

Synthesis of Novel Fluorine-Containing Poly(aryl ether nitrile)s Derived from 2,3,4,5,6-Pentafluorobenzonitrile

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ABSTRACT: 2,3,4,5,6-Pentafluorobenzonitrile (PFBN) is a valuable intermediate and it is available as a commercial product. In this paper, synthesis and characterization of novel fluorinated poly(ether nitrile)s (PEN) derived from PFBN is reported. Novel fluorinated PENs containing fluorine atoms in the main chain and pendant phenoxy group (2F-PEN) are synthesized by aromatic nucleophilic substitution reaction, of which M_n ranges from 1.77×10^4 to 5.16×10^4 . The obtained PENs show excellent solubilities in common solvents, and 2F-PEN(6FBA) and 2F-PEN(DPE) can be cast as tough transparent films. These polymers have high thermal stabilities with the 5% weight loss temperature in the range 509–562°C and the T_g of 142–235°C, which is highly dependent on the structures.

KEY WORDS Poly(ether nitrile) / Fluorine-Containing Polymer / 2,3,4,5,6-Pentafluorobenzonitrile / Nucleophilic Aromatic Substitution / Thermal Stability / High T_g / Solubility /

The high-performance fluorinated polymers have been receiving considerable attention as interesting advanced materials for applications as films, coatings for optical and microelectronics devices, gas separation membranes and so on.^{1–3} The incorporation of fluorine atoms into polymer chains leads to polymers with increased solubility, flame resistance, thermal stability and glass transition temperature, while also leading to decreased color, crystallinity, dielectric constant and moisture absorption. Owing these advantages, poly(aryl ether ketone)s (PEK) containing hexafluoroisopropylidene units had been prepared and studied for use in aerospace and electronic applications.⁴ Recently, PEKs containing 2,3,5,6-tetrafluoro-1,4-phenylene moieties were synthesized from perfluorobenzophenone.⁵

2,3,4,5,6-Pentafluorobenzoic acid (PFBA) is a valuable intermediate for pharmaceuticals, pesticides, perfumes, cosmetics and so on, and it is available as a commercial product. The authors had reported the synthesis and characterization of novel fluorinated PEKs containing 2,3,5,6-tetrafluoro-1,4-phenylene moieties derived from PFBA.^{6,7} These fluorinated PEKs showed excellent thermal stability and solubility into common organic solvents. Moreover, the films of these PEKs possess outstanding transparency and low dielectric constants. Therefore they are expected to use a optical and electronic materials and the application study is currently underway.

2,3,4,5,6-Pentafluorobenzonitrile (PFBN) is a raw material of PFBA and its commercial availability is much higher than PFBA. 2,6-Difluorobenzonitrile is commonly used as a monomer for poly(ether nitrile)s (PEN)⁸ and other types of fluorinated PENs had been previously synthesized from 2,4,5,6-tetrafluoroisophthalonitrile and bisphenols by interfacial polycondensation.⁹ However, polymers derived from PFBN have not been reported

to our knowledge. In this paper, synthesis and characterization of novel fluorinated PEN derived from PFBN is reported.

EXPERIMENTAL

Materials

PFBN was a gift from Nippon Shokubai Co. Ltd. Phenol, 2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (6FBA), 2,2-bis(4-hydroxyphenyl)propane (BisA), hydroquinone (HQ), phenolphthalein (PP), 4,4'-dihydroxydiphenyl ether (DPE), 1,4-bis(4-hydroxyphenyl)cyclohexane (CHB) and 4,4'-dihydroxybiphenyl (BP) were obtained from Aldrich Chemical Co., Inc. 9,9-bis(4-hydroxyphenyl)fluorene (HF) was obtained from Kennedy and Klim. Co., Inc. Bisphenols were purified by recrystallization. *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich Chemical Co. Inc. and used as received.

Synthesis of 4-Phenoxy-2,3,5,6-tetrafluorobenzonitrile (PTFB)

Into a 100 mL of three-neck flask equipped with a Dean-Stark trap, a condenser and a nitrogen inlet tube were placed 5.0 g of phenol (0.053 mol), 3.7 g of potassium carbonate (0.027 mol), 60 mL of NMP and 10 mL of toluene. The mixture was refluxed for 2 h with eliminating by-produced water by azeotropic distillation and then toluene was distilled over. The mixture was allowed to cool at 80°C and then 10.3 g of PFBN (0.053 mol) was added into the mixture. The reaction was allowed to keep at 80°C for 12 h. The reaction mixture was allowed to cool to room temperature and then poured into 200 mL of water, which was extracted with dichloromethane. The organic layer was collected, washed with water,

dried over sodium sulfate, filtered and evaporated. The unreacted PFBN was stripped off by distillation under reduced pressure and then the residual solids were recrystallized from ethanol. White crystals of 4-phenoxy-2,3,5,6-tetrafluorobenzonitrile (PTFB) were obtained at 5.4 g (38%). The product characteristics were as follows; T_m : 67–68°C, FT-IR (KBr) (cm^{-1}): 3047, 2932, 2243, 1651, 1593, 1492, 1437, 1319, 1203, 1169, 1119, 1074, 995, 957, 920, 781, 752, 735, 687.

Polymerization

Polymerization of PTFB with 6FBA is given as a typical example as follows. 1.26 g of 6FBA (3.74 mmol), 0.57 g of potassium carbonate (4.12 mmol), 8 mL of NMP and 10 mL of toluene were placed into a 50 mL of three-neck flask equipped with Dean–Stark trap, condenser, magnet stirrer and nitrogen inlet tube. The mixture was refluxed for 2 h with eliminating by-produced water by azeotrop distillation and then toluene was distilled over. The mixture was allowed to cool at 80°C and then 1.0 g of PTFB (3.74 mmol) was added into the mixture. The polymerization was allowed to keep at 80°C for 20 h. The reaction mixture was allowed to cool to room temperature and poured into rapidly stirred deionized water containing 1 wt% acetic acid to precipitate the polymer. The polymer was isolated by filtration, washed twice with deionized water and dried. The polymer {2F-PEN(6 FBA)} was purified by the reprecipitation of DMAc solution to methanol. The product characteristics were as follows. T_g : 163°C, FT-IR (KBr) (cm^{-1}): 3059, 2239, 1593, 1508, 1475, 1230, 1180, 1136, 1001, 962, 933, 831, 752, 696.

Characterization

NMR spectra were recorded on an Varian Unity-500 operating at 500 MHz (^1H), 125 MHz (^{13}C) and 470 MHz (^{19}F). CDCl_3 and $\text{DMSO}-d_6$ were used as the measuring solvents for monomer and polymers. In some cases, hexafluoroisopropanol was added into the solution to dissolve the samples completely. 4,4'-Difluorobenzophenone was used as an internal standard for ^{19}F NMR measurements. FT-IR measurements were performed on JASCO FT-IR 350. Glass transition temperature (T_g) was measured on a Perkin–Elmer DSC 7 at a scanning rate of $20^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Temperature and heat flow were calibrated using indium and zinc as the standards. Thermal stability was measured on a Perkin–Elmer TGA 7 at a heating rate of $20^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Reduced viscosity measurements were determined by using an Ostwald-Fenske viscometer in DMAc at a concentration of 0.5 g dL^{-1} and 25°C . Molecular weights were measured by TOSOH 8020 GPC. NMP was used as an eluent and column temperature was 40°C . Molecular weights were calculated with polystyrene standard. Dynamic mechanical measurement was performed on Orientech Rheovibron DDV-II-EP at 110 Hz with a scanning rate of 2°C min^{-1} .

RESULTS AND DISCUSSION

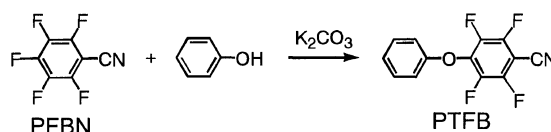
Monomer Synthesis

PFBN has three reactive positions for nucleophilic aromatic substitution reaction, that is, two *ortho*

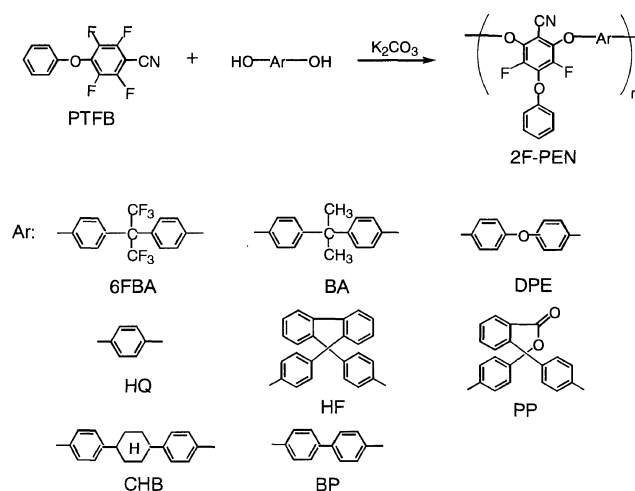
positions and one *para* position to cyano group. Multifunctional PFBN leads to crosslinking reaction during synthesis of PEN. Therefore, PTFB is designed in which the *para* position of PFBN is substituted by phenoxy group, and hence linear PENs can be obtained by the reaction between PTFB and bisphenols at *ortho* positions to cyano group of PTFB. PTFB was synthesized from PFBN and phenoxide by aromatic nucleophilic substitution as shown in Scheme 1. When the reaction was carried out over 100°C , phenoxide substituted at not only *para* position but *ortho* position. Hereby a small amount of diphenoxybenzonitrile was contaminated. The reaction was performed at 80°C to yield the only *para* substituted benzonitrile even though the yield became lower which was 38%. The chemical structure of PTFB was confirmed by ^1H , ^{13}C , ^{19}F NMR, and FT-IR spectroscopy. The spectrum of ^{19}F , ^1H NMR, and FT-IR are illustrated in Figures 1–3. Two peaks are observed in ^{19}F NMR spectrum at -140.7 and -122.2 ppm corresponding to two *meta* fluorines and two *ortho* fluorines to cyano group, respectively. In ^1H NMR spectrum, there exists three peaks at 7.36, 7.19, and 6.99 ppm corresponding to two *meta* protons, one *para* proton and two *ortho* protons to ether linkage, respectively. The peak of cyano group is clearly observed at 2243 cm^{-1} in FT-IR spectrum.

Polymer Synthesis

Novel eight PENs are synthesized from PTFB (2F-PEN) as shown in Scheme 2. Nucleophilic aromatic substitution polymerizations are typically performed in a high-boiling aprotic polar solvent in the presence of a base at high temperature. Polymerizations are carried out in NMP. The solids compositions are maintained at 25%. The potassium carbonate is used to convert the bisphenol into the more reactive anion. Irrespective of



Scheme 1. Monomer synthesis.



Scheme 2. Synthesis of fluorine-containing poly(ether nitrile)s.

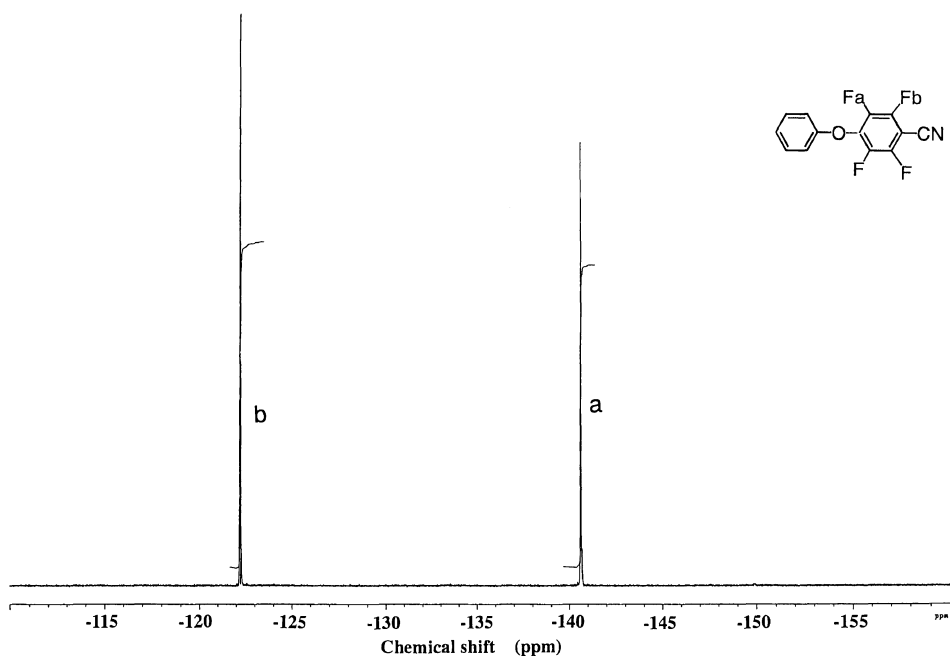


Figure 1. ^{19}F NMR spectrum of PTFB.

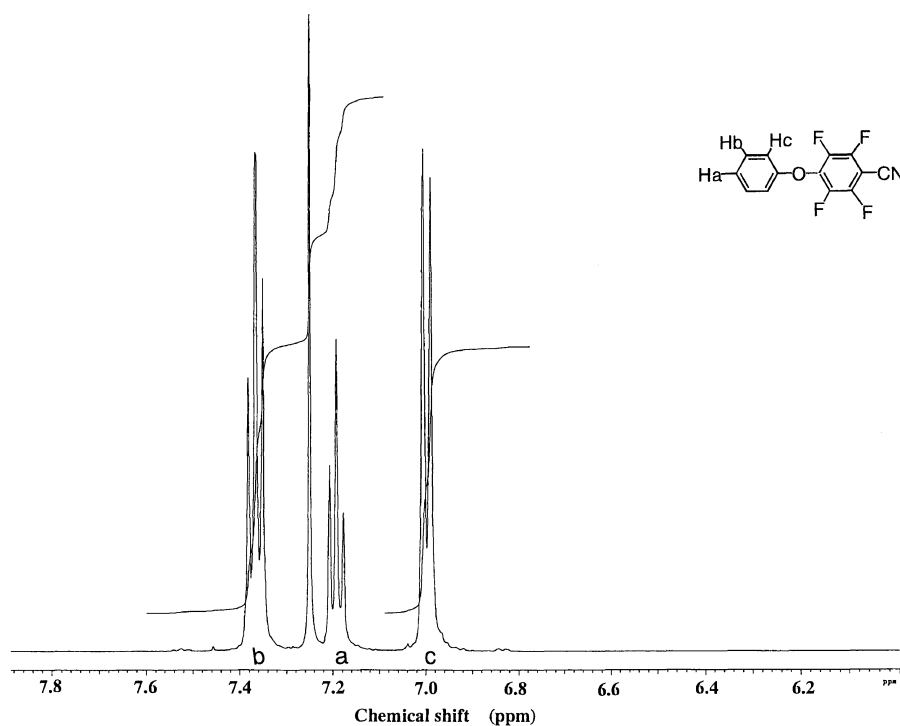


Figure 2. ^1H NMR spectrum of PTFB.

the solvents, toluene is used during the initial stages of the polymerizations to remove water generated by phenoxide formation as a toluene azeotrope.

Table I summarizes the results of polymerization. The polymerization of PTFB with 6FBA over 100°C yielded gels due to the crosslinking reaction, in which bisphenoxide substitutes at not only *ortho* position but *meta* position to cyano group in PTFB. In order to avoid the gelation, the polymerization was carried out at 80°C . The soluble 2F-PEN (6FBA) are obtained, of which the

viscosity is 0.66 dL g^{-1} . The polymerization of PTFB with other bisphenols was also carried out at 80°C . The soluble 2F-PENs were obtained, of which the viscosities range from 0.22 to 1.27 dL g^{-1} . The M_n s of these 2F-PENs range from 1.77×10^4 to 5.16×10^4 and the molecular weight distribution M_w/M_n are 2.02 – 6.81 . Among them, 2F-PEN (6FBA) and 2F-PEN (DPE) can be cast from toluene solutions into tough transparent films. The polymer structures are analyzed by ^{19}F , ^1H NMR, and FT-IR. ^{19}F and ^1H NMR spectra of 2F-PEN (6FBA) are

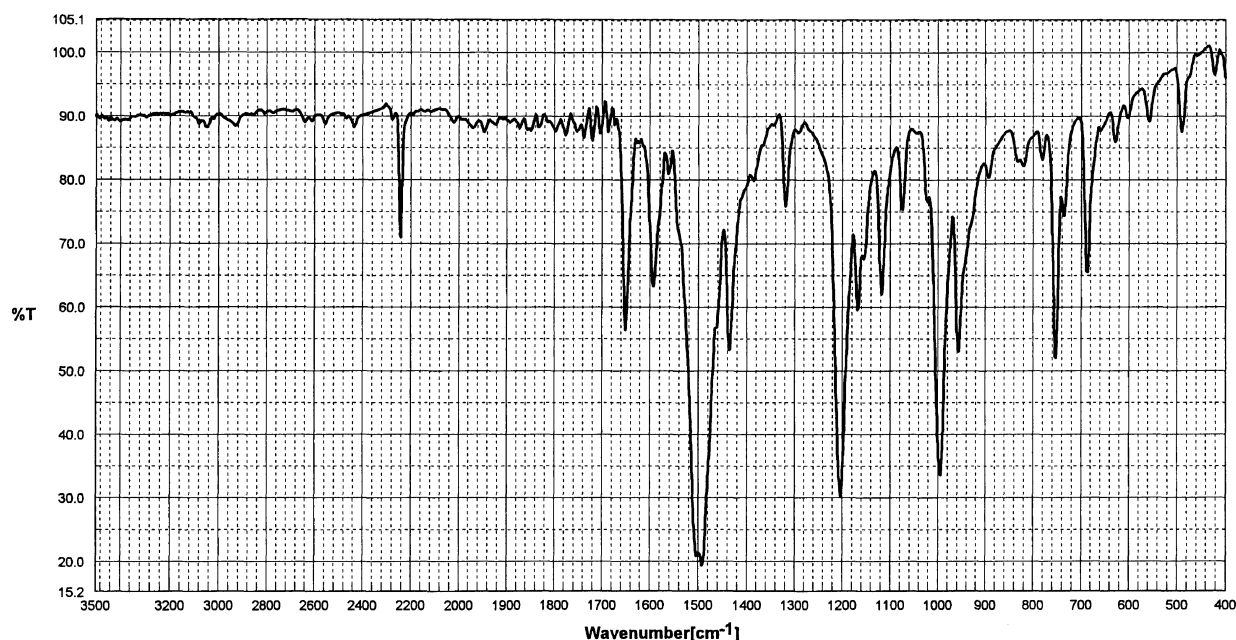


Figure 3. FT-IR spectrum of PTFB.

Table I. Polymerization of 4-phenoxy-2,3,5,6-tetrafluorobenzonitrile with various bisphenols^a

Polymer Code ^b	Temp.	Con.	Yield ^c	η_{sp}/c^d	M_n^e	M_w^e	M_w/M_n^e
	°C	wt/vol%	%	dL g ⁻¹	($\times 10^4$)	($\times 10^4$)	
2F-PEN-6FBA	80	25	86.0	0.66	5.16	29.07	5.63
2F-PEN-PP	80	25	94.9	0.44	2.82	11.22	3.98
2F-PEN-BisA	80	25	86.8	0.35	2.19	6.34	2.90
2F-PEN-HF	80	25	93.5	0.32	1.92	7.96	4.13
2F-PEN-HQ	80	25	85.5	0.34	2.00	4.03	2.02
2F-PEN-CHB	80	25	87.4	0.22	1.77	3.86	2.17
2F-PEN-DPE	80	25	87.1	1.27	2.98	20.33	6.81
2F-PEN-BP	80	25	90.7	0.57	3.17	7.57	2.39

^a Polymerizations were carried out in NMP for 20 h. ^b Polymer codes are shown in Scheme 2. ^c After purification by reprecipitation. ^d Viscosities were measured in DMAc at a concentration of 0.5 g dL⁻¹ and 25 °C. ^e Measured by GPC. Molecular weights are relative to polystyrene standards.

Table II. Solubility of 2F-PENs

Polymer code ^a	2F-PEN							
	6FBA	PP	BisA	HF	HQ	CHB	DPE	BP
Solubility ^b								
NMP	++	++	++	++	++	++	++	++
DMAc	++	++	++	++	++	++	++	++
Chloroform	++	++	++	++	+	++	++	++
THF	++	++	++	++	++	++	++	++
Toluene	++	++	++	++	+-	++	++	-

^a Polymer codes are shown in Scheme 2. ^b ++ Soluble at 25 °C, + soluble at 100 °C, +- partially soluble or swelling, - insoluble.

illustrated in Figures 4 and 5 as examples. Three peaks are observed in ¹⁹F NMR spectrum at -54.3 and -128.5 ppm corresponding to six aliphatic fluorines and two aromatic fluorines at *meta* position to cyano group, respectively. In ¹H NMR spectrum, there exists two peaks at 6.9–7.4 ppm corresponding to five different aromatic proton. The peak of cyano group is clearly observed at 2239 cm⁻¹ and the peak of ether linkage appear at 1230 cm⁻¹ in FT-IR spectrum of 2F-PEN (6FBA) as shown in Figure 6. It becomes clear from these results that nucleophilic aromatic substitution takes place at both *ortho*

positions to cyano group of PTFB and 2F-PEN (6FBA) has a linear structure without crosslinking.

Characteristics

Qualitative solubilities of the new 2F-PENs were determined in excess of solvents. Table II summarizes the results of solubilities. The 2F-PENs show good solubilities in aprotic polar solvents. Especially, 2F-PEN (6FBA), 2F-PEN (PP), 2F-PEN (BisA), 2F-PEN (HF), 2F-PEN (CHB), and 2F-PEN (DPE) exhibit wider solubilities in chloroform and toluene. PEN containing no fluo-

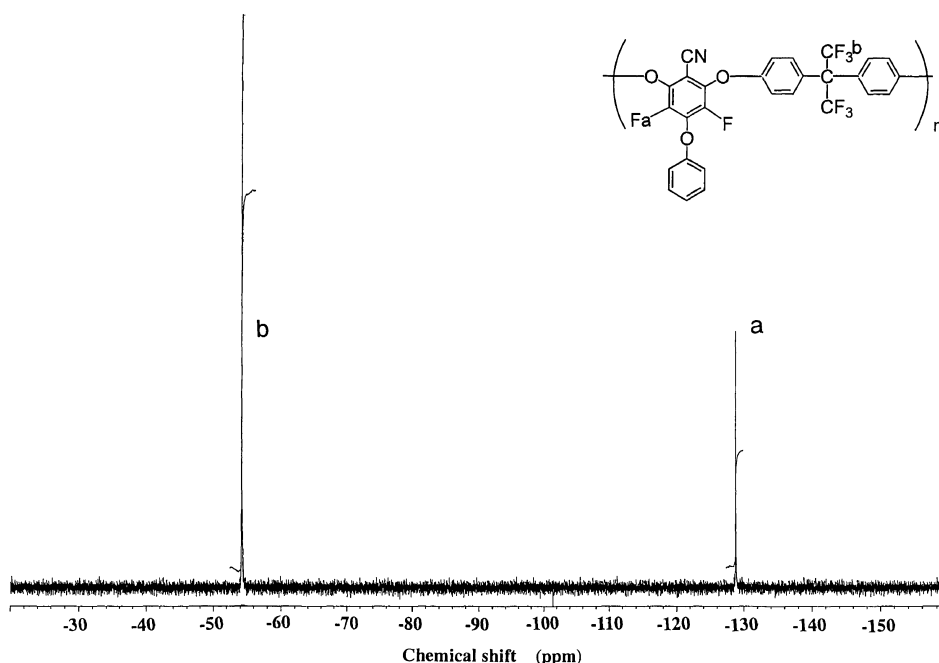


Figure 4. ^{19}F NMR spectrum of 2F-PEN (6FBA).

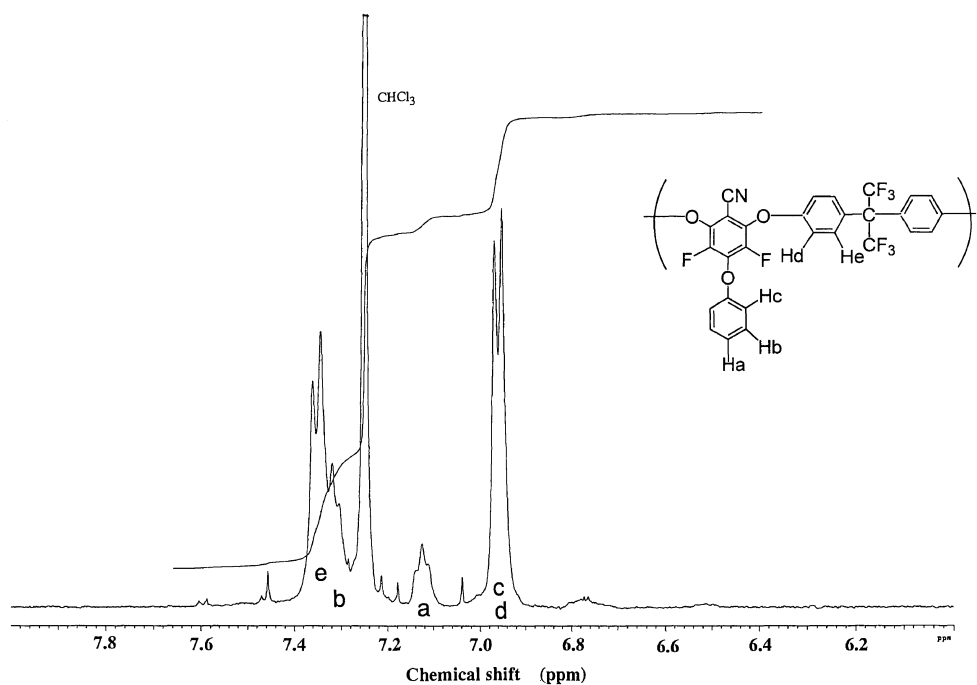


Figure 5. ^1H NMR spectrum of 2F-PEN (6FBA).

rine atoms is soluble only in polar solvents such as NMP and DMAc.⁸ The fluorine atoms, 1,3-connection of the back bone and furthermore, bulky phenoxy groups are the reasons to enhance the solubility very much.

Thermal properties are summarized in Table III. The T_g of the obtained fluorine-containing PENs is in the range 142–235°C depending on the chemical structures. Among them, 2F-PEN (HF) and 2F-PEN (PP) possess significantly high T_g and it is attributed to the presence of the large cyclic side groups in the polymer chain which is consistent with the previous work.⁵ 2F-PENs

obtained in this study do not show the endothermic peak on DSC profiles corresponded to melting and they are amorphous polymers.

Thermal stability was measured by TGA. The 5% weight loss in a nitrogen atmosphere is quite high, which is in the range 509–562°C. The char yields at 600°C in a nitrogen atmosphere are over 60% and those of 2F-PEN (HF), 2F-PEN (DPE), and 2F-PEN (BP) are over 80%. Among them, 2F-PEN (HF) exhibits outstanding thermal stability with the 5% weight loss temperature of 562°C and the char yield at 800°C of 70%. It is

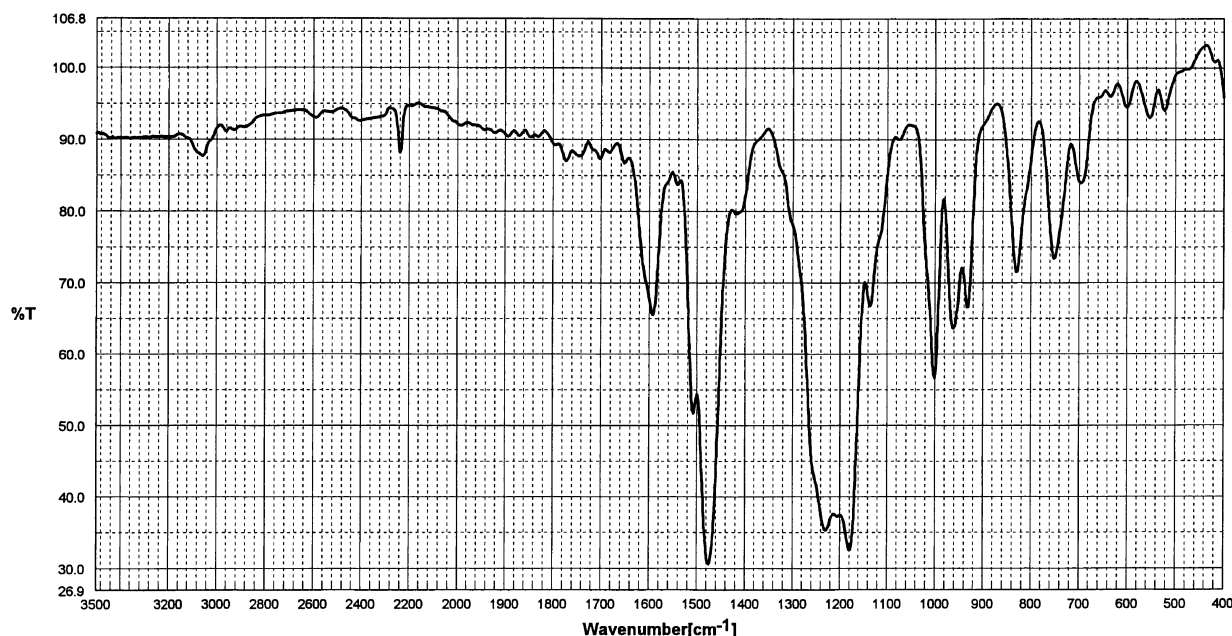


Figure 6. FT-IR spectrum of 2F-PEN (6FBA).

Table III. Thermal properties of 2F-PENs

Polymer Code ^a	T_g^b °C	5 wt% loss ^c °C	10 wt% loss ^c °C	Char Yield/wt% ^c		
				600°C	700°C	800°C
2F-PEN-6FBA	163.0	535	561	75	49	29
2F-PEN-PP	235.0	530	554	76	67	62
2F-PEN-BisA	143.6	531	546	68	60	56
2F-PEN-HF	232.2	562	593	89	75	70
2F-PEN-HQ	145.9	528	550	73	62	55
2F-PEN-CHB	151.8	509	522	60	54	51
2F-PEN-DPE	142.0	533	567	80	60	45
2F-PEN-BP	179.4	558	582	86	73	65

^a Polymer codes are shown in Scheme 2. ^b DSC was performed with $20^\circ\text{C min}^{-1}$ in nitrogen atmosphere. ^c TGA was performed with $20^\circ\text{C min}^{-1}$ in nitrogen atmosphere.

well known that the cyano groups afford triazine ring by an addition mechanism^{10,11} and previous study reported that poly(imide-amide)s containing pendant cyano group treated at high temperature lost a good solubility and this insolubility might be due to the formation of triazine rings from cyano groups at high temperature which led to the crosslinked structure.¹² In the case of 2 F-PENs, char remained at 600°C is not completely soluble in polar aprotic solvents. FT-IR measurement of the char shows very slight decrease in the relative intensity of the cyano absorption at 2239 cm^{-1} . But no characteristic absorption for the triazine ring formation could be unambiguously assigned because phenyl and triazine rings have very similar infrared absorption. Very high char yields of 2F-PENs may attributed to fluorine atoms as well as the formation of the triazine rings. From these results, they possess outstanding thermal stabilities.

Dynamic mechanical property of 2F-PEN (6FBA) is shown in Figure 7. Dynamic modulus at 25°C is $1.73 \times 10^{10}\text{ dyne cm}^{-2}$. It is almost constant up to 130°C and then decreased gradually due to α relaxation corresponding to glass transition. β relaxation is observed around 80°C. In poly(ether ether ketone) (PEEK) dynamic mechanical behavior, β relaxation was observed

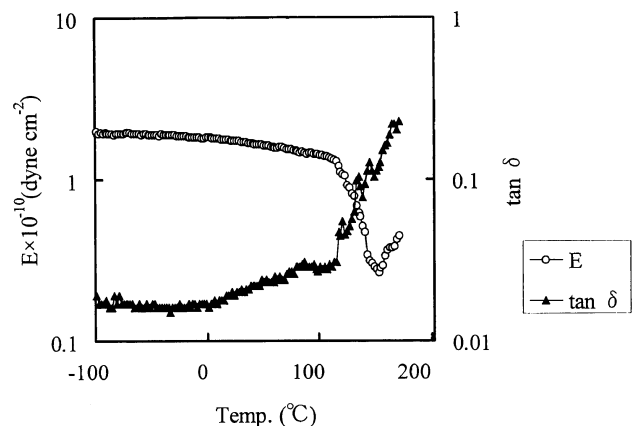


Figure 7. Dynamic mechanical scan of 2F-PEN (6FBA) at 110 Hz. Scanning rate was 2°C min^{-1} .

around 130°C and this behavior was interpreted as an effect of water^{13,14} or a counterrotational motion in diphenyl ether moiety.¹⁵ According to these previous discussions, β relaxation of 2F-PEN (6FBA) occurs at lower temperature than that of PEEK and its behavior seems to be attributable to rotational motion of pendant phe-

noxy group or cyano and fluoro substituted diphenyl ether moiety in polymer chain.

CONCLUSION

Novel fluorinated PENs containing fluorine atoms in the main chain and pendant phenoxy group are synthesized by aromatic nucleophilic substitution reaction, of which M_n ranges from 1.77×10^4 to 5.16×10^4 . The obtained PENs show excellent solubilities in common solvents, and 2F-PEN (6FBA) and 2F-PEN (DPE) can be cast as tough transparent films. These polymers have high thermal stabilities with the 5% weight loss temperature in the range 509–562°C and the T_g of 142–235°C, which is highly dependent on the structures.

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