Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 45 (2004) 3241–3247
polymer
www.elsevier.com/locate/polymer

Soluble aromatic poly(ether ketone)s with a pendant 3,5-ditrifluoromethylphenyl group

Baijun Liu[a,b], Wei Hu[a], Chunhai Chen[a], Zhenhua Jiang[a], Wanjin Zhang[a], Zhongwen Wu[a,*], Toshihiko Matsumoto[b,*]

[a]*Alan G. Macdiarmid Institute, Jilin University, 130023 Changchun, China*
[b]*Center for Nano Science and Technology, Tokyo Polytechnic University, 243-0297 Kanagawa, Japan*

Received 26 August 2003; received in revised form 1 March 2004; accepted 2 March 2004

Abstract

A novel bisphenol monomer, (3,5-ditrifluoromethyl)phenylhydroquinone (6F-PH), was synthesized in a three-step synthetic procedure. Three aromatic poly(ether ketone)s (PEKs) based on 6F-PH were prepared via a nucleophilic aromatic substitution polycondensation with three difluorinated aromatic ketones. These PEKs had a high thermal stability, and the temperatures at the 5% weight loss are above 532 °C in air. The solubility of the PEKs was improved by the introduction of bulky pendant groups. All the polymers formed transparent, strong, and flexible films with tensile strengths of 86.2–99.5 MPa, Young's moduli of 2.32–3.24 GPa, and elongations at break of 11–14%. These PEK films have low dielectric constants of 2.68–2.89 at 1 MHz and low water absorptions of 0.29–0.47%.

Keywords: Poly(ether ketone)s; Fluorinated; Soluble

1. Introduction

Aromatic poly(ether ketone)s (PEKs) are a class of high performance engineering thermoplastics known for their excellent combination of chemical, physical and mechanical properties. This class of advanced materials is currently receiving considerable attention for potential applications in aerospace, automobile, electronics, and other high technology fields [1–5]. In fact, it is difficult for PEKs to be used as thin films and coating materials because of their poor solubility. In addition, their poor solubility makes the polymerization conditions rigorous. To obtain the desired solubility, processability and other properties, the PEKs with pendant groups, such as phenyl, butyl, methyl, and bromomethyl moieties, have been successfully prepared so far [6–10].

There has been a continuous demand for high-temperature materials for use in microelectronic devices, such as the substrate for printed boards, insulating materials as interlayer dielectrics and intermetal dielectrics, and coatings as electronic packaging. Therefore, the aromatic polymers with a low dielectric constant, high thermal stability, low water absorption, excellent mechanical properties, and good solubility have been widely investigated. To meet these demands, a low dielectric constant is required. The introduction of fluorine substituent and bulky side groups into the polymer is regarded as effective ways to obtain a low dielectric constant property. Aromatic polyimides, poly(aryl ether)s, polybenzoxazoles, polyphenylenes and some other high temperature polymers are regarded as the promising low dielectric constant materials [11–15]. Fluorinated PEKs are desirable because they are economically accessible by both electrophilic and the nucleophilic substitution routes, and relatively less polar groups and more easily processed than polyimides. Thus, the PEKs with low dielectric constants could be achieved by introducing the fluorine groups and other functional moieties into their backbones [16,17].

The incorporation of fluorine into the polymer has been intensively explored because of the unique characteristics of fluorine substitution. Fluorine incorporation has been found to generally lower the dielectric constant and moisture absorption, to improve the optical properties, and also to

---

[*] Corresponding authors. Tel.: +81-46-242-9527; fax: +81-46-242-3000.
E-mail address: matumoto@nano.t-kougei.ac.jp (T. Matsumoto).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.03.015

increase the thermal stability. In particular, the polymers containing hexafluoroisopropyl moieties have been explored for applications in microelectronic devices, optical wave-guide materials, and gas-separation membranes [18–20]. For it is a fact that the fluorinated monomers are relatively hard and expensive as, few are commercially available.

We are interested in the synthesis of aromatic polymers with fluorinated bulky pendant groups. In the present article, we report the successful preparation of the higher fluorine-containing bisphenol monomer, (3,5-ditrifluoromethyl)phenylhydroquinone, based on a previous study [21]. Three aromatic PEKs containing 3,5-ditrifluoromethylphenyl side groups were synthesized via the nucleophilic aromatic substitution polymerization.

2. Experimental section

2.1. Materials

(3,5-Ditrifluoromethyl)aniline (Zhejiang Dongyang Reagent Co.), 1,4-benzoquinone (Dalian Jinzhou Chemical), zinc powder (Tianjin Chemical Reagent), hydrochloric acid (36%, 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 Jinzhou Oil Refinery and purified by distillation under reduced pressure. 4,4′-Difluorobenzophenone, 1,4-bis(4-fluorobenzoyl)benzene, 4,4′-bis(4-fluorobenzoyl)biphenyl and PEEK (Victrex®) were prepared in our lab according to the standard procedures.

2.2. Measurements

The FTIR spectra (KBr or film) were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. The ^{1}H (500 MHz), ^{13}C (125.7 MHz) and ^{19}F (479.5 MHz) NMR spectra were recorded using a Bruker 510 NMR spectrometer with tetramethylsilane (^{1}H NMR) or $CFCl_3$ (^{19}F NMR) as the reference. Inherent viscosity measurements were carried out with an Ubbelohde viscometer in concentrated sulfuric acid at 25 ± 0.1 °C. Gel permeation chromatograms (GPC) were obtained by a Waters 410 instrument with tetrahydrofuran (THF) as the eluent and polystyrene as the standard. The wide-angle X-ray diffractometer (WAXD) patterns were measured on a Rigaku D/Max-γA X-ray diffractometer with graphite-monochromated Cu$K\alpha$ radiation. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at the heating rate of 20 °C/min under nitrogen. The glass transition temperature (T_g) was taken from the DSC curve as the center of the step transition in the second heating run. The thermogravimetric analysis (TGA) was performed using a Netzch Sta 449c thermal analyzer system at the heating rate of 20 °C/min in air. The elemental analysis was carried out with a Thermoquest CHNS-O elemental analyzer. Mass spectra were obtained using a Finnigan 4510 mass spectrometer. 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 dielectric constants of the polymer films (diameter = 13 mm and thickness = 0.5 mm, prepared by compression molding, and then coated with silver by a vacuum evaporation method) were obtained using an HP 4192A LF impedance gain-phase analyzer with an HP-6047C capacitance meter at 1 MHz. The polarizability and dipole moments of the model compounds were calculated using WinMOPAC 3.0 software. CNDO/S method and MOS-F program were chosen after the geometry optimization by AM1 method in MOPAC 2000 program. The water uptakes of the polymer were measured by immersion of the polymer films ($5 \times 5 \times 0.5$ mm^3, prepared by compression molding) in deionized water at 100 °C for 2 h, followed by wiping with tissue paper for removal of any water on the surface. The water uptakes were calculated from the difference in the weights before and after this procedure.

2.3. Monomer synthesis

2.3.1. Synthesis of (3,5-ditrifluoromethyl)phenylquinone (6F-PQ)

In a 3000-ml beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer, 340 ml of hydrochloric acid, 200 ml of water and 200 g of ice were added. (3,5-Ditrifluoromethyl)aniline (229 g, 1.0 mol) was next added dropwise into the stirred mixture, and then a concentrated water solution of sodium nitrite (69 g, 1.0 mol) was added dropwise. The reaction mixture was stirred for another 1 h at 0–5 °C after dropping the solution which produced a (3,5-ditrifluoromethyl)phenyldiazonium chloride solution. The resulting solution was filtered, and then added dropwise to a mixture of 1,4-benzoquinone (86.4 g, 0.8 mol), sodium bicarbonate (252 g, 3.0 mol), and water (500 ml). The reaction mixture was stirred at about 12 °C for 1.5 h, and then at room temperature for another 1.5 h. The precipitate was collected, washed thoroughly with water, and dried at 60 °C in a vacuum oven. The product was recrystallized from butanol to give yellow crystals.

Yield: 45%. Mp: 83 °C (DSC). m/z : 320. Elem. Anal. Calcd for $C_{14}H_6F_6O_2$ (320.03 g/mol): C, 52.52%; H, 1.89%. Found: C, 52.39%; H, 1.86%. IR (KBr, cm^{-1}): 1639 (C=O), 1135 ($-CF_3$). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.98 (s, 1H), 7.95 (s, 2H), 6.97 (dd, $J = 8.5$, 2.0 Hz, 1H), 6.94 (s, 1H), 6.90 (dd, $J = 10.0$, 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 186.79, 185.74, 143.58, 137.28, 137.04, 134.97, 132.88, 132.48 (q, $J = 33.6$ Hz), 129.75, 124.01, 123.36 (q, $J = 272.8$ Hz). ^{19}F NMR ($CDCl_3$, δ, ppm): -63.16.

2.3.2. Synthesis of (3,5-ditrifluoromethyl)phenylhydroquinone (6F-PH)

Into a 1000-ml three-necked flask equipped with a mechanical stirrer, a dropping funnel and a condenser were placed 6F-PQ (160 g, 0.5 mol), zinc powder (98.1 g, 1.5 mol) and water (500 ml). Hydrochloric acid (120 ml) was added dropwise into the stirred mixture at reflux over a period of 4 h. After this addition, the reaction system was allowed to reflux for 2 h. The hot mixture was then filtered. The filtrate was poured into a large amount of water. The solid was then collected and dried in a vacuum oven. White crystals were obtained after recrystallization from the toluene.

Yield: 80%. Mp: 113 °C (DSC). *m/z* : 322. Elem. Anal. Calcd For $C_{14}H_6F_6O_2$ (322.04 g/mol): C, 52.19%; H, 2.50%. Found: C, 52.17%; H, 2.46%. IR (KBr, cm^{-1}): 3326 (–OH), 1132 ($-CF_3$). ^1H NMR ($CDCl_3$, δ, ppm): 8.00 (s, 2H), 7.85 (s, 1H), 6.80 (dd, $J = 8.3, 2.1$ Hz, 1H), 6.81 (s, 1H), 6.78 (dd, $J = 8.6, 2.1$ Hz, 1H), 4.66 (s, 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 149.92, 146.37, 139.58, 131.85 (q, $J = 33.3$ Hz), 129.45, 126.50, 123.40 (q, $J = 272.8$ Hz), 121.22, 117.63, 117.11, 117.00. ^{19}F NMR ($CDCl_3$, δ, ppm): −63.26.

2.4. Polymer synthesis

2.4.1. Poly(ether ether ketone) (6F-PEEK)

To a 250-ml three-necked flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer, and a Dean–Stark trap with a condenser, were added 6F-PH (16.10 g, 0.05 mol), 4,4′-difluorobenzophenone (10.90 g, 0.05 mol), anhydrous K_2CO_3 (8.97 g, 0.065 mol), TMS (90 ml) and toluene (65 ml). The system was allowed to reflux for 2 h, and then the toluene was removed. The reaction mixture was heated to 210 °C. After 4 h, the polymerization was complete. The viscous solution was then poured into water. The flexible threadlike polymer was pulverized into a powder using a blender. The polymer powder was washed several times with hot water and methanol, and dried at 120 °C for 24 h.

GPC: Number-average molecular weight ($\bar{M}_n$), 31,000. Polydispersity ($\bar{M}_w/\bar{M}_n$), 2.58.

IR (film, cm^{-1}): 1663 (C=O), 1224 (Ar–O–Ar), 1132 ($-CF_3$). ^1H NMR ($CDCl_3$, δ, ppm): 7.96 (s, 2H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.79 (s, 1H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.26–7.20 (m, 3H), 7.12 (d, $J = 9.1$ Hz, 1H), 7.10 (d, $J = 8.6$ Hz, 1H), 6.91 (d, $J = 9.8$ Hz, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), ^{13}C NMR ($CDCl_3$, δ, ppm): 193.83, 160.77, 153.00, 148.33, 138.32, 132.80, 132.34, 131.71 (q, $J = 34.0$ Hz), 129.17, 123.43, 123.41, 123.40 (q, $J = 273.0$ Hz), 122.25, 121.74, 121.52, 117.34, 116.23. ^{19}F NMR ($CDCl_3$, δ, ppm): −63.28.

2.4.2. Poly(ether ether ketone ketone) (6F-PEEKK)

6F-PEEKK was synthesized by the polymerization of 6F-PH with 1,4-bis(4-fluorobenzoyl)benzene. The procedure is similar to the synthesis of 6F-PEEK.

IR (film, cm^{-1}): 1662 (C=O), 1226 (Ar–O–Ar), 1137 ($-CF_3$). ^1H NMR ($CDCL_3$, δ, ppm): 7.97 (s, 2H), 7.91–7.73 (m, 9H), 7.30–7.07 (m, 3H), 7.14 (d, $J = 7.6$ Hz, 2H), 6.93 (d, $J = 7.6$ Hz, 2H).

2.4.3. Poly(ether ether ketone diphenyl ketone) (6F-PEEKDK)

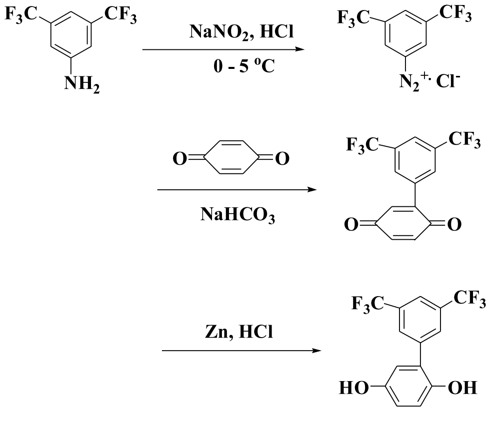
6F-PEEKDK was prepared from 6F-PH and 4,4′-bis(4-fluorobenzoyl)biphenyl, according to the same procedure used for 6F-PEEK.

IR (film, cm^{-1}): 1657 (C=O), 1225 (Ar–O–Ar), 1135 ($-CF_3$). ^1H NMR ($CDCL_3$, δ, ppm): 7.99 (s, 2H), 7.91 (d, $J = 8.0$ Hz, 4H), 7.84–7.72 (m, 9H), 7.30–7.08 (m, 3H), 7.15 (d, $J = 8.5$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H).

3. Results and discussion

3.1. Monomer synthesis

The synthetic route of a novel bisphenol, (3,5-ditrifluoromethyl)phenylhydroquinone (6F-PH) is shown in Scheme 1. The bisphenol was synthesized in a three-step synthetic process starting from the diazonium reaction of (3,5-ditrifluoromethyl)aniline in hydrochloric acid in the presence of sodium nitrite, followed by the coupling reaction of (3,5-ditrifluoromethyl)phenyldiazonium chloride with benzoquinone to yield (3,5-ditrifluoromethyl)benzoquinone (6F-PQ) [22]. 6F-PQ was then reduced with Zn/HCl to yield 6F-PH. The structures of 6F-PQ and 6F-PH were identified by mass spectrometry, IR, NMR spectroscopy, and elemental analysis. In the IR spectra, 6F-PQ showed an absorption band around 1639 cm^{-1} due to the carbonyl groups. After reduction, this characteristic absorption disappeared, and the characteristic band of the hydroxyl groups appeared around 3326 cm^{-1}. Fig. 1 shows the ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of 6F-PH. The signal at 4.66 ppm in ^1H NMR is assigned to the hydroxyl proton



Scheme 1. Synthesis of 6F-PH.

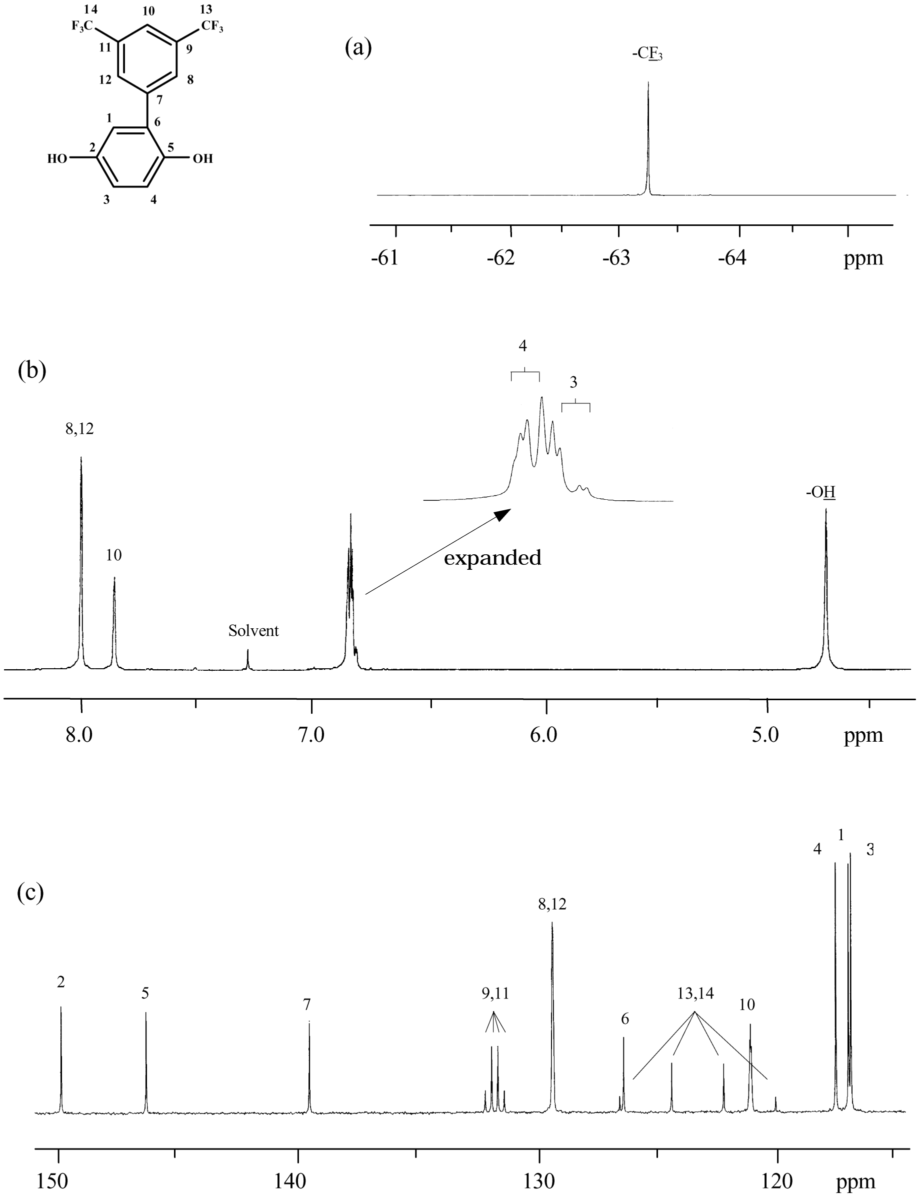


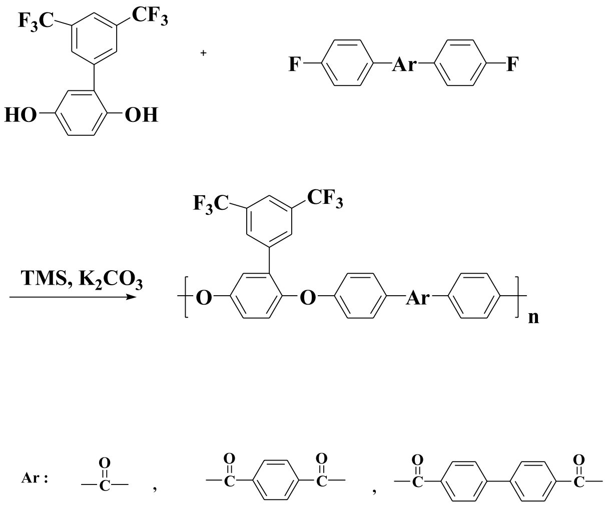
Fig. 1. ^{19}F NMR (a), ^1H NMR (b), and ^{13}C NMR (c) spectra of 6F-PH.

that could not be observed in the spectrum of 6F-PQ. Because of the symmetric structure of the (3,5-ditrifluoromethyl)phenyl group, the ^{13}C NMR spectra of both 6F-PQ and 6F-PH had 11 signals. The two quartet signals at 130–132 and 120–128 ppm in the ^{13}C NMR spectra of 6F-PQ and 6F-PH are due to the $^2J_{C-F}$ and $^1J_{C-F}$ coupling of the carbons with fluorines in the trifluoromethyl groups. A single signal around −63.2 ppm in ^{19}F NMR spectra of 6F-PQ and 6F-PH is characteristic of fluorines in trifluoromethyl groups.

3.2. Polymer synthesis

Polymerization of 6F-PH with three different difluorinated aromatic ketones was carried out in the presence of K_2CO_3 in TMS as the solvent at 210 °C after removing the water from the reaction system by the azeotropic distillation of toluene, as shown in Scheme 2. High molecular weight polymers were readily obtained in 4 h. The inherent viscosities of the resulting polymers ranged from 0.71 to 0.82 dl/g in concentrated sulfuric acid (Table 1).

The chain structure of the polymers was confirmed by FTIR and NMR spectroscopies. The FTIR spectra of the polymer films showed the characteristic absorption bands around 1660 cm^{-1} due to aryl carbonyl groups, around 1220 cm^{-1} based on aryl ether linkages, and 1135 cm^{-1} corresponding to trifluoromethyl moieties. In the ^1H NMR spectra of the polymers, the signals at 7.99–6.89 ppm are assigned to the aromatic protons in the polymer chains. The chemical shifts of the corresponding protons beside the carbonyl exhibited a little difference because of the asymmetric substitution of 3,5-ditrifluoromethylphenyl



Scheme 2. Synthesis of novel aromatic poly(ether ketone)s.

group. A typical set of NMR spectra of 6F-PEEK is shown in Fig. 2, and the spectra agreed with the proposed polymer structure.

The crystallinity of the PEKs was evaluated by wide-angle X-ray diffraction (WAXD). All the polymers exhibited amorphous patterns. The amorphous behavior of the polymers was mainly due to the existence of the bulky substituents, which disrupted the regularity of the molecular chains and inhibited their close packing.

3.3. Thermal properties of polymers

The thermal properties of the polymers were evaluated by DSC and TGA, as summarized in Table 1. The T_g's of 6F-PEEK, 6F-PEEKK and 6F-PEEKDK were 150, 163 and 183 °C, respectively. It was obvious that the T_g's of the polymers increased in the following order: 6F-PEEK < 6F-PEEKK < 6F-PEEKDK. 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 polymers. No melting endotherms were observed in the DSC traces, which further confirmed the amorphous nature of the polymers.

Table 1
Inherent viscosity (η_{iv}) and thermal properties of polymers

Polymer	η_{iv} (dl/g)[a]	T_g (°C)[b]	DT_5 (°C)[c]	DT_{10} (°C)[d]
6F-PEEK	0.76	150	562	580
6F-PEEKK	0.71	163	543	558
6F-PEEKDK	0.82	183	532	569

[a] Measured at a polymer concentration of 0.5 g/dl in H_2SO_4 at 25 ± 0.1 °C.

[b] From the second heating trace of DSC measurements conducted at a heating rate of 20 °C/min.

[c] 5% weight loss temperatures measured by TGA at a heating rate of 20 °C/min in air.

[d] 10% weight loss temperatures measured by TGA at a heating rate of 20 °C/min in air.

The polymers had excellent stabilities against thermal decomposition. The temperatures at a 5% weight loss (TD_5) are above 532 °C and the temperatures at a 10% weight loss (TD_{10}) are above 558 °C in air. The high thermal stability is attributed to the aromatic chains and strong C–F bonds.

3.4. Solubility and mechanical properties of the polymers

The solubility behavior of the polymers in some solvents is listed in Table 2. It is well known that the conventional PEEK could not be dissolved in most known organic solvents. In sharp contrast, 6F-PEEK was soluble at room temperature in aprotic polar solvents such as NMP, DMAc and DMF as well as in the less polar solvents such as chloroform and tetrahydrofuran (THF). The good solubility of 6F-PEEK could be attributed to the introduction of the bulky 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. However, the solubilities of 6F-PEEKK and 6F-PEEKDK are quite lower with the incorporation of the rigid carbonyl and biphenyl moieties. They could be soluble in DMAc, DMF, chloroform and THF with heating. At room temperature, they could only be dissolved in NMP. All the polymers were found to be soluble in concentrated sulfuric acid like PEEK (Victrex®).

The mechanical properties of the polymer thin film cast from NMP are summarized in Table 3. All the films were transparent, strong, and flexible. The polymer films had tensile strengths of 86.2–99.5 MPa, Young's moduli of 2.32–3.24 GPa, and elongations at break of 11–14%, indicating that they are strong materials.

3.5. Water absorption and dielectric constants

Table 4 summarizes the water absorption and dielectric constants of the polymers. The polymer films showed water absorptions in the range of 0.29–0.47%. The low water absorption of the polymers is attributed to the hydrophobicity of the fluorine-containing groups. Compared with 6F-PEEKK and 6F-PEEKDK, 6F-PEEK with the higher fluorine content had a lower absorption. The dielectric constants of the polymers were measured on the films. The

Table 2
Solubility of polymers

Polymers	$CHCl_3$	THF	DMF	DMAc	NMP	H_2SO_4
PEEK	−−	−−	−−	−−	−−	++
6F-PEEK	++	++	++	++	++	++
6F-PEEKK	+−	+−	+−	+−	++	++
6F-PEEKDK	+−	+−	+−	+−	++	++

++, Soluble at room temperature; +−, soluble on heating; −−, insoluble. $CHCl_3$, chloroform; THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; H_2SO_4, concentrated sulfur acid.

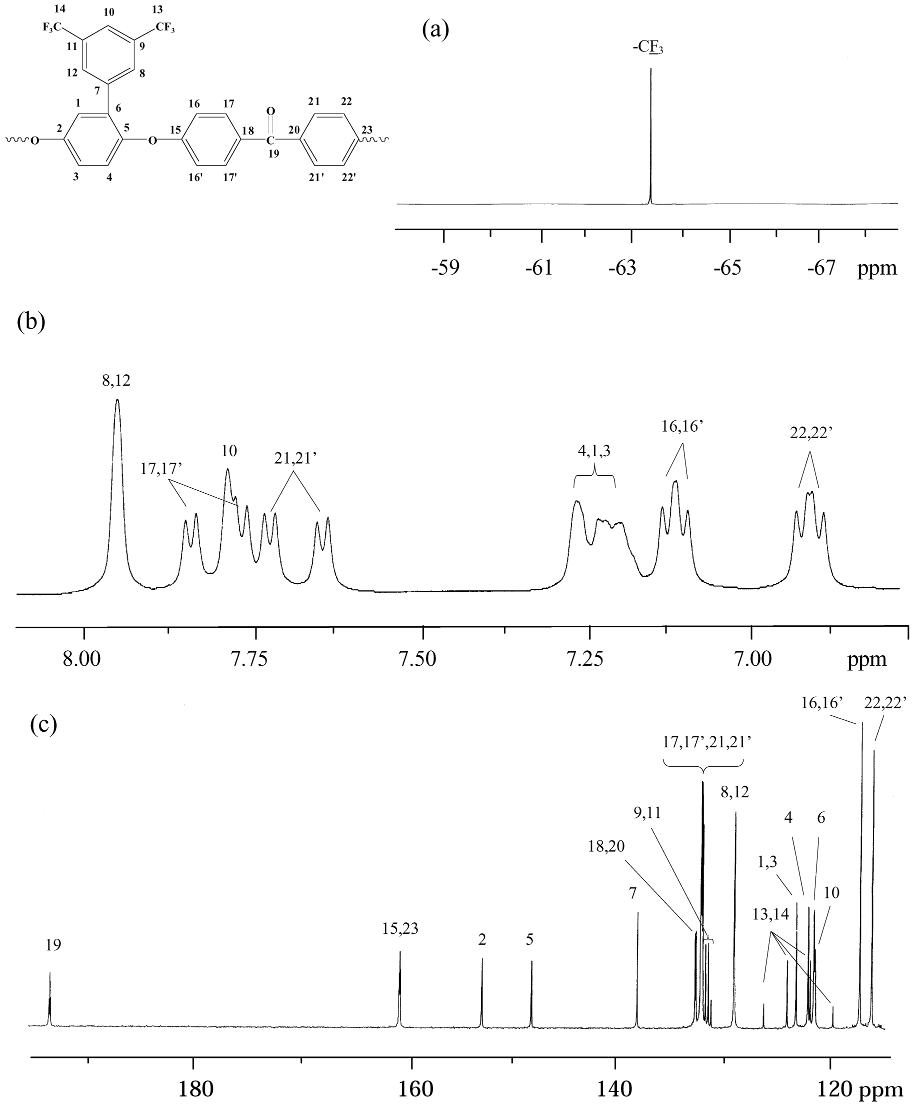


Fig. 2. ^{19}F NMR (a), ^{1}H NMR (b), and ^{13}C NMR (c) spectra of 6F-PEEK.

dielectric constants of these films ($\varepsilon = 2.68$–2.89 at 1 MHz) were lower than PEEK ($\varepsilon = 3.27$ at 1 MHz) under the same measurement conditions. In addition, the dielectric constants decreased as the content of fluorinated substitution increased.

Compared with m-TPEEK and 3F-PEEK [21], the dielectric constant of 6F-PEEK was not markedly decreased. We tried to use molecular orbital (MO) calculation of the corresponding model compounds to explain this result. As shown in Table 5, the trifluoromethylated compounds showed lower static and dynamic polarizability than the methylated compound. It is well known that low polarizability would lead to lower dielectric constant. However, the trifluomethyl substituents would change the dielectric constants due to the increase of the dipole moments. This possible explanation is well agreed with

Table 3
Mechanical properties of polymers

Polymer	Tensile strength (MPa)	Young's modulus (Gpa)	Elongation at break (%)
6F-PEEK	86.2	2.32	14
6F-PEEKK	89.3	2.67	12
6F-PEEKDK	99.5	3.24	11

Table 4
Water absorption and dielectric constant of polymers

Polymer	Water Absorption (%)[a]	Dielectric Constant (At 1 MHz)[b]
PEEK[c]	0.50	3.27
6F-PEEK	0.29	2.68
6F-PEEKK	0.45	2.78
6F-PEEKDK	0.47	2.89

[a] Calculated from the difference in the weights before and after immersion of the polymer films in water.

[b] The dry dielectric constants measured at room temperatures.

[c] A reference PEEK prepared from hydroquinone and 4,4′-Difluorobenzophenone

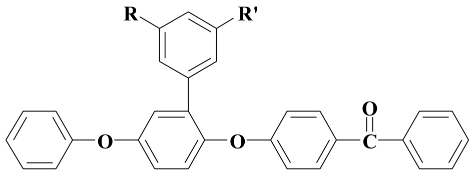
Table 5
The polarizability and dipole moments of the corresponding models for m-TPEEK, 3F-PEEK and 6F-PEEK

Polymer	Static polarizability (10^{-24} cm^3)	Dynamic		Dipole Moment (Debye)
		Incident light (eV)	Polarizability (10^{-24} cm^3)	
m-TPEEK	32.91	0.2	32.95	5.439
		1.0	33.86	
		2.0	37.13	
3F-PEEK	32.77	0.2	32.81	6.648
		1.0	33.72	
		2.0	36.97	
6F-PEEK	32.85	0.2	32.89	7.587
		1.0	33.81	
		2.0	37.09	

the results reported by Hougham et al. The introduction of fluorinated substitution into the polymers could decrease the dielectric constants by the ways of increased free volume, lower electronic polarizability, and decreased moisture absorptions. In the case of asymmetric substitution, the incorporation of fluorines into the polymer chains will increase the dipole moments and thus has the potential to increase dielectric constants. It was suggested that other effects overcame these increases, if indeed they were occurring [15,23] (Scheme 3).

4. Conclusion

A new hydroquinone monomer, 6F-PH has been successfully synthesized in a three-step procedure. Three fluorinated aromatic PEKs were prepared from 6F-PH via the nucleophilic aromatic substitution polycondensation with three fluoro compounds. The resulting PEKs are amorphous and exhibited outstanding thermochemical stabilities in air. These polymers have remarkably improved solubilities in common organic solvents over the unsubstituted PEEK. These novel PEKs have high tensile strengths, high moduli, low dielectric constants and low water absorptions. These polymers may be considered as good potential candidates for high-temperature microelectronic devices, optical materials and gas-separation membranes.



	R	R'
m-TPEEK	**H**	**-CH$_3$**
3F-PEEK	**H**	**-CF$_3$**
6F-PEEK	**-CF$_3$**	**-CF$_3$**

Scheme 3. Structures of the model compounds for m-TPEEK, 3F-PEEK and 6F-PEEK.

Acknowledgements

The authors thank the Chinese High Technology and Development Program and Japan Academic Frontier Program for the financial support.

References

[1] Ji XL, Zhang WJ, Wu ZW. Polymer 1996;37:4205.
[2] Cao JK, Su WC, Wu ZW, Kitayama T, Hatada K. Polymer 1994;35:3549.
[3] Ji XL, Yu DH, Zhang WJ, Wu ZW. Polymer 1997;38:3501.
[4] Rose JB. Polymer 1974;15:456.
[5] Rao VL. J Macromol Sci Rev, Macromol Chem Phys 1995;C35:661.
[6] Bennett GS, Farris RJ, Thompson SA. Polymer 1991;32:1633.
[7] Wang F, Roovers J, Toporowski PM. Macromolecules 1993;26:3826.
[8] Wang F, Roovers J. J Polym Sci, Polym Chem 1994;32:2413.
[9] Singh R, Hay AS. Macromolecules 1991;24:2637.
[10] Risse W, Sogah DY. Macromolecules 1990;23:4029.
[11] Cassidy PE, Aminabhavi TM, Fartley JM. J Macromol Sci Rev, Macromol Chem Phy 1989;29:365.
[12] Maier G. Prog Polym Sci 2001;26:3.
[13] Mercer F, Goodman T, Wojtowicz J, Duff D. J Polym Sci, Polym Chem 1992;30:1767.
[14] Hsiao SH, Li CT. J Polym Sci, Polym Chem 1999;37:1403.
[15] Hougham G, Tesoro G, Viehbeck A, Chapple-Sokol JD. Macromolecules 1994;27:5964.
[16] Gronewald S, Cassidy PE, Fitch JW, Arbaugh J, Herbold H, Jurek D. High Perform Polym 2001;13:117.
[17] Mercer FW, Mckenzie MT, Merlino G, Fone MM. J Appl Polym Sci 1995;56:1397.
[18] Banerjee S, Maier G. Chem Mater 1999;11:2179.
[19] Goodwin AA, Mercer FW, McKenzie MT. Macromolecules 1997;30:2767.
[20] Harris FW, Hsu SLC. High Perform Polym 1989;1:3.
[21] Liu BJ, Wang GB, Hu W, Jin YH, Chen CH, Jiang ZH, Zhang WJ, Wu ZW, Wei Y. J Polym Sci, Polym Chem 2002;40:3392.
[22] Wang B. Organic synthesis reaction. Beijing: Science Press; 1985. p. 763.
[23] Hougham G, Tesoro G, Viehbeck A. Macromolecules 1996;29:3453.