Fluorinated Poly(aryl thioether)s and Poly(aryl sulfone)s Derived from 2,3,4,5,6-Pentafluorobenzoic Acid

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ABSTRACT: Poly(aryl thioether)s (F-PTEs) containing 2,3,5,6-tetrafluoro-1,4-phenylene moiety and polar moiety, such as 1,3,4-ozadiazole, ether ketone, and amide groups, were synthesized by nucleophilic aromatic substitution reaction of aryl fluorides and 4,4′-thiobisbenzenthiol. F-PTEs were amorphous with good thermal properties including high glass transition temperature (T_g) and thermal stability, solubility, and hydrophobicity. F-PTEs were transformed into poly(aryl sulfone)s (F-PSs) by the oxidation reaction with hydrogen peroxide in acetic acid. Because of the sulfone group, the T_gs of the F-PSs were 30–40°C higher than those of the corresponding F-PTEs. F-PSs maintained solubility in polar aprotic solvents and exhibited hydrophobicity in spite of the content of polar sulfone groups due to the highly substituted fluorine atoms. These F-PTEs and F-PSs were a new class of high-performance polymers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 498–503, 2008

Key words: fluoropolymers; poly(aryl thioether); poly(aryl sulfone); high-performance polymers; pentafluorobenzoic acid

INTRODUCTION

Fluorinated aromatic polymers are characterized by many advantages such as their high glass transition temperature, excellent thermal stability, good solubility, high transparency, low dielectric constant, low moisture absorption, and so on. Many types of the fluorinated aromatic polymers have been synthesized as high-performance materials for optical and microelectronics devices, aerospace application, gas separation membranes.[1–4] Fluorinated aromatic polymers containing 2,3,5,6-tetrafluoro-1,4-phenylene moiety had been prepared from 2,3,4,5,6-pentafluorobenzoic acid (PFBA), such as poly(aryl ether ketone)s,[5] poly (aryl ether amide)s,[6] and poly(aryl ether oxadiazole)s.[7] The obtained polymers showed excellent solubility into less polar solvents such as toluene and chloroform, and could be cast into tough transparent films. They also exhibited high T_g and outstanding thermal stability. Recently, various types of fluorine-containing aromatic polymers such as poly(aryl ether ketone), poly(aryl ether sulfone), and poly(aryl ether phosphine oxide) containing 2,3,5,6-tetrafluoro-1,4-phenylene moiety have been synthesized for optical guide[8–11] and the demand for these fluorine-containing aromatic polymers is continuously increasing.

Sulfur-containing polymers also play an important role in the development of high-performance polymers. For instance, poly(aryl thioether)s (F-PTEs) and poly(aryl sulfone)s (F-PSs) are semicrystalline polymers with the characteristics of good thermooxidative stability, high glass transition temperature, and excellent mechanical properties including stiffness, dimensional stability, and high toughness.[12–15]

This article aims to describe the synthesis and characterization of F-PTEs and F-PSs derived from PFBA.

EXPERIMENTAL

Materials

PFBA was a gift from Nippon Shokubai (Osaka, Japan). 4,4′-Thiobisbenzenthiol (TBT) was obtained from Aldrich (St. Louis, MO) and purified by recrystallization from methanol. 2,5-Bis(2,3,4,5,6-pentafluorophenyl)-1,3,4-oxadiazole (**1a**),[16,17] 4,4′-bis(2,3,4,5,6-pentafluorobenzoyl)diphenyl (**1b**),[5] and 1,4-bis(2,3,4,5,6-pentafluorobenzamido)benzene (**1c**)[6] were synthesized from PFBA according to the literature procedures. *N,N*-Dimethylformamide (DMF) and 1-methy-2-pyrrolidinone (NMP) were purchased from Aldrich. DMF was purified by distillation over calcium hydride. NMP was used without further purification.
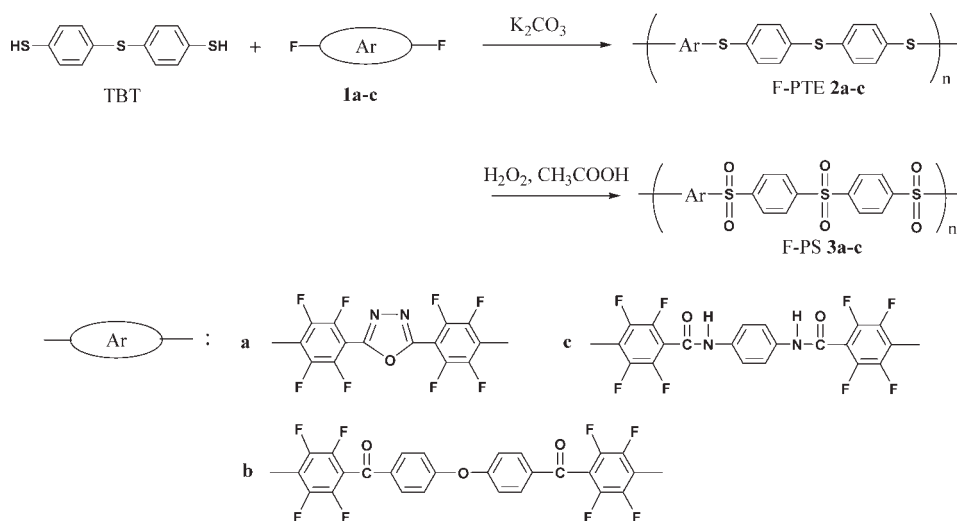
Scheme 1 Synthesis of F-PTEs and F-PSs.

Measurements

NMR spectra were recorded on a JOEL AL300 SC-NMR at 300 MHz (^{1}H) and 283 MHz (^{19}F). DMSO-d_6 and chloroform-d with a small amount of trifluoroacetic acid were used as the measuring solvents for monomers and polymers, respectively. 4,4′-Difluorobenzophenone was used as an internal standard for ^{19}F-NMR measurements. Infrared (IR) spectra were measured on a JASCO FT/IR-410 spectrometer. T_gs were measured by differential scanning calorimetry on a Perkin-Elmer DSC 7 at a scanning rate of 20°C min^{-1} in N$_2$. Temperature and heat flow were calibrated using indium and zinc as the standards. Thermal stability was measured by thermogravimetric analysis on a Perkin-Elmer TGA 7 at a heating rate of 20°C min^{-1} in N$_2$. Water contact angle of films was measured on a Kyowa Kaimen CA-D contact angle meter. Reduced viscosities (η_{sp}/C) were measured with an Ostwald-Fenske viscometer in NMP at a concentration of 0.5 dL g^{-1} at 25°C. Solubility tests were carried out at a concentration of 50 mg mL^{-1} in various solvents at 25°C.

General procedure for the synthesis of F-PTE

1a (1.00 g, 2.5 mmol), anhydrous potassium carbonate (0.40 g, 2.9 mmol), and DMF (20 mL) were taken in a three-neck round-bottom flask equipped with a Dean-Stark trap, a condenser, a magnetic stirrer, and a nitrogen inlet tube. The solution of TBT (0.62 g, 2.5 mmol) and DMF (13 mL) was slowly added through a dropping funnel at 25°C and the reaction mixture was stirred at 25°C for 15 min. Then, the reaction mixture was poured into rapidly stirred water containing 1 wt % acetic acid. The precipitated polymer was isolated by filtration and washed twice with water. After drying at 50°C under vacuum for 24 h, F-PTE **2a** was obtained as a powder (1.47 g, 93% yield).

General procedure for the synthesis of F-PS[15,18]

F-PTE **2a** (0.60 g) was suspended in 6.6 mL of 50% acetic acid and 4.5 mL of 30% aq. hydrogen peroxide by stirring. The mixture was heated at 100°C for 3 h. The product was filtrated, washed with methanol,

TABLE I
Results of Polymerizations[a]

| Polymer code | Polymerization conditions | | Yield (%) | η_{sp}/C^b (dL g^{-1}) | Insoluble residue[c] (wt %) |
	Temp. (°C)	Time (h)			
F-PTE **2a**	25	0.25	93	0.71	0.2
	25	1	88	Gelation	–
F-PTE **2b**	80	20	96	0.41	0
F-PTE **2c**	30	5	91	0.70	0

[a] Polymerizations were carried out in DMF at a concentration of 5.0 wt %.
[b] Reduced viscosities were measured in NMP at a concentration of 0.5 g dL^{-1} and 25°C.
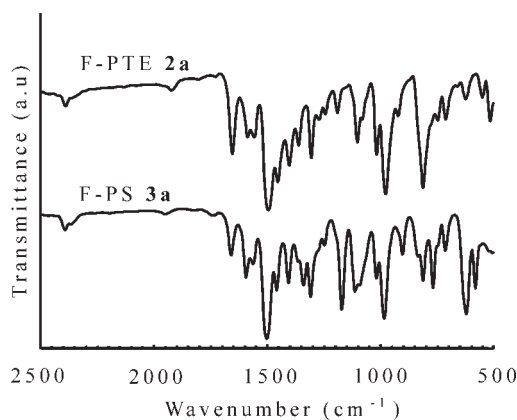[c] Insoluble part in NMP.

Figure 1 IR spectra of F-PTE **2a** and F-PS **3a**.

Figure 2 ^{19}F-NMR spectra of **1a** and F-PTE **2a**.

and dried at 50°C under vacuum for 24 h to give F-PS **3a**.

RESULTS AND DISCUSSION

Synthesis and characterization of F-PTEs

Fluorinated poly(aryl ether)s containing 2,3,5,6-tetra-fluoro-1,4-phenylene moiety had been prepared by the nucleophilic aromatic substitution reactions of **1a–c** and various bisphenoxides in the presence of potassium carbonate at low temperature.[5–7] In the preparation of poly(aryl ether)s, the polymerization temperature and time were of importance to prepare the linear polymers and avoid the crosslinking reaction at ortho positions of aryl fluorides. It is expected that the crosslinking reaction will occur more easily in the preparation of F-PTEs due to the higher nucleophilicity of bisthiophenoxide than bisphenoxide. Polymerization conditions were optimized to prepare uncrosslinked F-PTE as depicted in Scheme 1 and the results were presented in Table I. Polymerizations were carried out in DMF at a concentration of 5.0 wt % at various temperatures. Potassium carbonate was used to convert the TBT into the more reactive thiophenoxide. On the basis of the preparation of fluorinated poly(aryl ether)s,[5–7] the polymerization of **1a** with TBT was carried out at 80°C. The crosslinking reaction occurred rapidly and insoluble gels were formed. Then the polymerization was carried out at lower temperature. The polymerization proceeded even at 25°C and insoluble gels were formed after 1 h. The polymerization was stopped after 15 min. F-PTE **2a** was isolated by the precipitation into water containing 1 wt % acetic acid with the yield of 93%. The content of insoluble residues in NMP was only 0.2 wt % and η_{sp}/C was 0.71 dL g^{-1}. Flexible and tough film of F-PTE **2a** was obtained by the casting method as described later and this indicates that the η_{sp}/C of 0.71 dL g^{-1} was
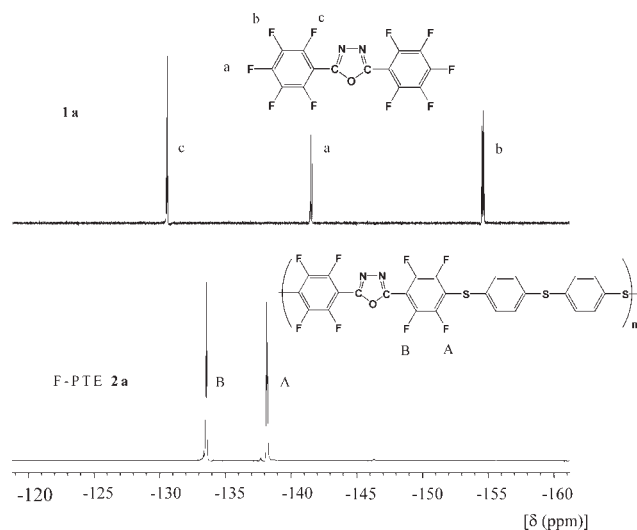
enough to make high molecular weight films. Figures 1 and 2 show IR and ^{19}F-NMR spectra of F-PTE **2a**. With respect to IR spectra, characteristic peaks of the 1,3,4-oxadiazole ring were observed at 1500 and 993 cm^{-1}, and a peak of the thioether linkage was also done at 810 cm^{-1}. In the ^{19}F-NMR spectrum, only two peaks were clearly detected at δ of −133.4 and −138.2 ppm, corresponding to aromatic fluorine atoms at ortho and meta position to the 1,3,4-oxadiazole ring. The peak at −141.3 ppm corresponding to
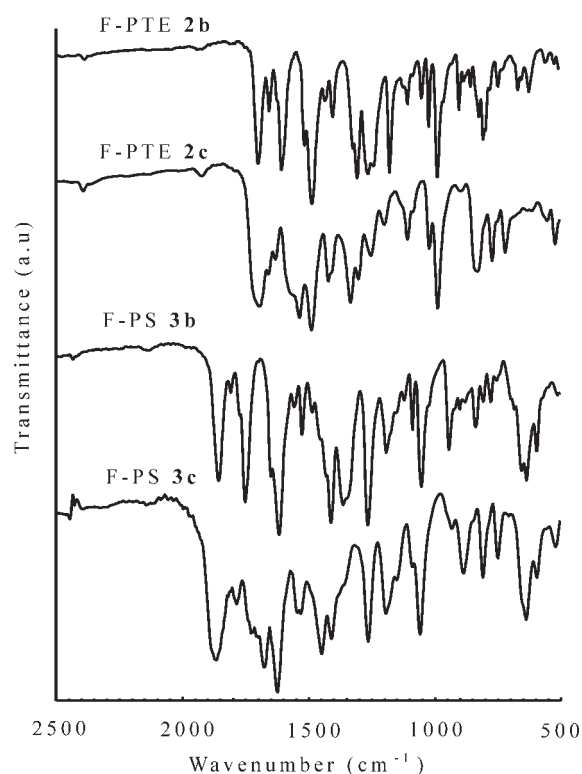

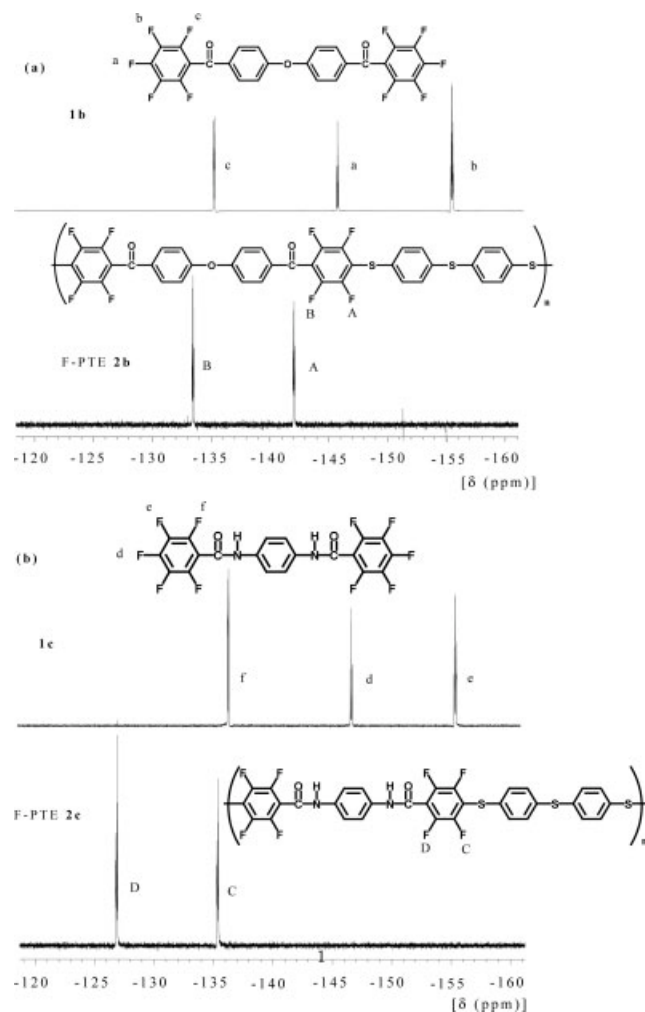**Figure 3** IR spectra of F-PTE **2b**, **2c**, F-PS **3b**, and **3c**.

Figure 4 ^{19}F-NMR spectra of (a) **1b** and F-PTE **2b**, and (b) **1c** and F-PTE **2c**.

TABLE II
Results of Solubility Test[a]

Polymer code	H$_2$SO$_4$[a]	NMP	DMAc	THF	CHCl$_3$	Toluene
F-PTE **2a**	+	+	+	+−	+−	−
F-PS **3a**	+	+	+	−	−	−
F-PTE **2b**	+	+	+	−	−	−
F-PS **3b**	+	+	+	−	−	−
F-PTE **2c**	+	+	+	−	−	−
F-PS **3c**	+	+	+	−	−	−

Solubility tests were carried out at a concentration of 0.5 g dL^{-1} and 25°C.
+: soluble; +−: partially soluble; −: insoluble.
[a] H$_2$SO$_4$, NMP, DMAc, THF, CHCl$_3$, and toluene are the solvents used.

tion conditions of **1b** and **1c** with TBT were also optimized, and soluble F-PTE **2b** and **2c** were obtained at 80°C for 20 h and at 30°C for 5 h with the η_{sp}/C of 0.41 and 0.70 dL g^{-1}, respectively. The chemical structures of F-PTE **2b** and **2c** were also analyzed by IR and ^{19}F-NMR spectra as shown in Figures 3 and 4. These spectra reveal that F-PTE **2b** and **2c** were also para-connected linear structures.

Quantitative solubility of the obtained polymers was determined in excess of solvents. F-PTEs have high solubility in 97% sulfuric acid and polar aprotic solvents such as NMP and N,N-dimethylacetoamide (DMAc) as shown in Table II. F-PTE **2a** was partially soluble into THF and chloroform. Thermal properties such as T_g and thermal stability of F-PTEs were summarized in Table III. T_gs were in the range of 148–183°C. F-PTE **2c** containing amide linkages possesses higher T_g due to the hydrogen bonding effect. These polymers did not possess melting temperature and they were amorphous. The 10% wt loss temperatures in N$_2$ of F-PTEs **2a** and **2b** were 501 and 541°C, respectively. Char yields at 600°C in N$_2$ were 56 and 72%. They exhibited excellent thermal stability. The 10% wt loss temperature and the char yield of F-PTE **2c** were 382°C and 39%, respectively. F-PTE **2c** exhibited slightly lower thermal stability

the fluorine atoms para to the 1,3,4-oxadiazole ring in **1a** was not completely detected. These spectra showed that the nucleophilic aromatic substitution occurred only at the carbons para to 1,3,4-oxadiazole ring in **1a** up to 15 min and the resulting F-PTE **2a** was para-connected linear structure. The polymeriza-

TABLE III
Characterization of Various Polymers

Polymer code	η_{sp}/C[a] (dL g^{-1})	Content of sulfone group (%)	T_g[b] (°C)	TGA[a]		Water contact angle (°)
				10 wt % loss temperature (°C)	Char yield[c] (wt %)	
F-PTE **2a**	0.71	0	148	501	56	90.1
F-PS **3a**	0.39	82	188	416	60	90.2
F-PTE **2b**	0.41	0	166	540	72	90.3
F-PS **3b**	0.24	70	175	446	65	−[d]
F-PTE **2c**	0.70	0	183	382	39	90.5
F-PS **3c**	0.59	70	215	413	54	90.0

[a] TGA was performed with a heating rate of 20°C min^{-1}.
[b] T_gs were measured on DSC with a heating rate of 20°C min^{-1}.
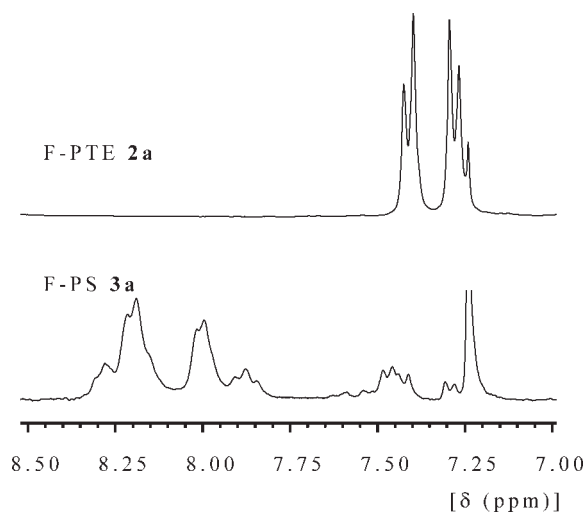[c] Char yield at 600°C in N$_2$.
[d] Not measured.

Figure 5 ^{1}H-NMR spectra of F-PTE **2a** and F-PS **3a**.

than F-PTE **2a** and **2b** due to the less thermal stability of amide linkage than 1,3,4-oxadiazole ring, ether linkage, and ketone linkage.

Transparent, flexible, and tough films of the F-PTEs could be obtained by the casting method from NMP solutions. Water contact angle was measured on the film surfaces as also presented in Table III. The angles of F-PTEs were higher than 90°, ranging from 90.1° to 90.5°, and they were hydrophobic due to the existence of fluorine atoms.

Conversion and characterization of F-PSs

F-PSs **3a–c** were prepared by oxidation of corresponding F-PTEs **2a–c** as depicted in Scheme 1. From the viewpoint of the convenience for the preparation of F-PTEs, the chemical conversion to F-PSs is of great advantage.[15,18,19] A typical example is the synthesis of F-PS **3a** by the oxidation of F-PTE **2a** with hydrogen peroxide in acid medium. The oxidation reactions were carried out in suspension of F-PTE **2a** in acetic acid with hydrogen peroxide at

100°C. The IR spectrum of F-PS **3a** is shown in Figure 1. Characteristic peaks of the 1,3,4-oxadiazole ring were clearly observed at 1500 and 993 cm^{-1}. A peak of the thioether linkage at 810 cm^{-1} was still observed but the relative peak intensity became smaller compared with F-PTE **2a**. Peaks at 1326 and 1160 cm^{-1} were newly detected in F-PS **3a**, which were assignable to sulfone groups. Completion of the reaction was confirmed by ^{1}H-NMR studies. A comparison of ^{1}H-NMR spectra of F-PTE **2a** and F-PS **3a** is shown in Figure 5. Because of the strong electron withdrawability of sulfone group, proton signals adjacent to the sulfone groups moved to much lower field at δ of 7.75–8.50 ppm compared with the corresponding F-PTE. However, the signals at δ of 7.10–7.70 ppm were observed with the weak intensity, and they are assignable to the proton signals adjacent to the sulfoxide groups[20] and unreacted sulfide groups. The molar ratio of sulfone, sulfoxide, and sulfide groups were estimated by ^{1}H-NMR and summarized in Table IV. The molar ratio of sulfone group increased with time and it became 82% after 3 h. The molar ratio of sulfone groups was leveled off at 3 h, but the η$_{sp}$/C and the recovery yield decreased with time due to the polymer chain scission. The optimal condition was determined as 100°C for 3 h. F-PS **3a** prepared under this condition contained 82% of sulfone groups, 15% of sulfoxide groups, and 3% sulfide groups. F-PSs **3b** and **3c** were also converted from F-PTEs **2b** and **2c** by the oxidation at 100°C for 3 h and 100°C for 2 h, respectively. Conversion to sulfone and the chemical structures of F-PS **3b** and **3c** were confirmed by IR as shown in Figure 3 and the molar ratio of sulfone, sulfoxide, and sulfide groups estimated by ^{1}H-NMR were also summarized in Table IV. F-PS **3c** containing amide linkages was not stable in the acid medium due to the hydrolysis of amide linkages. The residual ratio of sulfide groups in F-PS **3b** was the highest than the others. It is well known that the sulfide groups adjacent with the electro withdrawing

TABLE IV
Results of Oxidation[a]

Polymer code	Time (h)	Recovery yield (%)	η$_{sp}$/C[b] (dL g^{-1})	Content (%)		
				—SO$_2$—	—SO—	—S—
F-PS **3a**	1	92	0.42	55	39	6
	3	87	0.39	82	15	3
	5	47	—[c]	82	17	1
F-PS **3b**	3	80	0.24	70	9	21
F-PS **3c**	2	81	0.59	70	27	3
	3	27	—[c]	67	27	6

[a] Oxidation reactions were carried out at 100°C.
[b] Reduced viscosities were measured in NMP at a concentration of 0.5 g dL^{-1} and 25°C.
[c] Not measured.

TABLE V
^{19}F-NMR Chemical Shifts of Monomers

Monomer code	^{19}F chemical shift[a] (ppm)		
	ortho	meta	para
1a	−131.5	−155.0	−142.5
1b	−144.3	−164.0	−154.5
1c	−136.2	−155.7	−147.0

[a] ^{19}F chemical shifts were reported in ppm relative to 4,4′-difluorobenzophenone (−101.1 ppm).

group are more susceptible for the oxidation reaction. To clarify the susceptibility for the oxidation reaction, ^{19}F chemical shifts of **1a–c** were investigated as summarized in Table V. ^{19}F spectroscopy can be used to probe the π-electron density at the actual site of reaction and it is a sensitive tool in regards to the nucleophilic aromatic substitution.[21–26] ^{19}F chemical shift is corresponding to the π-electron density and the fluorine shifting lower field is more reactive for the oxidation reaction due to the higher electrophilicity. As shown in Figures 2 and 4, the chemical shifts of fluorine atoms para position of **1a**, **1b**, and **1c** are −142.5, −154.5, and −147.0 ppm, respectively. These results strongly indicate that the sulfide groups in **1a** and **1c** are more susceptible to the oxidation reaction than those in **1b**, and this result is identical with the residual content of sulfide groups.

Although F-PSs were slightly less soluble than the corresponding F-PTEs, they still exhibited good solubility into 97% sulfuric acid, NMP, and DMAc due to the 2,3,5,6-tetrafluoro-1,4-phenylene moiety as also shown in Table II. Because of the introduction of the sulfone group, T_gs of F-PSs are 30–40°C higher than those of the corresponding F-PTEs. Ten percent wt loss temperatures in N_2 of F-PS **3a–c** were from 413 to 446°C, and char yields at 600°C in N_2 were in the range of 54–65 wt %. They also exhibited excellent thermal stability.

F-PS **3a** and **3c** were coated on glass plates and the water contact angle was measured on the coated surface. FS-PS **3b** did not form uniform and smooth film surface on the glass plate and the contact angle of PF-**3b** could not measured. The angles were also higher than 90.0° and they still maintained the hydrophobicity in spite of the presence of polar sulfone groups.

CONCLUSIONS

F-PTEs containing 2,3,5,6-tetrafluoro-1,4-phenylene moiety were obtained by the low-temperature nucleophilic aromatic substitution reaction. They were amorphous polymers with outstanding thermal properties including high T_g and thermal stability, solubility into polar aprotic solvents such as NMP and DMAc, and hydrophobicity. F-PTEs were transformed into F-PSs by the oxidation reaction with hydrogen peroxide in acetic acid. F-PSs also exhibited higher T_gs and hydrophobicity in spite of the presence of polar sulfone groups due to the highly substituted fluorine atoms.

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