Poly(aryl ether ketone)s with (3-Methyl)phenyl and (3-Trifluoromethyl)phenyl Side Groups

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ABSTRACT: New bisphenol monomers, (3-methyl)phenylhydroquinone and (3-trifluoromethyl)phenylhydroquinone, were prepared in a two-step synthesis. A series of poly(aryl ether ketone)s were derived from these bisphenols via a nucleophilic aromatic substitution polycondensation with various bisfluoro compounds. The polycondensation proceeded quantitatively in tetramethylene sulfone in the presence of anhydrous potassium carbonate and afforded the polymers with inherent viscosities of 0.63–0.91 dL/g. The fluorinated polymers showed lower glass-transition temperatures and higher thermal-decomposition temperatures than the corresponding nonfluorinated polymers. The solubility of the polymers was improved by the introduction of bulky pendant groups. All the polymers formed transparent, strong, and flexible films, with tensile strengths of 86.4–102.0 MPa, Young's moduli of 2.28–3.03 GPa, and elongations at break of 14–42%. All the polymers had low dielectric constants of 2.70–2.83 at 1 MHz. Compared with the methylated polymers, the trifluoromethylated polymers exhibited lower water sorption, which was attributed to the stronger hydrophobicity of the fluorine-containing groups. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 3392–3398, 2002

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INTRODUCTION

Poly(aryl ether ketone)s (PAEKs), including poly(ether ether ketone) (PEEK), poly(ether ether ketone ketone) (PEEKK), and poly(ether ether ketone diphenyl ketone) (PEEKDK), are a family of high-performance engineering thermoplastics, known for their excellent thermal, mechanical, and electrical properties. This class of advanced materials is currently receiving considerable attention for potential applications in aerospace, automobile, electronics, and other high technology fields.[1–3] However, it is difficult for PAEKs to be used as thin films and coatings because they have low solubility in almost all known solvents except for concentrated sulfuric acid. A great deal of research on PAEKs has been concentrated on the introduction of pendant groups to improve the solubility, processability, and other desired properties. To meet various demands without thermal stability being sacrificed, PAEKs with phenyl, methyl, butyl, and bromomethyl side groups have been successfully prepared.[4–7]

The need has become particularly acute for high-temperature materials used in microelectronic devices, such as the substrates for printed circuit boards, dielectric and insulating layers in multilayer structures, and coatings in electronic packaging. Therefore, aromatic polymers with low dielectric constants, high thermal stability,

low water absorption, and good solubility have been studied extensively. A low dielectric constant is one of the most important requirements. The introduction of fluorine substitution and bulky side groups and the formation of nanofoam are regarded as effective ways to reduce the dielectric constant.[8–13]
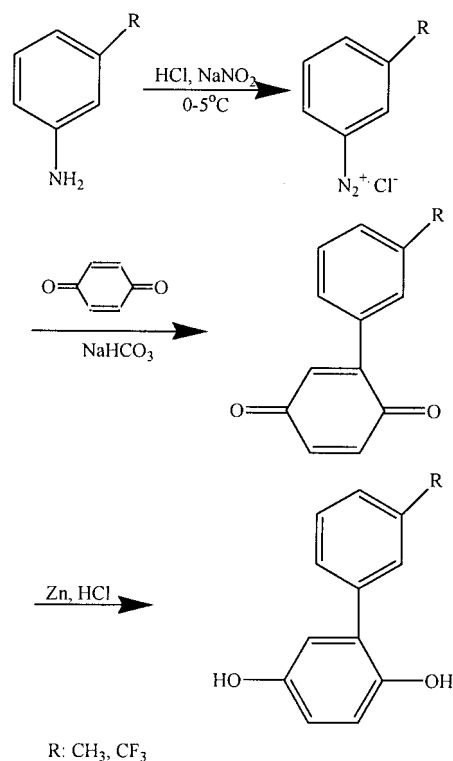
Because of the unique characteristics of fluorine substitution, including high electronegativity, low polarity, and low surface free energy, many fluorine-containing polymers have been prepared. In particular, the polymers containing hexafluoroisopropyl moieties have been exploited for applications as optical wave-guide materials, microelectronic devices, and gas-separation membranes. In general, the incorporation of fluorinated substituents into the polymers will decrease the dielectric constants, moisture absorption, and refractive index and increase the free volume, solubility, and thermal stability.[14–16]

We are interested in the synthesis of aromatic polymers with both nonfluorinated and fluorinated bulky pendant groups. In this article, we present the successful preparation of two new bisphenol monomers, (3-methyl)phenylhydroquinone and (3-trifluoro methyl)phenylhydroquinone. The nucleophilic aromatic substitution polymerization of these bisphenol monomers with various difluoro-substituted aromatic compounds affords new PAEKs with many interesting properties.

EXPERIMENTAL

Materials

m-Toluidine (Shanghai Chemical Reagent Co.), (3-trifluoromethyl)aniline (Zhejiang Dongyang Reagent Co.), 1,4-benzoquinone (Dalian Jizhou Chemical), zinc powder (Tianjin Chemical Reagent), hydrochloric acid (Beijing Chemical Reagent), sodium nitrite (Beijing Chemical Reagent), sodium bicarbonate (Beijing Chemical Reagent), and toluene (Beijing Chemical Reagent) were used as received. Tetramethylene sulfone (TMS) was purchased from Jizhou Oil Refinery and purified by distillation under reduced pressure. 4,4′-Difluorobenzophenone (mp = 103–104 °C), 1,4-di(4′-fluorobezoyl)benzene (mp = 219–220 °C), and 4,4′-bis(4-fluorobenzoyl)-biphenyl (mp = 269–270 °C) were prepared in our laboratory according to the standard procedures. The syntheses of the new bisphenol monomers
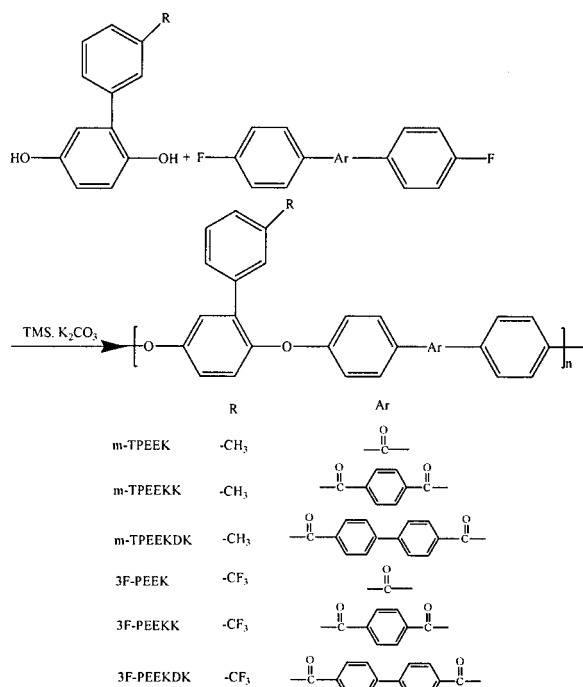

Scheme 1. Synthesis of the bisphenol monomers.

and polymers are illustrated in Schemes 1 and 2, respectively.

Measurements

IR spectra (KBr pellets or films) were measured on a Nicolet Impact 410 Fourier transform infrared (FTIR) spectrometer. ^{1}H (500 MHz), ^{13}C (125.7 MHz), and ^{19}F (470.5 MHz) NMR spectra were recorded on a Bruker 510 NMR spectrometer with tetramethyl silane (^{1}H and ^{13}C NMR) or CFCl$_3$ (^{19}F NMR) as a reference. Gel permeation chromatograms were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1.00 mL/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 20 °C/min under nitrogen. The glass-transition temperature (T_g) was taken in DSC curve as the center of the step transition in the second heating run. Thermogravimetric analysis (TGA) was performed on a Netzch Sta 449c thermal analyzer system at a heating rate of 10 °C/min in air. The elemental analysis was carried out with a Thermoquest CHNS-O elemental analyzer. Mass spectra were

Scheme 2. Synthesis of the *m*-T polymers and 3F polymers.

obtained on a Finnigan 4510 mass spectrometer. Inherent viscosity measurements were carried out with a Ubbelohde viscometer in concentrated sulfuric acid at 25 ± 0.1 °C. The polymer thin films for stress–strain tests were cast from *N*-methyl-2-pyrrolidinone (NMP) solutions onto glass plates, and this was followed by evaporation of the solvent and drying at 100 °C for 1 h, at 150 °C for 1 h, and at 200 °C in vacuo for 2 h. The completeness of the solvent removal from the films was confirmed by TGA and DSC measurements. The stress–strain behavior of such films was evaluated at room temperature at a strain rate of 10 mm/min. The dielectric constants of thin polymer films were measured on an HP 1645 B/4194A impedance gain-phase analyzer with a round-board electrode.

Monomer Synthesis

Synthesis of (3-Methyl)benzoquinone (m-*TBQ*)

Into a 2000-mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer were placed hydrochloric acid (11.8 M, 340 mL), water (200 mL), and ice (200 g). *m*-Toluidine (107 g, 1.0 mol) was added dropwise into the stirred mixture through the dropping funnel, and then a

concentrated water solution of sodium nitrite (69 g, 1.0 mol) was added dropwise. The mixture was stirred for 2 h at 0–5 °C and yielded a clear solution.

The resulting solution was filtered and added dropwise to a mixture of 1,4-benzoquinone (108 g, 1.0 mol), sodium bicarbonate (252 g, 3.0 mol), and water (500 mL). The reaction mixture was stirred at 8–12 °C for about 2 h and then at room temperature for 2 h. The precipitate was collected by filtration, washed thoroughly with water, and dried at 60 °C in a vacuum oven. The product was recrystallized from *n*-butanol and gave yellow crystals.

Yield: 82%. mp: 92 °C (DSC). *m/z*: 198. ELEM. ANAL. Calcd. for $C_{13}H_{10}O_2$ (198.21 g/mol): C, 78.77%, H, 5.08%. Found: C, 79.02%; H, 5.11%. IR (KBr, ν, cm^{-1}): 3061, 2950, 1647, 1589, 1454, 1345, 1296, 1099, 901, 888, 834, 780, 697. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.33 (t, *J* = 6.5 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.28 (s, 1H), 6.86 (d, *J* = 13 Hz, 1H), 6.85 (s, 1H), 6.81 (dd, *J* = 10.0 Hz, 2.5 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (CDCl$_3$, δ, ppm): 187.61, 186.69, 146.17, 138.25, 137.07, 136.21, 132.69, 132.59, 130.92, 129.84, 128.45, 126.40, 21.41.

Synthesis of (3-Trifluoromethyl)benzoquinone (3F-BQ)

The procedure was similar to the synthesis of *m*-TBQ, except that (3-trifluoromethyl)aniline was used as the starting material.

Yield: 90%. mp: 68 °C (DSC). *m/z*: 252. ELEM. ANAL. Calcd. for $C_{13}H_7F_3O_2$ (252.186 g/mol): C, 61.91%, H, 2.79%. Found: C, 61.62%, H, 2.72%. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.75 (s,1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 10.0 Hz, 1H), 6.91 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (CDCl$_3$, δ, ppm): 187.13, 186.01, 144.62, 137.02, 136.47, 133.48, 133.46, 132.55, 131.16 (q, *J* = 32.5 Hz), 129.11, 126.73, 126.12, 125.50 (q, *J* = 272.4 Hz, —CF$_3$). ^{19}F NMR (CDCl$_3$, δ, ppm): −63.16 (s, —CF$_3$). IR (KBr, ν, cm^{-1}): 3051, 1660, 1608, 1585, 1434, 1327, 1252, 1196, 1128, 1074, 922, 846, 808, 695.

Synthesis of (3-Methyl)phenylhydroquinone (m-*TPH*)

m-TPQ (99 g, 0.50 mol), Zn powder (98.1 g, 1.50 mol), and 400 mL of deionized water were placed into a 1000-mL, three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping

funnel. The mixture was heated to 90 °C with stirring, which was followed by the addition of 120 mL of HCl (11.8 M) dropwise at a rate of 0.5 drops per second. After complete addition, the reaction mixture was allowed to reflux for 3 h. Then, the hot mixture was filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. The white solid was collected and recrystallized from toluene.

Yield: 70%. mp: 92 °C (DSC). m/z: 200. ELEM. ANAL. Calcd. for $C_{13}H_{12}O_2$ (200.23 g/mol): C, 77.97%, H, 6.04%. Found: C, 77.72%, H, 5.98%. IR (KBr, ν, cm^{-1}): 3277, 3015, 2917, 1602, 1496, 1396, 1191, 1170, 931, 870, 804, 774, 730, 702, 433. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.33 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 4.5 Hz, 1H), 7.22 (d, J = 4.5 Hz, 1H), 7.20 (s, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.73 (dd, J = 8.5 Hz, 3.0 Hz, 1H), 6.72 (s, 1H), 4.90 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (CDCl$_3$, δ, ppm): 149.25, 146.46, 139.11, 136.82, 129.65, 129.20, 128.99, 128.78, 125.93, 116.67, 116.62, 115.79, 21.46.

Synthesis of (3-Trifluoromethyl) phenylhydroquinone (3F-PH)

The procedure was similar to the synthesis of m-TPH, except that m-TPQ was replaced by 3F-PQ as the starting material.

Yield: 78%. mp: 88 °C (DSC). m/z: 254. ELEM. ANAL. Calcd. for $C_{13}H_9F_3O_2$ (254.20 g/mol): C, 61.42%; H, 3.56%. Found: C, 61.43%; H, 3.49%. IR (KBr, ν, cm^{-1}): 3274, 3012, 1613, 1592, 1491, 1454, 1431, 1287, 1275, 1195, 1167, 1117, 1073, 867, 782, 707, 700. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.74 (s, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 6.82 (dd, J = 6.0 Hz, 3.5 Hz, 1H), 6.75 (s, 1H), 6.74 (dd, J = 6.5 Hz, 3.0 Hz, 1H), 4.78 (s, 2H). ^{13}C NMR (CDCl$_3$, δ, ppm): 149.61, 146.37, 138.03, 132.42, 131.37 (q, J = 32.3 Hz), 129.33, 127.79, 126.03, 124.52, 124.05 (q, J = 272.3 Hz, —CF$_3$), 117.33, 116.97, 116.43. ^{19}F NMR (CDCl$_3$, δ, ppm): −63.20 (s, CF$_3$).

Polymer Synthesis

m-TPEEK

m-TPH (10.00 g, 50 mmol), 10.90 g (50 mmol) of 4,4′-difluorobenzophenone, 8.79 g (65 mmol) of anhydrous K$_2$CO$_3$, 70 mL of TMS, and 80 mL of toluene were placed in a 500-mL, three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser. The reaction mixture was allowed to reflux for

2 h. The toluene was removed by distillation. The system was heated to 220 °C. The polymerization was complete after 2.5 h. The viscous mixture was poured into 2000 mL of water. The threadlike polymer was pulverized into a powder after cooling. The powder was washed with hot methanol and water several times and dried at 120 °C for 24 h. The white polymer powder was obtained in a quantitative yield.

Gel permeation chromatography (GPC) in THF: Number-average molecular weight (M_n), 32,500; weight-average molecular weight/number-average molecular weight (M_w/M_n), 2.82. IR (film, ν, cm^{-1}): 3038, 2918, 1654, 1598, 1479, 1277, 1221, 1158, 927, 864, 765, 700. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.83 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.27–6.92 (m, 11H), 2.32 (s, 3H). ^{13}C NMR (CDCl$_3$, δ, ppm): 194.47, 162.05, 161.62, 153.02, 148.88, 138.32, 136.85, 136.72, 132.66, 132.54, 132.48, 132.25, 130.01, 129.02, 128.58, 126.41, 123.51, 123.04, 120.56, 117.57, 116.70, 21.81.

3F-PEEK

3F-PEEK was synthesized from the polymerization of 1 equiv of 3F-PH and 1 equiv of 4,4′-difluorobenzophenone. The procedure was similar to the synthesis of m-TPEEK, except that the polymerization period was prolonged to 4 h.

GPC in THF: M_n, 28,800; M_w/M_n, 2.48. IR (film, ν, cm^{-1}): 3066, 1654, 1699, 1497, 1485, 1333, 1225, 1161, 1126, 928, 865, 766, 701. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.84 (d, J = 8.8 Hz, 1H), 7.18 (s, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.26–7.18 (m, 3H), 7.11–6.89 (m, 4H). ^{13}C NMR (CDCl$_3$, δ, ppm): 193.98, 161.18, 152.93, 148.43, 137.17, 134.70, 132.72, 132.25, 130.83 (q, J = 31.7 Hz), 128.90, 125.92, 124.64, 123.99 (q, J = 272.4 Hz, —CF$_3$), 123.37, 122.47, 121.03, 117.35, 116.28. ^{19}F NMR (CDCl$_3$, δ, ppm): −63.49 (s, CF$_3$).

m-TPEEKK, m-TPEEKDK, 3F-PEEKK, and 3F-PEEKDK

m-TPEEKK and m-TPEEKDK were prepared from the polymerization of 1 equiv of m-TPH with 1,4-di(4′-fluorobenzoyl)benzene and 4,4′-bis(4-fluorobenzoyl) biphenyl, respectively, according to the same procedure used for m-TPEEK. 3F-PEEKK and 3F-PEEKDK were synthesized from 3F-PH with 1,4-di(4′-fluorobenzoyl)benzene and

4,4′-bis(4-fluorobenzoyl)biphenyl, respectively, in the same manner as 3F-PEEK.

RESULTS AND DISCUSSION

Monomer Synthesis

The bisphenol monomers m-TPH and 3F-PH were synthesized in two steps by the coupling reaction[17] of (3-methyl)phenyldiazonium chloride and (3-trifluoromethyl)phenyldiazonium chloride with 1,4-benzoquinone in the presence of $NaHCO_3$ to yield m-TBQ and 3F-BQ, respectively, followed by reduction with Zn/HCl (see Scheme 1). The structures of m-TBQ, 3F-BQ, m-TPH, and 3F-PH were confirmed by mass spectrometry, IR, NMR spectroscopy, and elemental analysis. In the IR spectra, m-TBQ and 3F-BQ show an absorption band around 1660 cm^{-1} due to symmetric stretching of carbonyl groups. After reduction, this characteristic absorption disappeared, and the characteristic bands of hydroxy groups around 3270 cm^{-1} appeared. The peak at 4.50–5.00 ppm in ^{1}H NMR spectra of m-TPH is assigned to the hydroxy proton that is absent in the spectrum of m-TPQ. The peaks at 2.40 and 7.33–6.72 ppm are assigned to the methyl and aromatic protons, respectively. ^{13}C NMR spectra of m-TPQ, m-TPH, 3F-PQ, and 3F-PH all exhibit 13 peaks. Two quartet peaks at 130–132 and 120–128 ppm in ^{13}C NMR spectra of both 3F-PQ and 3F-PH are attributed to the $^2J_{C-F}$ and $^1J_{C-F}$ coupling of the carbons with fluorine atoms in trifluoromethyl groups. In the ^{19}F NMR spectrum of 3F-PH, a single peak at −63.20 ppm is characteristic of the fluorine atoms in trifluoromethyl groups.

Poly(ether ketone) Synthesis

The polymerizations of two bisphenol monomers with stoichiometric amounts of three different bisfluoro monomers were carried out in the presence of excess potassium carbonate as a base in TMS, as shown in Scheme 2. The polymerizations were completed at a solid content of about 20%, and toluene was used for the azeotropic removal of water. The reaction temperature for bisphenolate formation was first governed by the amount of toluene under reflux. The water generated from deprotonation of the bisphenols was removed through the Dean–Stark trap. After the completion of bisphenolate formation in about 2 h, the reaction temperature was increased to 220 °C.

Table 1. Inherent Viscosity (η_{iv}) and Thermal Properties of PAEKs

Polymer	η_{iv} (dL/g)	DT$_5$ (°C)	DT$_{10}$ (°C)	T_g (°C)
m-TPEEK	0.72	505	520	148
m-TPEEKK	0.91	516	537	159
m-TPEEKDK	0.81	516	538	182
3F-PEEK	0.63	545	569	136
3F-PEEKK	0.89	525	549	147
3F-PEEKDK	0.79	522	566	170

High molecular weight polymers were readily obtained in 2.5–4 h. The existence of bulky pendant groups in the monomers did not have a significant effect on the polymerization. The molecular weight of the polymers could be adjusted by variations in the feed ratios of the bisphenols and bisfluoro monomers. It is very interesting to note that the polymerization periods of m-TPEEK, m-TPEEKK, and m-TPEEKDK were very short. Dramatically increased viscosity of the reaction systems was observed only about 0.5 h after the completion of bisphenolate formation. The resulting polymers had high inherent viscosities of 0.63–0.91 dL/g (Table 1).

The FTIR spectra of all the polymers support their structures. 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. In ^{1}H and ^{13}C NMR spectra of m-TPEEK, the assignments of the peaks are in good agreement with the proposed structures. The signals at 6.92–7.83 ppm in ^{1}H NMR spectra are assigned to the aromatic protons in the polymer backbone. The peak at 2.32 ppm in the ^{1}H NMR spectrum of m-TPEEK is attributed to the methyl protons. The ^{13}C NMR spectrum of m-TPEEK shows 22 peaks corresponding to the 22 distinguishable carbons. There are only 18 signals in the ^{13}C NMR spectrum of 3F-PEEK because of the overlap of chemical shifts of two phenyl carbons that are not attached to the carbonyl group. Two quartet peaks at 130–132 and 120–128 ppm arise from the $^1J_{C-F}$ and $^2J_{C-F}$ coupling of the carbon with fluorine atoms in the pendant groups. A single peak was also observed at −63.49 ppm in the ^{19}F NMR spectrum of 3F-PEEK, as expected.

The crystallinity of the PAEKs was examined by wide-angle X-ray diffraction. All the PAEKs exhibited amorphous patterns. These results

Table 2. Mechanical Properties of PAEKs

Polymer	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
3F-PEEK	93.5	2.72	36
3F-PEEKK	95.6	2.54	29
3F-PEEKDK	102.0	3.03	17
m-TPEEK	94.1	2.66	42
m-TPEEKK	86.4	2.28	26
m-TPEEKDK	99.1	2.82	14

could be explained by the presence of bulky pendant groups, which disrupted the regularity of molecular chains and inhibited the close packing of the polymer chains.

Thermal Properties of PAEKs

The thermal properties of the new PAEKs, fluorinated or nonfluorinated, were evaluated by DSC and TGA. The T_g's of the PAEKs were 136–182 °C, and no melting endotherms were observed in DSC traces. These observations further confirm the amorphous nature of the PAEKs. As depicted in Table 1, the T_g values of the 3F polymers are 12 °C lower than those of their corresponding *m*-T polymers. A possible explanation for the lower T_g values of 3F polymers is that the substitution of methyl with trifluoromethyl would lead to an internal plasticization in addition to the geometry and free-volume factors.[18]

The PAEKs exhibit good thermal stability. As summarized in Table 1, the temperatures at 5% weight loss (DT_5) are above 505 °C and the temperatures at 10% weight loss (DT_{10}) are above 520 °C in air. As anticipated, fluorinated (3F) polymers show a higher thermal stability than the corresponding nonfluorinated (*m*-T) polymers. This is attributed to the stronger C—F bond in comparison with C—H bonds.

Solubility of the PAEKs and Their Mechanical Properties

The solubility of the new PAEKs is greatly improved by the incorporation of (3-methyl)phenyl and (3-trifluoromethyl)phenyl groups. Conventional PEEKs without side groups could not be dissolved in most known organic solvents. In sharp contrast, *m*-TPEEK and 3F-PEEK have significant solubility in NMP, *N,N*-dimethylform-amide (DMF), *N,N*-dimethylacetamide (DMAc), chloroform, and THF at room temperature. The excellent solubility of *m*-TPEEK and 3F-PEEK could be attributed to the presence of bulky pendant groups, which led to increased free volume. However, with the incorporation of rigid carbonyl and biphenyl moieties, the solubility of the polymers is relatively lower. *m*-TPEEKK, *m*-TPEEKDK, 3F-PEEKK, and 3F-PEEKDK were found to be soluble in chloroform, DMF, and THF with heating. At room temperature, they could only be dissolved in NMP.

The mechanical properties of PAEK thin films cast from hot NMP are summarized in Table 2. All the films were transparent, strong, and flexible. The films had tensile strengths of 86.4–102.0 MPa, Young's moduli of 2.28–3.03 GPa, and elongations at break of 14–42%.

Dielectric Constants and Water Sorption

The dielectric constants of the polymers, as listed in Table 3, were measured on the thin films. At 1 MHz, the dielectric constant of conventional PEEK without pendant groups was 3.3. The dielectric constants of the polymers decreased when the bulky (3-trifluoromethyl)phenyl and (3-methyl)phenyl pendant groups were incorporated into the polymer chains. There are two related factors that could explain the observed effect of bulky pendant groups on the dielectric properties of polymers. First, the bulky side groups attached to the polymer main chains might have pushed the neighboring chains apart, and this resulted in loosely packed polymers and a low dielectric constant. By the same token, the incorporation of bulky pendant groups disrupted the crystallinity, leading to a less dense amorphous structure and a decreased dielectric constant.

Table 3. Dielectric Constant and Water Sorption of PAEKs

Polymer	Dielectric Constant (at 1 MHz)	Water Sorption (%)
m-TPEEK	2.70	0.51
m-TPEEKK	2.75	0.54
m-TPEEKDK	2.83	0.64
3F-PEEK	2.70	0.31
3F-PEEKK	2.76	0.46
3F-PEEKDK	2.82	0.50

Both nonfluorinated and fluorinated polymers were found to have similar dielectric constants. There are two competing factors to be considered. First, the nonsymmetrical substitution of —CF_3 for —CH_3 should result in an increase in the dipole moment and dielectric constant. However, the fluorine substitution would reduce moisture sorption and increase the free volume, leading to a lower dielectric constant.[19] In the case of 3F polymers, two factors might have approximately offset each other. In other words, the bulkiness of the pendant groups, (3-methyl)phenyl and (3-trifluoromethyl)phenyl, is the main reason for the decreased dielectric constants of the polymers.

The water uptakes of the polymers were measured by the immersion of the polymer films (5 $\times$ 5 $\times$ 0.5 mm^3) in water at 100 °C for 2 h, which was followed by wiping with tissue paper for the removal of water on the surface. The water uptakes were calculated from the difference in the weights before and after this procedure. The results show that the water uptakes by the polymers are in a general range of 0.31–0.64% (Table 3). Compared with *m*-T polymers, 3F polymers exhibit appreciably lower water sorption. The low water sorption of fluorine-containing polymers is attributed to the increase in hydrophobicity due to the introduction of trifluoromethyl groups.

CONCLUSIONS

A series of methylphenyl and trifluormethylphenyl-substituted PAEKs have been successfully synthesized from two new bisphenol monomers, *m*-TPH and 3F-PH, respectively. All the polymers have remarkably improved solubility in common organic solvents, such as NMP, DMF, DMAc, THF, and chloroform, over their unsubstituted counterparts. These polymers form transparent, strong, and flexible films with tensile strengths of 86.4–102.0 MPa, Young's moduli of 2.28–3.03 GPa, and elongations at break of 14–42%. All the polymers are amorphous and exhibit low dielectric constants ranging from 2.70 to 2.83 at 1 MHz. Compared with the methylphenyl-substituted polymers, the trifluoromethylphenyl-substituted polymers show lower T_g's, higher thermal stability, and lower water sorption.

REFERENCES AND NOTES

1. Rose, J. B. Polymer 1974, 15, 456.
2. Ohno, M.; Takata, T.; Endo, T. J Polym Sci Polym Chem Ed 1975, 33, 2647.
3. Ji, X. L.; Yu, D. H.; Zhang, W. J.; Wu, Z. W. Polymer 1997, 38, 3501.
4. Wang, F.; Roovers, J.; Toporowski, P. M. Macromolecules 1993, 26, 3826.
5. Higashi, F.; Kim, J.; Ong, C. J Polym Sci Part A: Polym Chem 1999, 32, 2413.
6. Bennett, G. S.; Farris, R. J.; Thimpson, S. A. Polymer 1991, 32, 1633.
7. Wang, F.; Roovers, J. J Polym Sci Part A: Polym Chem 1994, 32, 2413.
8. Tummala, R. R.; Rymaszewski, E. J. Microelectronics Packaging Handbook; Van Nostrand Reinhold: New York, 1989.
9. Minges, M. L. Electronic Materials Handbook; ASM International: Materials Park, Ohio, 1989.
10. Singer, P. Semicond Int 1996, 5, 88.
11. Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. Macromolecules 1991, 24, 5001.
12. Maier, G.; Banerjee, S. STEPI 5 Proceedings; Technip: Paris, 1999.
13. Miller, R. D.; Volksen, W.; Hawker, C. J.; Yoon, D. Y.; Rusell, T. P.; McGrath, J. E.; Briber, R. M. Adv Polym Sci 1998, 141, 1.
14. Mercer, F.; Goodman, T.; Wojtowicz, J.; Duff, D. J Polym Sci Part A: Polym Chem 1992, 30, 1767.
15. Cassidy, P. E.; Aminabhavi, T. M.; Fartley, J. M. J Macromol Sci Rev Macromol Chem Phys 1989, 29, 365.
16. Harris, F. W.; Hsu, S. L. C. High Perform Polym 1989, 1, 3.
17. Wang, B. L. Organic Synthesis Reaction (Part II); Science Press: Beijing, 1985.
18. Hougham, G.; Tesoro, G.; Viehbeck, A.; Chapple-Sokol, J. D. Macromolecules 1994, 27, 5964.
19. Hougham, G.; Tesoro, G.; Viehbeck, A. Macromolecules 1996, 29, 3453.