm/min. Samples with dimensions of $4.0 \times 6.0 \times 55 \text{ mm}^3$ were cut from the 55-mm^2 molding. Wide-angle X-ray diffraction (WAXD) was measured with a Rigaku D/MAX-IIA X-ray diffractometer using $\text{Cu K}\alpha$ radiation at 30 kV and 20 mA. The diffractograms were recorded at room temperature over the range of $10\text{--}40^\circ$. Samples were powdered and heat-treated at 200°C for 30 min.

RESULTS AND DISCUSSION

The route to the synthesis of a new monomer (BPOBDP or **2**) is shown in Scheme 1. Precursor **1** was conveniently obtained by the Friedel-Crafts acylation reaction of 4-bromobenzoyl chloride and diphenyl in *o*-dichlorobenzene at 90°C . The condensation of **1** with phenol for the preparation of **2** was carried out in NMP in the presence of potassium hydroxide and potassium carbonate at 200°C . **2** was obtained as a pure material after recrystallization from DMF. FTIR, NMR, and MS spectroscopy and elemental analysis were applied to confirm the structure of compound **2**. In the IR spectra, the key structural features include the following absorptions: aromatic C-H at 3065 cm^{-1} , aromatic ketone C=O at 1644 cm^{-1} , and aromatic ether Ar-O-Ar at 1266 cm^{-1} . In the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of compound **2**, all the signals corresponding to the proposed structure can be clearly observed. The $^1\text{H-NMR}$ spectrum of compound **2** is shown in Figure 1.

Aromatic PEKDKKs were synthesized by an improved electrophilic Friedel-Crafts copolycondensation of BPOBDP with a mixture of IPC and TPC

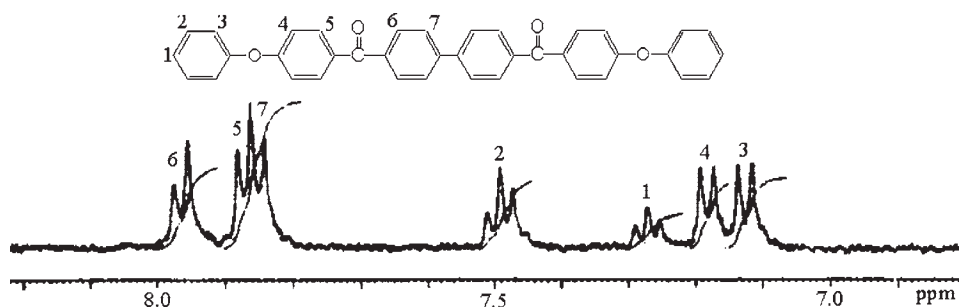


Figure 1 $^1\text{H-NMR}$ spectrum of BPOBDP ($\text{DMSO-}d_6$).

over a wide range of IPC/TPC molar ratios, as shown in Scheme 2. It is generally accepted that premature polymer precipitation from an initially homogeneous solution in electrophilic polycondensation syntheses prevents further macromolecular chain growth reactions and produces a polymer of undesirably low molecular weight and poor thermal stability. Furthermore, such precipitation Friedel–Crafts polymerizations generally have produced an intractable reaction product difficult to remove from the reaction vessel and purify. It is well known that in Friedel–Crafts polymerizations, ortho substitution and alkylation of the polymer are more likely to occur if the reaction is conducted at elevated temperatures and for a relatively long reaction time. Janson and Gors²¹ found that the Friedel–Crafts polymerization reaction can be controlled by the addition of a controlling agent to achieve the desired melt-processable, high-molecular-weight, substantially linear PAEKs. The controlling agent can efficiently suppress undesirable side reactions, particularly ortho substitution of activated aryloxy groups and alkylation of the polymer. Preferred controlling agents for the polymerization are organic Lewis bases such as DMF, *N,N*-dimethylacetamide (DMAc), and NMP. The Lewis acid (AlCl_3)/Lewis base complex appears to act as a solvent for the polymer–Lewis acid complex formed during the reaction, thereby maintaining the polymer in solution or in a reactive gel state. Furthermore, the reaction mixture is more tractable, and this makes workup of the polymer easier and ensures effective removal of catalyst residues during purification. The solubilization property of the Lewis acid (AlCl_3)/Lewis base complex is particularly significant in the preparation of para-linked PAEKs.

Initially, the influence of the reaction conditions on the preparation of PEKDKEKK by Friedel–Crafts acylation of BPOBDP and IPC in DCE with anhydrous AlCl_3 as a catalyst and NMP as a Lewis base was examined. The following factors were considered: catalyst quantity, Lewis base quantity, monomer ratio, and monomer concentration. The preparation of PAEKs by the electrophilic route gen-

erally starts at a low temperature. The initial low temperature is needed to maintain control over the reaction rate. A reaction temperature of about -15 to -5°C has been found to be particularly effective. Thereafter, the reaction temperature is slowly increased, and this is continued at room temperature. In general, Friedel–Crafts acylation gives a 1 : 1 complex of AlCl_3 and the carbonyl group formed.^{22,23} Therefore, an excess of AlCl_3 with respect to the carbonyl group formed should be used to catalyze the reaction. In the preparation of PAEKs, formations of the same types of complexes have been reported.²⁴ In our improved Friedel–Crafts acylation polycondensation, because of the addition of a Lewis base (NMP) as the controlling agent, an additional amount of AlCl_3 was required for the formation of a 1 : 1 complex of AlCl_3 and NMP. The effect of the quantity of AlCl_3 is shown in Table I. As shown in Table I, the reaction with 6.6 equiv of AlCl_3 with respect to IPC yielded a polymer with a low inherent viscosity of 0.25 dL/g because of the absence of a catalytic amount of AlCl_3 ; at least a molar equivalent excess of AlCl_3 over the monomer was necessary to obtain polymers with higher viscosity. When the molar ratio of AlCl_3 to IPC was between about 7.6 and 8.4, a polymer with a high inherent viscosity (>1.0 dL/g) could be obtained.

TABLE I
Effect of the AlCl_3 Quantity on the Polymerization of PEKDKEKKs

AlCl_3 (molar ratio with respect to IPC)	Yield (%)	Inherent viscosity (dL/g) ^a
6.6	88.5	0.25
7.2	95.4	0.76
7.6	95.8	1.04
8.0	96.3	1.17
8.4	96.0	1.09
9.0	92.5	0.93

Polymerization was conducted at 20°C with 5 mmol of BPOBDP, 5 mmol of IPC, and 13 mmol of NMP in 15 mL of DCE for 8 h.

^a Measured at a concentration of 0.2 g/dL in 95% sulfuric acid at 25°C .

TABLE II
Effect of the NMP Quantity on the Polymerization of PEKDKEKs

NMP (molar ratio to IPC)	Yield (%)	Inherent viscosity (dL/g) ^a
0	92.2	0.54
1.8	94.3	0.76
2.2	95.4	0.95
2.6	96.3	1.17
3.0	96.1	1.02
3.4	95.8	0.81

Polymerization was conducted at 20°C with 5 mmol of BPOBDP, 5 mmol of IPC, and 27 mmol of AlCl₃ in 15 mL of DCE for 8 h. In addition, 1 mol equiv of AlCl₃ with respect to NMP was required to form a 1 : 1 complex of AlCl₃ and NMP.

^a Measured at a concentration of 0.2 g/dL in 95% sulfuric acid at 25°C.

However, a large excess of AlCl₃ (e.g., a 9-fold excess) seemed to induce unfavorable side reactions because the polymer obtained under this condition contained a fraction that was insoluble in 95% sulfuric acid. Therefore, a suitable quantity of AlCl₃ was about 8 mol equiv with respect to IPC.

The effect of the Lewis base (NMP) quantity on polymerization was investigated, and the results are summarized in Table II. As shown in Table II, the precipitation polycondensation reaction without NMP afforded a polymer with a lower inherent viscosity of 0.54 dL/g. The inherent viscosity of the polymer increased with an increase in the molar ratio of NMP to IPC from 1.8 to 2.6 because the polymer was kept in solution or in a reactive gel state, but further increasing the quantity of NMP resulted in a decrease in the inherent viscosity of the polymer because of the decrease in the rate of the polymerization reaction. Therefore, an optimum quantity of NMP was about 2.6 mol equiv with respect to IPC.

In classical polycondensation of two monomers, the molecular weight of the polymer that is formed is strongly dependent on the monomer stoichiometric ratio. An excess of one of the two monomers usually results in a dramatic decrease in the molecular weight of the product. Table III shows the effect of the BPOBDP/IPC feed ratio on the inherent viscosity of the polymer obtained. From Table III, we can see that a monomer ratio of 1 : 1 gave the maximum inherent viscosity, and deviations from the stoichiometry gave lower viscosities. However, it is still possible to obtain high-viscosity polymers with a 1 mol % excess of BPOBDP or IPC; therefore, the resulting polymers will be end groups of phenoxy or acyl chloride. It is well known that the acyl chloride group is reactive and the phenoxy group is non-reactive and thermally stable. Therefore, the polymer

TABLE III
Effect of the Monomer Ratio on the Polymerization of PEKDKEKs

Monomer ratio		Yield (%)	Inherent viscosity (dL/g) ^a
BPOBDP	IPC		
1.00	0.98	92.8	0.48
1.00	0.99	96.1	0.95
1.00	1.00	96.3	1.17
1.00	1.01	95.8	0.83
1.00	1.02	92.0	0.40

Polymerization was conducted at 20°C with 5 mmol of BPOBDP, 13 mmol of NMP, and 40 mmol of AlCl₃ in 15 mL of DCE for 8 h.

^a Measured at a concentration of 0.2 g/dL in 95% sulfuric acid at 25°C.

with end groups of phenoxy will exhibit higher thermal stability and lower melting viscosity than the polymer with end groups of acyl chloride.

The Friedel-Crafts acylation polymerization also showed a characteristic effect of the monomer concentration on the inherent viscosity of the polymers. Table IV shows the influence of the monomer concentration on the polymer viscosity in the course of the preparation of PEKDKEKs. As shown in Table IV, a polymer with a high viscosity was obtained with monomer concentrations between about 0.36 and 0.25 mol/L. A higher monomer concentration resulted in lower viscosity because the polymerization reaction was too fast and a gelatinous mass was formed after 4 h. However, too low a monomer concentration (e.g., a monomer concentration of 0.17 mol/L) also yielded a polymer with a low viscosity because of the low rate of the polymerization reaction.

Under the optimum polymerization reaction conditions, a series of novel PEKDKEKs were synthesized by the variation of the molar ratio of IPC to TPC. Feed ratios and some of the properties of the

TABLE IV
Effect of the Monomer Concentration on the Polymerization of PEKDKEKs

Monomer concentration (mol/L)	Yield (%)	Inherent viscosity (dL/g) ^a
0.50	93.7	0.62
0.42	94.4	0.86
0.36	95.6	1.08
0.33	96.3	1.17
0.29	96.0	1.14
0.25	95.8	1.01
0.20	95.6	0.78
0.17	93.8	0.57

Polymerization was conducted at 20°C with 5 mmol of BPOBDP, 5 mmol of IPC, 13 mmol of NMP, and 40 mmol of AlCl₃ for 8 h.

^a Measured at a concentration of 0.2 g/dL in 95% sulfuric acid at 25°C.

TABLE V
Conditions and Viscosities of the Polymers

Polymer	IPC (mol %)	TPC (mol %)	Yield (%)	Inherent viscosity ^a
I	100	0	96.3	1.17
II	90	10	96.7	1.18
III	80	20	96.1	1.26
IV	70	30	95.9	1.27
V	60	40	97.0	1.21
VI	50	50	95.7	1.18
VII	0	100	96.6	1.16

Polymerization was conducted at 20°C with 5 mmol of BPOBDP, 5 mmol of IPC and TPC, 13 mmol of NMP, and 40 mmol of AlCl₃ in 15 mL of DCE for 8 h.

^a Measured at a concentration of 0.2 g/dL in 95% sulfuric acid at 25°C.

polymers are listed in Table V. The inherent viscosity values reveal that high-molecular-weight polymers were obtained in the DCE/NMP medium because the inherent viscosity values of the polymers were higher than the critical inherent viscosity value of the macromolecule. Thus, the improved electrophilic solution polycondensation route is appropriate.

The synthesized PEKDKEKKs were characterized by FTIR spectroscopic analysis. The FTIR spectra of all the polymers show no absorption at about 1740 cm⁻¹, indicating the absence of -COCl groups. All the spectra show characteristic bands at 1655 (S, νC=O), 1587 (S, νC=C), 1496 (S, νC=C), and 1241 cm⁻¹ (S, νC-O). The FTIR spectrum of polymer IV is shown in Figure 2.

The thermal properties of the new PEKDKEKKs were evaluated by DSC and TGA, and the results are given in Table VI. Samples were heated up to 430°C at the rate of 10°C/min in N₂, quenched to -50°C, and rerun to obtain *T_g*. The *T_g* values of the PEKDKEKKs were 174–185°C, and they were signifi-

TABLE VI
Thermal Properties of the Polymers

Polymer	<i>T_g</i> (°C)	<i>T_m</i> (°C)	<i>T_c</i> (°C)	<i>T_d</i> (°C) ^a
I	175	354	240	553
II	174	353	255	559
III	176	342	254	552
IV	176	358	238	550
V	176	363	234	546
VI	178	371	227	544
VII	185	403	242	547

^a Observed by TGA.

cantly higher than that (170°C) of the all para-linked poly(aryl ether ketone ketone) (*p*-PEKK).²⁵ This was attributed to the presence of rigid diphenyl moieties in the main chain. The *T_g* values of copolymers II–VI increased with an increase in the concentration of TPC in the polymer, but the increase was marginal. However, all para-linked polymer VII had the highest *T_g* of 185°C because of the high regularity of the molecular chains. The crystallization temperature (*T_c*) values of the PEKDKEKKs were 227–255°C. The *T_m* values of the PEKDKEKKs were 342–403°C, and the polymers with a high concentration of IPC had lower *T_m* values because of the decrease in the regularity of the molecular chains with the introduction of the *meta*-phenylene linkages. The *T_m* values of copolymers III–VI increased with an increase in the concentration of TPC in the polymer, and all para-linked polymer VII had the highest *T_m* of 403°C because of the existence of diphenyl and the high regularity of the molecular chains. *p*-PEKK also had a high *T_g* of 170°C, but its too high *T_m* of 384°C made it unsuitable for melt processing. However, polymer III with an IPC/TPC molar ratio of 80 : 20 had not only a high *T_g* of 176°C but also a moderate *T_m* of 342°C. A typical DSC curve of polymer III is illustrated in Figure 3.

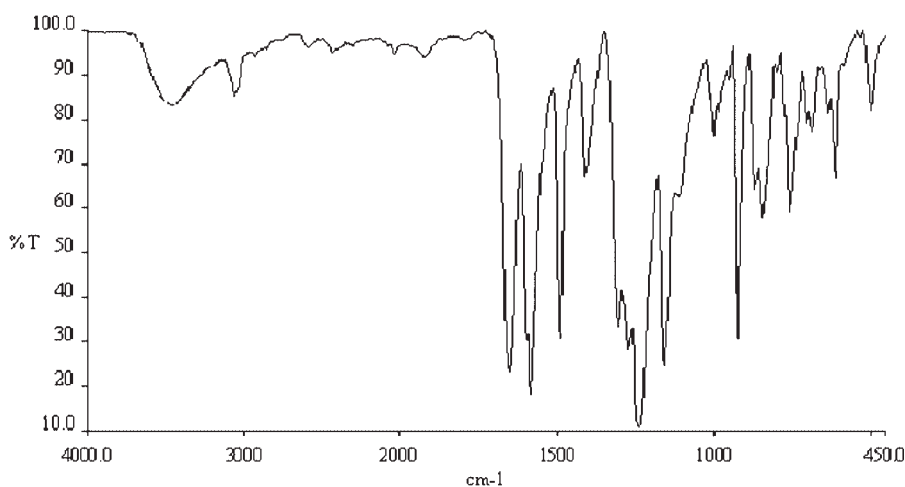


Figure 2 FTIR spectrum of polymer IV.

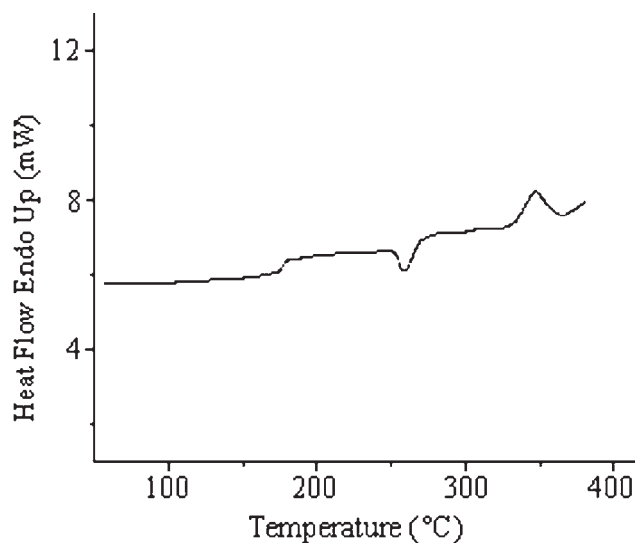


Figure 3 DSC curve of polymer III.

The PEKDKEKKs exhibited excellent thermal stability. As summarized in Table VI, the temperature at 5% weight loss (T_d) for all the polymers was above 544°C in N_2 . The temperature difference between T_m and T_d of polymers I–III was large, so melt processing could be accomplished. We measured the mechanical properties of polymers I–VI, and the results are presented in Table VII. From these data, it can be seen that the polymers had tensile strengths of 100.4–103.8 MPa, Young's moduli of 3.29–3.45 GPa, and elongations at break of 7–13%, which indicated that they were strong materials.

The crystallinities of the polymers were evaluated by WAXD. All the polymers exhibited semicrystalline patterns. The WAXD patterns of polymers I, III, and VI are presented in Figure 4. *p*-PEKK had four major diffraction peaks at 2θ values of 18.7 (110), 20.8 (111), 23.3 (200), and 28.9° (211).⁹ The WAXD patterns of polymers I, III, and VI fundamentally bore the same number and site of the diffraction peak of every crystal plane in comparison with that of *p*-PEKK. These results indicated that the PEKDKEKKs had a chain similar to that of *p*-PEKK to form the crystal that was included in the orthorhombic system with *p*-PEKK.

TABLE VII
Mechanical Properties of the Polymers

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
I	102.2	3.34	12
II	101.9	3.36	13
III	103.5	3.29	11
IV	103.8	3.31	12
V	101.8	3.38	10
VI	100.4	3.45	7

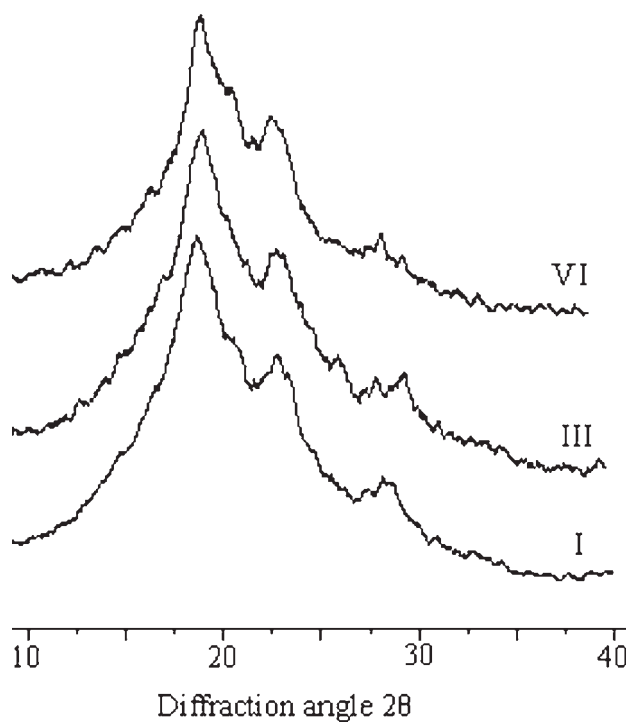


Figure 4 WAXD patterns of polymers I, III, and VI.

The solubility behavior of the polymers prepared in this study was determined for powdery samples in excess solvents at room temperature for 24 h. All prepared polymers were insoluble in common solvents such as tetrahydrofuran, $CHCl_3$, DCE, ethanol, and toluene. They were also insoluble in highly polar solvents such as DMF, DMAc, NMP, and DMSO. The excellent behavior of resistance to organic solvents can be ascribed to the close packing and higher regularity of the polymer chain due to the presence of rigid diphenyl moieties. The PEKDKEKKs were also insoluble in 30% aqueous NaOH or 30% aqueous HCl but not in concentrated sulfuric acid. Thus, on the basis of these results, we concluded that the semicrystalline PEKDKEKKs had excellent resistance to organic solvents, acidity, and alkalinity.

CONCLUSIONS

Novel high-molecular-weight PEKDKEKKs were conveniently synthesized by the electrophilic Friedel-Crafts solution copolycondensation of BPOBDP with a mixture of IPC and TPC over a wide range of IPC/TPC molar ratios under very mild conditions.

The incorporation of diphenyl into the polymers greatly increased T_g , and the T_m values of the polymers could be adjusted to a moderate value by the variation of the molar ratio of IPC to TPC. Copolymer III with an IPC/TPC molar ratio of 80 : 20 had not only a high T_g of 176°C but also a moderate T_m of 342°C. Copolymer III had a tensile strength of

103.5 MPa, a Young's modulus of 3.29 GPa, and an elongation at break of 11%.

The novel PEKDKEKs were semicrystalline and exhibited outstanding thermal stability and excellent resistance to organic solvents, acidity, and alkalinity.

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