Synthesis and Characterization of Novel Aromatic Poly(ether sulfone ketones)

Yang-Kyoo Han,* Sung Dae Chi, and Young Ha Kim

Polymer Chemistry Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Byung Kyu Park

Chemical Division, Cheil Industries Inc., 62, Pyongyo Dong, Yocheon Si, Cheon Nam 555-210, Korea

Jung-Il Jin

Department of Chemistry, College of Sciences, Korea University, 1-Anam Dong, Sungbuk Gu, Seoul 136-701, Korea

Received August 2, 1994®

ABSTRACT: New aromatic poly(ether sulfone ketones) were prepared by polycondensation of 4-fluoro-4′-(((fluorobenzoyl)phenyl)oxy)diphenyl sulfone, a new ordered-sequence aromatic dihalide, and conventional aromatic diols such as Bisphenol A, hydroquinone, 4,4′-biphenol, resorcinol, or 2,6-naphthalenediol in sulfolane solvent in the presence of anhydrous potassium carbonate. The resulting high molecular weight polymers were found to be amorphous by X-ray diffractometry, and their glass transition temperatures ranged from 167 to 206 °C. According to the results of thermogravimetric analyses, they exhibited excellent thermal stability, showing 10% weight loss at 525–562 °C depending on their composition. They also exhibited good mechanical properties with moduli of 2400–3100 MPa. Tough and transparent thin films could easily be cast from their chloroform solutions. Their optical transmittance was over 80% in the wavelength range from 380 to 900 nm.

Introduction

High-performance engineering thermoplastics with excellent heat resistance are currently receiving considerable interest as advanced materials. Among them, poly(arylene ether ketones), well known in the form of poly(ether ether ketone) (Victrex PEEK) and poly(ether ketones) (PEK), are being used as matrix resins for advanced composite materials for aircraft and automobiles because of their high mechanical strength, excellent thermal stability, and good chemical resistance.[1,2] However, poly(arylene ether ketones) have several limitations in preparation,[3] molding, and processing[4] due to their crystalline structure and low thermooxidative stability[5] at or above the melting temperature. Compared with amorphous poly(arylene ether sulfones), they also have relatively low glass transition temperatures. It is well established that the modulus of elasticity decreases near T_g.[6,7] To overcome these disadvantages, blends[8,9] or block copolymerization[10] of PEEK and poly(ether sulfone) have been examined. The latter is one of the commercially available amorphous superengineering plastics.

In addition, high molecular weight poly(arylene ether ketones) are very difficult to synthesize because of their lack of solubility. Thus, a number of researchers have dealt with modification of poly(arylene ethers) to enhance their solubility. Several suggested methods include incorporation of alkyl substituents onto the polymer main chain,[11] introduction of the hexafluoroisopropylidene group into the PEK backbone,[12] and random copolymerization employing combinations of aromatic dihalides (or aromatic diols) such as dichlorodiphenyl sulfone, dichlorobenzophenone, 4,4′-bis(4-fluorobenzoyl)diphenyl ketone, and so on.[13,14] Sogah et al.[15] also reported a new approach to the synthesis of high molecular weight PEEK through the preparation of a soluble amorphous prepolymer that contains removable bulky substituents.

On the other hand, it has been well recognized that poly(arylene ether sulfones) such as Udel [poly(sulfone)], Radel [poly(aryl sulfone)], and Victrex [poly(ether sulfone); PES] are amorphous engineering thermoplastics having excellent heat resistance, oxidative stability, steam resistance, optical transparency, and solubility. These characteristics arise from a high resonance effect of the sulfone group incorporated into the corresponding polymer chain. The ether linkage also provides inherent toughness to the polymers.[16,17]

The purpose of this research is to synthesize a new class of poly(arylene ethers) possessing characteristics of both poly(arylene ether ketones) and poly(arylene ether sulfones) from 4-fluoro-4′-(((fluorobenzoyl)phenyl)-oxy)diphenyl sulfone (FBPODS), a sequentially ordered aromatic difluoride monomer. This paper reports the synthesis and characterization of a series of novel aromatic poly(ether sulfone ketones) (PESKs) prepared via a nucleophilic substitution reaction of FBPODS with conventional aromatic diols. Their thermal properties, solubility, transparency, and mechanical properties will also be described.

Experimental Section

Materials. Sulfolane and dimethyl sulfoxide (DMSO) were distilled from sodium hydroxide and calcium hydride, respectively, prior to use. 4,4′-Difluorodiphenyl sulfone (FPS) was recrystallized from ethanol. 4-Fluoro-4′-hydroxybenzophenone (FHB), Bisphenol A (BPA), and resorcinol were purified by recrystallization from toluene. Hydroquinone was recrystallized from acetone. 4,4′-Biphenol supplied by Aldrich was used without further purification. 2,6-Dihydroxynaphthalene was recrystallized from an 80/20 (v/v) mixture of water and acetone.

* To whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* January 15, 1995.

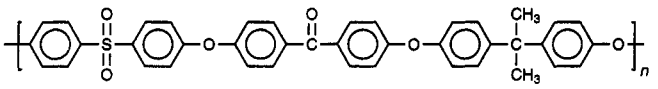
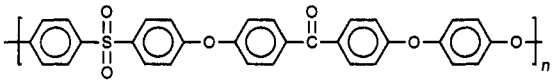
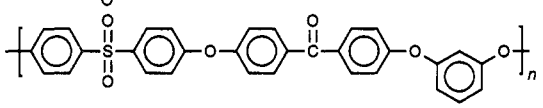
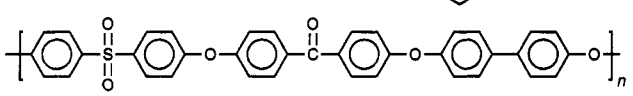
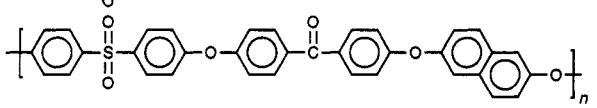
0024-9297/95/2228-0916$09.00/0

Table 1. Polymerization Conditions for the Preparation of PESK-1 from Bisphenol and FBPODS

expt no.	solvent	base	base/BPA (mole ratio)	FBPODS/BPA (mole ratio)	temp (°C)	time (h)	yield (wt %)	η_{red}[a] (dL/g)
1	DMSO	KOH	1.0	1.0	160	6	92	0.36
2	sulfolane	K_2CO_3	1.05	1.05	160	6	94	0.37
3	sulfolane	K_2CO_3	1.05	1.02	160 and 220	3 and 3	95	0.55
4	sulfolane	K_2CO_3	1.05	1.01	160 and 220	3 and 3	96	0.40
5	sulfolane	K_2CO_3	1.05	1.01	220	24	94	0.43

[a] The reduced viscosity was measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

Table 2. Structure and Results of PESKs

PESK	repeating unit	yield (%)	η_{red} (d L/g)	M_w[a]	M_n[a]	M_w/M_n
PESK-1		96	0.40	41 800	14 800	2.8
PESK-2		95	0.71	84 000	23 000	3.6
PESK-3		92	0.30	22 200	7 800	2.8
PESK-4		98	0.91	105 600	37 200	2.8
PESK-5		97	0.89	91 800	26 400	3.5

[a] Determined by GPC based on polystyrene standards.

Anhydrous potassium carbonate (Merck) was employed without further drying.

Synthesis of 4-Fluoro-4'-(((fluorobenzoyl)phenyl)oxy)-diphenyl Sulfone (FBPODS). A three-neck, 250 mL flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet adapter was charged with FPS (13.60 g, 53.5 mmol), FHB (11.46 g, 53.0 mmol), and 80 mL of sulfolane. After 10 min of stirring at room temperature, anhydrous potassium carbonate (3.85 g, 27.85 mmol) was added, and the reaction mixture was then stirred at 160 °C for 6 h in an oil bath. The brown solution was allowed to cool to 50 °C. The hot solution was poured into 800 mL of water. The precipitate was filtered and washed three times with hot water and methanol in turn and then dried. The crude product was distilled at 0.1 Torr and 296 °C for 6 h to give 17.89 g (75% yield) of FBPODS as a white solid, mp 162 °C. ^{1}H-NMR ($CDCl_3$): 8.1–7.8 (m, 8 H), 7.3–7.0 (m, 8 H). Anal. Calcd for $C_{25}H_{16}O_4F_2S$: C, 66.66; H, 3.58; F, 8.44; S, 7.12. Found: C, 66.64; H, 3.56; F, 8.40; S, 7.09.

Polymer Synthesis. A three-neck, 100 mL flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet adapter was charged with 5.76 g (12.8 mmol) of FBPODS, 2.90 g (12.7 mmol) of Bisphenol A, and 27 mL of sulfolane. After 10 min of stirring at room temperature, 1.84 g (13.3 mmol, 5% excess) of anhydrous potassium carbonate was added to the reaction mixture. The mixture was heated to and maintained at 160 °C for 3 h under a nitrogen atmosphere and then further at 220 °C for 3 h. After completing the polymerization, the viscous solution was dissolved in 200 mL of chloroform to remove residual potassium carbonate and potassium fluoride formed during the polymerization. The filtrate solution was poured into 800 mL of methanol to give a white polymer precipitate. The crude polymer was redissolved in chloroform, reprecipitated in methanol, and dried *in vacuo* at 80 °C for 24 h to obtain a fiber-shaped polymer.

Other polymers were also prepared under the same conditions. Analytical data for the polymers and results of the polymerizations are summarized in Tables 1 and 2.

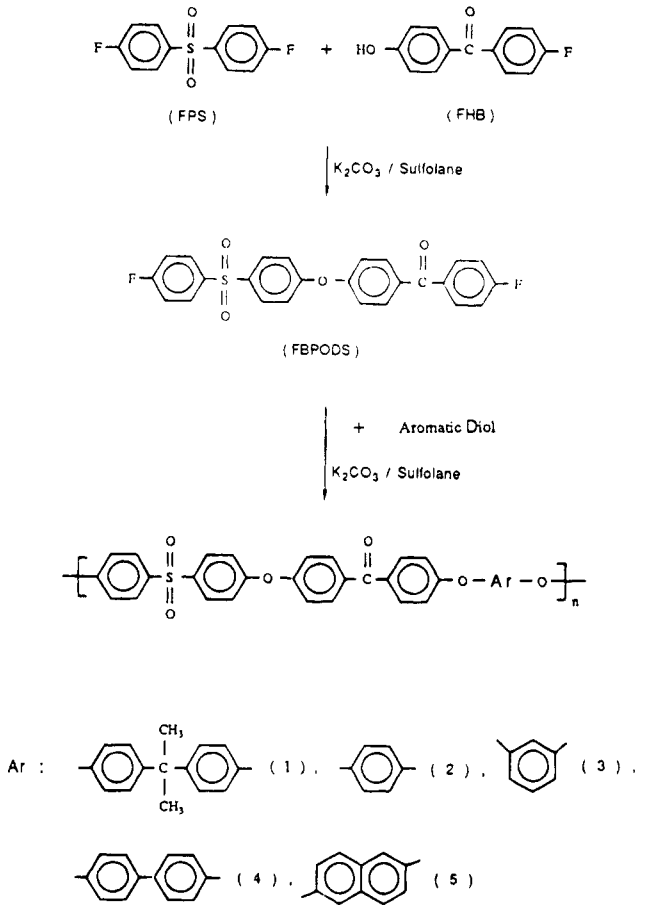
Characterization. Elemental analysis was performed on a Perkin-Elmer 240DS. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini-300 spectrometer. FT-IR spectra were obtained on a Mattson Alpha Centauri instrument. Viscosities of polymer solutions were measured at a concentration of 0.5 g/dL in chloroform at 25 °C using a Schott-Gerate AVS 400 Ubbelohde automatic viscometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were made on a DuPont 2000 thermal analyzer at a heating rate of 10 °C/min. Linear thermal expansion coefficients were measured with a Polymer Laboratories PL-TMA 100 at a heating rate of 10 °C/min. Dynamic mechanical properties were examined on an Orientec Rheovibron DDV-II-C with a heating rate of 3 °C/min (110 Hz). Dielectric constants were measured on an Ando AG-430 LCR meter at a frequency of 1 kHz after deposition of gold on the polymeric thin film coated onto an ITO glass plate. Mechanical properties (ASTM D882) of the films 40–90 μm thick were studied on an Instron Model TTD tensile tester at a strain rate of 10 mm/min.

Transmittance of the polymeric thin films was recorded on a Shimadzu UV-240 spectrophotometer. X-ray diffraction patterns were obtained on a JEOL JDX-11 using Ni-filtered Cu K radiation. Molecular weight determinations were performed with a Spectra Physics-SP8810 GPC using GMHXL, G6000HXL, and G2500HXL columns with chloroform as solvent and polystyrene for calibration. Density measurements (ASTM D1505-C) were carried out with a density gradient column charged with 150/50 and 80/120 (v/v) mixtures of carbon tetrachloride and toluene for calibration. Water absorption (ASTM D570) was calculated from the difference of the dry weight of the polymer films with a 1 × 1 cm template and the wet weight after immersion into water for 6 h in a thermostat at 23 °C.

Results and Discussion

Synthesis of FBPODS as a New Ordered-Sequence Monomer. In order to produce the polymers suitable for this research objective, we synthesized FBPODS, a new ordered-sequence monomer from FPS and FHB, as shown in Scheme 1. FBPODS was prepared by nucleophilic aromatic substitution of FPS with an alkali salt of FHB in a highly polar solvent such as

Scheme 1. Synthetic Route of PESKs



sulfolane or DMSO. FBPODS could be obtained in high yield only when an equivalent molar ratio of KOH to FHB was used. At the same time water generated during the reaction should be removed by azeotropic distillation with toluene. Otherwise, the water decreases the nucleophilicity of the resulting FHB potassium salt toward FPS and consequently it causes a decrease of the yield of FBPODS.

On the other hand, it has been reported that using anhydrous potassium carbonate instead of KOH can solve difficulties in stoichiometry and azeotrope,[18] and this was confirmed even in our work. That is, although anhydrous potassium carbonate was used in excess of 5.0–25 mol % without accompanying azeotropic distillation, FBPODS was obtained in a yield of 75–70%. The reaction temperature and time were dependent on the solvent used, but FBPODS was produced with the highest yield in the sulfolane solvent when the reaction temperature and the time were 160 °C and 6 h, respectively.

In the IR spectrum of Figure 1, FBPODS shows characteristic bands at 1650, 1250, and 1160 cm^{-1} assignable to aromatic ketone, ether, and sulfone groups, respectively. The structure of FBPODS was also confirmed by ^{13}C-NMR spectroscopy, in which the carbonyl carbon peak appears at 188 ppm and a number of characteristic bands between 162 and 110 ppm correspond to the aromatic carbons, as shown in Figure 2. The monomer had a sharp melting temperature at 162 °C in a DSC measurement. Its purity was reconfirmed by a HPLC analysis. The results of elemental analysis also match well with the presumed structure of FBPODS.

Synthesis of New Aromatic PESKs. The synthesis of PESKs was achieved through a polycondensation of

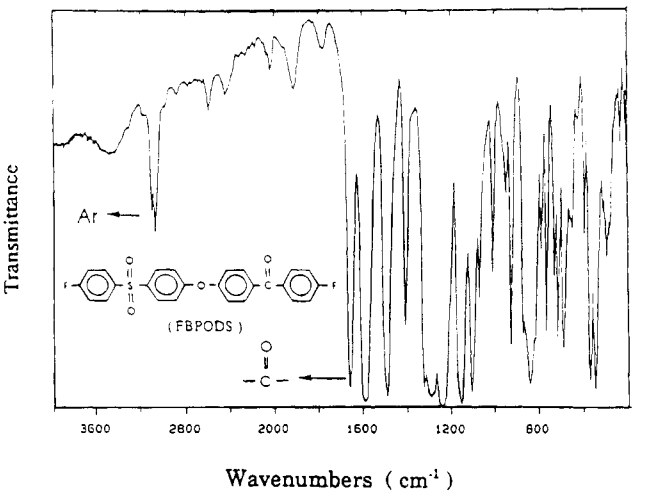


Figure 1. FT-IR spectrum of FBPODS.

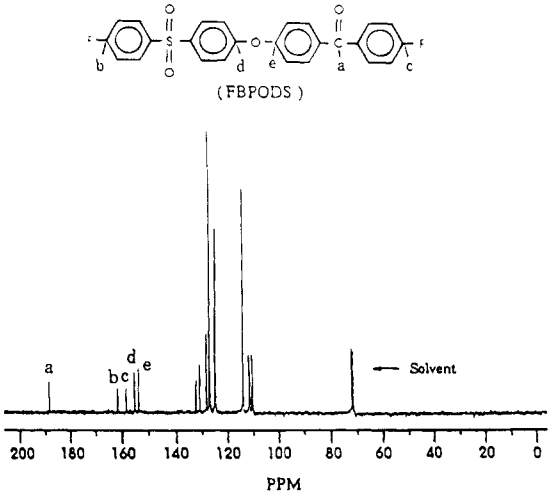


Figure 2. ^{13}C-NMR spectrum of FBPODS.

FBPODS, a new ordered-sequence aromatic difluoride, with conventional aromatic diols in dipolar aprotic solvent in the presence of a base, as shown in Scheme 1. BPA, hydroquinone, 4,4′-biphenol, resorcinol, and 2,6-naphthalenediol were used as aromatic diol monomers.

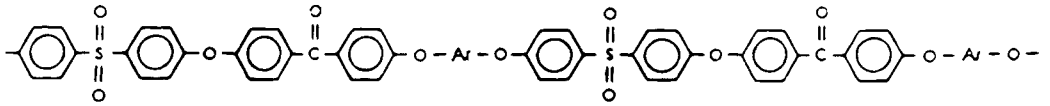
Table 1 shows a representative polymerization condition for the preparation of PESK-1 from BPA and FBPODS. In this study anhydrous potassium carbonate, a weak base, was employed to form a bisphenolate ion in the initial stage of polymerization. Unlike the strong base KOH, the use of potassium carbonate provides two main merits in the polymerization. One advantage lies in the fact that it is unnecessary to remove the water generated during the polymerization and the other is that the addition of excess potassium carbonate hardly causes any hydrolytic side reactions responsible for the formation of branched polymers. However, we found that we obtained the best results when potassium carbonate was in 1.0–5.0 mol % excess compared with the amount of aromatic diol used. On the contrary, when KOH, a strong base, was used, the lowest molecular weight polymers were obtained. This is probably due to the reported hydrolytic side reactions occurring via a hydrogen abstraction of phenoxide ion, which exists at the ends of growing polymer chains.[18,19] These branching reactions have also been reported to be dependent on polymerization temperature and time.[20] Therefore, both polymerization temperature and time

Table 3. Characterization Data for PESKs

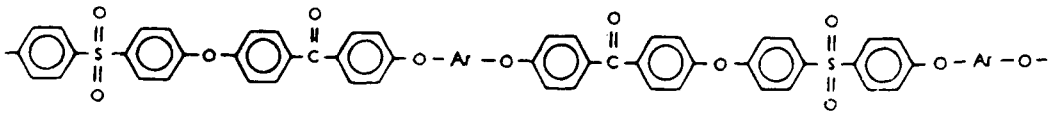
PESK	IR (KBr) (cm^{-1})	^{1}H-NMR[a] (ppm)	^{13}C-NMR[a] (ppm)	elem anal. % found	elem anal. % calcd
PESK-1	1650 (s, C=O) 1380 (s, CH_3) 1250 (s, −O−)	8.0−6.8 (m, ArH, 24H) 1.7 (s, CH_3, 6H)	157.0−112.0 (ArC, 36C) 189.0 (C=O) 25.7 (CH_3) 37.3 (−C−)	C: 74.30 H: 4.64 S: 5.31	C: 75.22 H: 4.73 S: 5.02
PESK-2	1650 (s, C=O) 1250 (s, −O−)	8.0−6.9 (m, ArH, 20H)	162.1−117.1 (ArC, 30C) 194.1 (C=O)	C: 71.48 H: 3.85 S: 6.02	C: 71.53 H: 3.87 S: 6.16
PESK-3	1650 (s, C=O) 1250 (s, −O−)	8.0−6.7 (m, ArH, 20H)	162.1−117.1 (ArC, 30C) 194.1 (C=O)	C: 71.50 H: 3.84 S: 6.09	C: 71.53 H: 3.87 S: 6.16
PESK-4	1650 (s, C=O) 1250 (s, −O−)	8.0−7.0 (m, ArH, 24H)	161.4−115.7 (ArC, 36C) 194.0 (C=O)	C: 72.90 H: 3.85 S: 5.75	C: 74.48 H: 4.05 S: 5.37
PESK-5	1650 (s, C=O) 1250 (s, −O−)	8.0−7.0 (m, ArH, 22H)	162.0−116.3 (ArC, 34C) 194.1 (C=O)	C: 73.52 H: 3.89 S: 6.48	C: 73.67 H: 3.89 S: 5.62

[a] In $CDCl_3$.

Chart 1



A



B

should be reduced to decrease the amount of branched polymers formed as much as possible.

We, however, have observed in this work that the effect of polymerization temperature and time on molecular weight was not very high, and molecular weight somewhat increased with increasing temperature from 160 to 220 °C. When the polymerization temperature was increased stepwise from the initial reaction temperature of 160 to 220 °C, the polymer produced was of the highest molecular weight. In addition, since FBPODS not only suppresses the formation of the branched polymers originating from the bisphenoxide ion of BPA but also plays an important role in controlling the molecular weight of the final polymers, it is preferred to use a slight excess (1.0−5.0 mol %) of FBPODS against aromatic diols.

The GPC chromatogram of PESK-1 exhibits one peak, indicating that no branching reactions occurred during polymerization.[20] Thus the PESKs derived from hydroquinone, resorcinol, biphenol, and 1,6-naphthalenediol were prepared under the same conditions as those of experiment 3 in Table 1. The weight-average molecular weights of the corresponding polymers were in the range of 41 000−106 000 except PESK-3 from resorcinol, as shown in Table 2. The molecular weight was observed to increase with increasing rigidity of the aromatic diols used: biphenol > naphthalenediol > hydroquinone > BPA > resorcinol. The PESKs show molecular weight distributions of 2.8−3.6, which are within the range of many polycondensed polymers.

Structure Analysis of Polymer. The structure of the PESKs was confirmed by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra and also by elemental analysis Table 3 shows the analytical data of the polymers and they coincide reasonably well with the structures shown in Table 2. However, the real chemical microstructure of the polymers is likely to consist of a random distribution of diad structures A (head-to-tail) and B (head-to-head) (Chart 1) due to the unsymmetrical structure of FBPODS and, thus, the difference in the relative reactivity of fluoride groups, which exist at both ends of the monomer and growing polymer chains, toward the phenoxide ions of the aromatic diols.

Table 4. Thermal Properties of PESKs and Specialty Engineering Plastics

PESK	T_g (°C)	initial decomp temp[a] (°C)	temp of 10% wt loss (°C)	char wt % at 700 °C
PESK-1	175	475	525	43
PESK-2	186	505	562	49
PESK-3	167	462	527	48
PESK-4	206	506	558	55
PESK-5	199	500	545	55
Udel-P1700	190	492	523	35
PES-5200P	220	497	555	47
PEEK-450P	144	547	577	56

[a] Temperature of 1.0% weight loss.

All the PESKs were found to be amorphous, supported by their wide-angle X-ray diffractograms and diffraction patterns, although they are not presented in this article. DSC thermograms also show no evidence for crystal melting, supporting that the present PESKs are of amorphous morphology. This is supposed to result from the structural irregularity along the chain and also from the introduction of the aryl sulfonyl linkage having a tetrahedral configuration,[13] which inhibits close packing of polymer chain and consequently suppresses crystallization.

Thermal Properties. Table 4 exhibits a comparison of the thermal properties of the PESKs with other conventional superengineering plastics. The thermal

properties of the present PESKs were compared with those of polysulfone (Udel-P1700, pellet from Amoco), PES-5200P (pellet from ICI), and PEEK-450P (powder from ICI). The glass transition temperatures (T_g) obtained by DSC for the PESKs ranged from 167 to 206 °C. It, especially, is necessary to note that the T_g values of PESK-1 and -2 from BPA and hydroquinone, respectively, are almost the average of the component T_g values of each pair of the polysulfone–PEK (T_g = 154 °C) and PES–PEEK commercial products. This verifies that the present PESKs have chemical structures of random sequence of an arylene ether ketone unit and an arylene ether sulfone unit, although they are composed of a random distribution of structures A and B.

Generally, T_g is known to depend on the rigidity of the polymer main chain: the increase of the rigidity of the polymer backbones increases the energy barrier for segmental motion and hence T_g increases. As expected, PESK-4 containing a biphenyl group in the polymer backbone reveals the highest T_g because of its rigidity. On the other hand, PESK-3 from resorcinol shows the lowest T_g, which results from the kink structure of the diol. PESK-5 shows a slightly lower T_g value than PESK-4 due to the slight kinky nature of the 1,6-naphthalenediol moiety when compared with the straight biphenyl moiety. PESK-2 from hydroquinone was observed to have a T_g about 11 °C higher than that of PESK-1. This is consistent with the earlier observation reported by Clendinning et al.[21]

From TGA thermograms, the PESKs were found to show high thermal stability as summarized in Table 4. On the basis of the temperatures for 1% weight loss, the initial decomposition temperature of the PESKs ranged from 462 to 506 °C depending on their structure. The temperature of 10% weight loss was in the range of 525–562 °C and all the PESKs displayed char yields of 43–55% at 700 °C under a nitrogen atmosphere. The thermal properties of PESK-1 and -3 were much inferior to those of the remaining PESKs, which is ascribed to the structural factors of BPA and resorcinol moieties.

Comparing these data with those of conventional advanced materials such as polysulfone, PES, and PEEK, all the PESKs showed a lower thermal stability than crystalline PEEK but a better stability than the corresponding amorphous polysulfone and PES. The order of thermal properties is as follows: PEEK > PESK-2, -4, -5 ≫ PES ≫ PESK-3 > PESK-1 ≫ PSF. In addition, the linear thermal expansion coefficients of the PESKs were about 10^{-5} m/m °C, in the same range as those of the conventional specialty engineering plastics.

Mechanical Properties. The mechanical properties of the PESKs were compared with those of commercially available advanced materials, Stabar-S100 (PES) and Stabar-XK300 (PEEK) films from ICI. Udel-P1700 (polysulfone) from Amoco and the PESKs were cast into thin films 40–90 μm thick from chloroform solution (5%). Mechanical tests were performed on four specimens (60 mm × 5 mm) for each sample.

Tensile properties of the PESKs and commercial products are shown in Table 5. Moduli of the PESKs had values between 2400 and 3100 MPa, which are comparable to those of commercially available samples. The modulus of PESK-4, in particular, was almost same as that of PEEK, which is well known for its excellent mechanical properties. In stress–strain curves, all the PESKs were observed to decrease in tensile stress at the yield point and thereafter to elongate. This demonstrates that the synthesized polymers have tough–

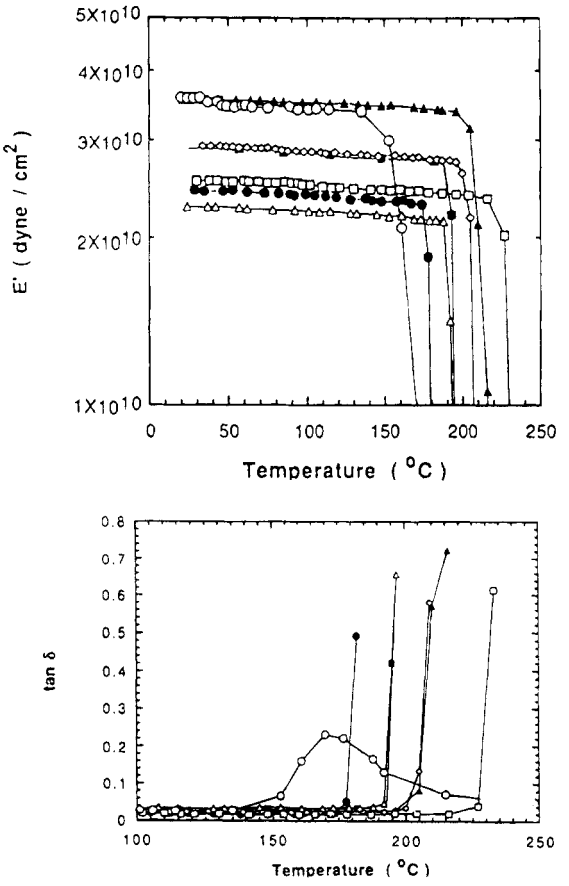


Figure 3. Storage tensile modulus and tan δ versus temperature of PESKs: (●), PESK-1; (■) PESK-2; (▲), PESK-4; (◇) PESK-5; (△), Udel-P1700; (□), Stabar-S100; (○), Stabar-XK300.

Table 5. Mechanical Properties of PESKs

PESK	modulus (MPa)	tensile stress at yield (MPa)	tensile stress at break (MPa)	elongation at break (%)
PESK-1	2400	76	65	5
PESK-2	2700	82	71	9
PESK-4	3100	88	80	20
PESK-5	2800	84	78	4
Udel-P1700	2100	75	61	26
Stabar-S100	2400	74	60	24
Stabar-XK300	3200	105	99	130

ductile mechanical properties. Except PESK-4, the elongation of the other PESKs, however, was not as high as expected. These abnormal results are believed to result, most probably, from the quality of the film specimens rather than the inherent property of the polymers.

The dynamic mechanical behaviors of the polymers are shown in Figure 3. The PESKs exhibited storage modulus values lying between those for amorphous polysulfone and crystalline PEEK. They also showed a rapid decrease in storage modulus at T_g. It is, moreover, worth noting that the storage modulus of PESK-4, similarly to that of PEEK, remains unchanged up to 206 °C, T_g. This indicates that PESK-4 has a very excellent dimensional stability. The storage moduli results showed a trend similar to that of the thermal behavior and tensile properties. The change of damping (tan δ) with time also revealed a good agreement with DSC results; that is, tan δ displayed a maximum value at T_g. It, therefore, can be emphasized that incorporating the aromatic ether ketone moiety, which is derived from

FBPODS, a sequentially ordered aromatic difluoride monomer, into the poly(arylene ether sulfone) backbone improves mechanical properties as well as thermal stability.

Solubility and Film Transparency. FBPODS was freely soluble in most organic solvents except methanol, water, *n*-hexane, and toluene. PESK-1 was soluble in common solvents such as chloroform, tetrahydrofuran, and 1,4-dioxane as well as polar solvents like *N,N*-dimethylformamide, DMSO, sulfolane, aniline, and *m*-cresol. However, other polymers were soluble only in chloroform, sulfolane, aniline, *m*-cresol, and *N,N*-dimethylformamide, and they were only swollen in DMSO.

The solvent-cast films showed a high optical transmittance of over 80% in the wavelength range 350–900 nm. Especially, the optical transparency of PESK-1 was over 95%, which is comparable to that of amorphous polysulfone, one of the best superengineering plastics in optical clarity. On the other hand, PESK-3 failed to produce a high-quality film because of its low molecular weight.

Other Properties. The PESKs had excellent electrical resistance: dielectric constants ranged from 3.03 to 3.08 and dissipation factors were approximately 10^{-3}. They also had low water absorptions of 0.19–0.27%, except PESK-5, exhibiting 0.5% absorption. Densities of the PESKs were in the range 1.30–1.34.

Conclusion

Synthesis of new amorphous poly(arylene ether sulfone ketones) was achieved through a nucleophilic aromatic substitution between a sequentially ordered aromatic difluoride monomer (FBPODS) and conventional aromatic diols. The resulting polymers with high optical transparency showed excellent thermal and mechanical properties, which are comparable to those of commercially available superengineering plastics such as polysulfone, PES, and PEEK. They show excellent promise as advanced materials for electronic and composite applications with high thermal and mechanical performances.

Acknowledgment. This work was supported by the Korea Ministry of Science and Technology (MOST), Grants N4830 and M3840.

References and Notes

(1) Rose, J. B.; Staniland, P. A. US Patent 4,320,224, 1982.
(2) Mijovic, J. *Polym. News* **1989**, *14*, 177.
(3) Critchley, J. P.; Knight, G. J.; Wright, W. W. *Heat Resistant Polymers*; Plenum Press: New York, 1983.
(4) Mullins, M. J.; Woo, E. P. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1987**, *C27* (2), 313.
(5) Day, M.; Suprunphuk, T.; Cooney, J. D.; Wiles, D. M. *J. Appl. Polym. Sci.* **1988**, *36*, 1097.
(6) Willats, D. J. *SAMPE J.* **1984**, *20*, 6.
(7) Griffiths, G. R.; Damon, J. W.; Lawson, T. T. *SAMPE J.* **1984**, *20*, 32.
(8) Wu, Z.; Zheng, Y.; Nakamura, T.; Yosomiya, R. *Makromol. Chem.* **1989**, *171*, 119.
(9) Harris, J. E.; Gavula, C. A. Eur. Pat. Appl. 166450, 1986.
(10) Wu, Z.; Zheng, Y.; Yan, H.; Nakamura, T.; Nozawa, T.; Yosomiya, R. *Makromol. Chem.* **1989**, *173*, 163.
(11) Lee, J.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *29*, 2189.
(12) Tullos, G. L.; Cassidy, P. E. *Macromolecules* **1991**, *24*, 6059.
(13) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, R. J.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1096.
(14) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.
(15) Risse, W.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4029.
(16) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2375.
(17) Seymour, R. B.; Kirshenbaum, G. S. *High Performance Polymers: Their Origin and Development*; Elsevier: New York, 1986.
(18) Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1827.
(19) Devaux, J.; Daoust, D.; Legras, R.; Dereppe, J. M.; Nield, E. *Polymer* **1989**, *30*, 161.
(20) Attwood, T. E.; King, T.; Mckenzie, I. D.; Rose, J. B. *Polymer* **1977**, *18*, 365.
(21) Clendinning, R. A.; EI-Hibri, M. J.; Matzner, M.; Kwiatkowski, G. T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (2), 166.

MA9411437