

Aromatic Polyamides Bearing Ether and Isopropylidene or Hexafluoroisopropylidene Links in the Main Chain

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Abstract: Two multiring, flexible dicarboxylic acids, 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**3**) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**3-F**), were synthesized through the nucleophilic fluorodisplacement of *p*-fluorobenzonitrile by the dipotassium bisphenolates of the corresponding bisphenol precursors followed by alkaline hydrolysis. Two series of aromatic polyamides **5_{a-k}** and **5_{a-k-F}** containing both ether and isopropylidene or hexafluoroisopropylidene linkages between phenylene units were prepared by direct polycondensation of diacids **3** and **3-F**, respectively, with various aromatic diamines using triphenyl phosphite and pyridine as condensing agents in a *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride. The resulting polyamides of **5** and **5-F** series have inherent viscosities of 0.92-1.29 dL/g and 0.60-0.92 dL/g, respectively. Most of these polymers are amorphous in nature, are soluble in polar solvents such as NMP, *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF), and can afford tough and flexible films by solution casting. Differential scanning calorimetry shows T_g s ranging from 175 to 239 °C for the **5** series polyamides and ranging from 172 to 267 °C for the **5-F** series polymers. Both classes of polyamides show good thermal stability, with the **5-F** series polyamides being more stable.

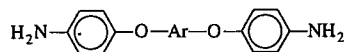
Keywords: Aromatic polyamides, Isopropylidene, Hexafluoro-isopropylidene, Direct polycondensation, Triphenyl phosphite.

Introduction

Aromatic polyamides are well known as high-performance polymer materials for their high thermal stability and excellent mechanical properties [1, 2]. However, their industrial applications were rather restricted by difficulty in fabrication due to their extremely high T_g s or melting temperatures and insolubility in most organic solvents. Therefore, numerous attempts have been tried to improve their processability. One of the useful approaches is the introduction of flexibilizing groups such as aryl ether, aryl sulfide, isopropylidene, or hexafluoroisopropylidene linkage into the aromatic polyamide backbone [3-9].

The traditional synthetic route to prepare polyamides is through the polycondensation reaction of diamine monomers with dicarboxylic acids or their derivatives. Thus, if the flexible linkages were incorporated into the monomer components first, flex-

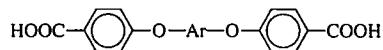
ible polyamides could be obtained by the polycondensation of these monomers. For example, the bis(ether amine)s with the following general structure:



could be obtained easily by the reduction of bis(4-nitrophenoxy) compounds which were synthesized by the nucleophilic substitution of aromatic diols such as naphthalenediols, benzenediols or bisphenols with *p*-chloronitrobenzene. Many organic-soluble aromatic polyamides have been prepared from these diamines and aromatic dicarboxylic acids [9-15]. Using the same logic, the fluoro-displacement reaction of *p*-fluorobenzonitrile with aromatic diols could lead to the bis(4-cyanophenoxy) compounds [16-19], which could be subsequently hydrolyzed to the bis(ether-carboxylic acid)s with the following gen-

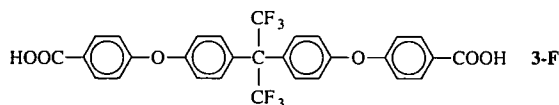
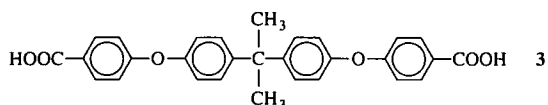
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eral structure:



Then, the bis(ether-carboxylic acid)s or their derivatives were polycondensated with aromatic diamines to form the polyamides containing aryl ether and other flexible groups existing in the -Ar- unit. Thus, the goal of processability enhancement could be achieved.

The present investigation follows the synthetic procedure mentioned above to prepare two dicarboxylic acids **3** and **3-F** containing aryl ether and isopropylidene or hexafluoroisopropylidene groups starting from 4,4'-isopropylidenediphenol (bisphenol A), 4,4'-hexafluoroisopropylidene-diphenol (bisphenol AF), and *p*-fluorobenzonitrile. To understand the "structure-property" relationships, the two dicarboxylic acids **3** and **3-F** were directly polycondensed with a series of diamines with one to five aromatic rings between the amino functional groups, through the activation of triphenyl phosphite and pyridine, to obtain two series of polyamides. The effect of fluorine atoms on the properties of these polyamides such as solubility, crystallinity, tensile properties and thermal properties are discussed in this study. Although the syntheses and properties of some polyamides derived from dicarboxylic acids **3** and **3-F** have been published recently [7, 8], polyamides prepared from these diacids are not investigated in detail. Therefore, a more systematic study of these polyamides was made in the present work in order to further understand their characteristics.



Experimental

1. Materials

The reagents used to synthesize dicarboxylic acids **3** and **3-F** including 4,4'-isopropylidenediphenol (bisphenol A) (Wako), 4,4'-hexafluoroisopropylidenediphenol (bisphenol AF; from Chriskev), *p*-fluorobenzonitrile (Wako), K₂CO₃ (Fluka), *N,N*-dimethylformamide (DMF) (Fluka), toluene (Alps), ethanol (95%), KOH were used as received without previous purification.

p-Phenylenediamine (**4_a**) (TCI) and benzidine

(**4_c**) (TCI) were purified by sublimation, and *m*-phenylenediamine (**4_b**) (Janssen) was purified by vacuum distillation. According to a procedure in the literature [9], 4,4'-bis(4-aminophenoxy)biphenyl (**4_i**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**4_j**), and α,α' -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**4_k**) were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenols, i.e., 4,4'-biphenol (Fluka), 2,2-bis(4-hydroxyphenyl)propane (Wako), and α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene and *p*-chloronitrobenzene in the presence of potassium carbonate, giving the bis(*p*-nitrophenoxy) compounds and subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst. Other diamines that included 4,4'-diaminodiphenyl ether (**4_d**) (TCI), 3,4'-diaminodiphenyl ether (**4_e**), 4,4'-diaminodiphenylmethane (**4_f**) (TCI), 4,4'-diaminobenzanilide (**4_g**) (Chriskev), and 1,4-bis(*p*-aminophenoxy)benzene (**4_h**) (TCI) were used without previous purification. *N,N*-Dimethylacetamide (DMAC) and *N*-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) (TCI) was purified by distillation under reduced pressure. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180 °C for 8 hrs.

2. Monomer synthesis

2.1 4,4'-[Isopropylidenebis(1,4-phenylene)dioxy]dibenzonitrile (**2**)

In a 250 mL round-bottomed flask, K₂CO₃ (24.3 g ; 0.176 mol) were suspended in a solution of bisphenol A (20 g ; 0.088 mol) in a mixture of 100 mL of DMF and 70 mL of toluene and heated at reflux temperature using a Dean-Stark trap to remove the water azeotropically. After toluene was removed completely, *p*-fluorobenzonitrile (22.52 g ; 0.175 mol) was added and heating was continued at 140 °C for 6 hrs. The reaction mixture was allowed to cool and poured into 600 mL of water. The product was separated as an oily viscous layer in the bottom of the container. After washing with water several times, the dinitrile was extracted with 300 mL of chloroform. The crude product was obtained after distilling off chloroform in a rotatory evaporator and then recrystallizing from methanol to afford white needles. The product had a melting point of 122-123 °C (lit. [7] 124 °C) in 73.5% (27.7 g) yield.

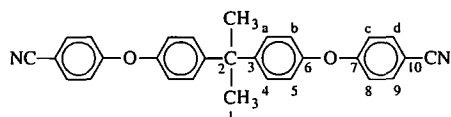
IR (KBr): 2222 cm⁻¹ [C≡N str.], 1408-1597 cm⁻¹ [arom. C=C str.], 1257 cm⁻¹ [C-O-C str.].

¹H NMR (CDCl₃): δ 7.59 (d, H_d, 4H), 7.27 (d,

H_a, 4H), 7.01 (d, H_c, 4H), 6.99 ppm (d, H_b, 4H).

¹³C NMR (CDCl₃): δ 161.60 (C⁶), 152.62 (C⁷), 147.19 (C³), 134.04 (C⁹), 128.43 (C⁴), 119.81 (C⁸), 118.79 (C≡N), 117.80 (C⁵), 105.69 (C¹⁰), 42.38 (C²), 30.90 ppm (C¹).

Anal. Calcd for C₂₉H₂₂N₂O₂ (430.51): C, 80.91%; H, 5.15%; N, 6.51%; Found: C, 80.91%; H, 5.15%; N, 6.28%.



2.2 4,4'-[Hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzo-nitrile (2-F)

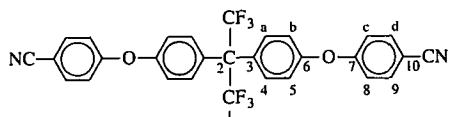
Dinitrile 2-F was prepared from bisphenol AF (1-F) and *p*-fluorobenzonitrile in a similar method. It was recrystallized from acetonitrile to provide colorless flakes with a melting point of 166 °C (lit. [8] 167 °C) in 78.75% (31.5 g) yield.

IR (KBr): 2232 cm⁻¹ [C≡N str.], 1415-1599 cm⁻¹ [arom. C=C str.], 1247 cm⁻¹ [C-O-C str.], 1214 cm⁻¹ [C-F str.].

¹H NMR (CDCl₃): δ 7.65 (d, H_d, 4H), 7.44 (d, H_a, 4H), 7.09 (d, H_c, 4H), 7.06 ppm (d, H_b, 4H).

¹³C NMR (CDCl₃): δ 166.27 (C⁶), 155.80 (C⁷), 134.28 (C⁹), 132.08 (C⁴), 129.32 (C³), 124.01 (C¹, quartet, with ¹J_{CF} = -288.2 Hz), 119.28 (C⁵), 118.88 (C⁸), 118.51 (C≡N), 106.92 (C¹⁰), 63.75 (C², multiplet, with ²J_{CF} = 20.9 Hz).

Anal. Calcd for C₂₉H₁₆N₂O₂F₆ (538.45): C, 64.69%; H, 3.21%; N, 5.22%; Found: C, 64.38%; H, 3.14%; N, 4.94%.



2.3 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (3)

The dicarboxylic acid 3 was obtained by alkaline hydrolysis of the dinitrile 2. A suspension of 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzonitrile (2) (23.5 g ; 0.0545 mol) in 400 mL of a 1:1 volume mixture of water and ethanol containing 61.2 g (1.09 mol) of KOH in a 1000 mL flask was refluxed at 90 °C. The suspension solution turned into a clear solution after about 2 hrs, then heating was continued until no further ammonia was generated. The resulting hot clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and was acidified by concentrated HCl to pH = 2-3, then the white precipitate was filtered off, washed with water to neu-

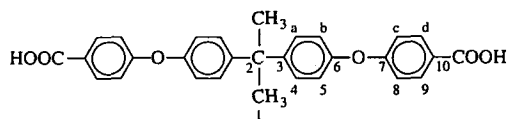
tral and dried *in vacuo*, giving 23 g (90.2% yield) of 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (3) without further purification; m.p. 276 °C (lit. [7] 279 °C).

IR (KBr): 2500-3500 cm⁻¹ [O-H str.], 1686 cm⁻¹ [C=O str.], 1247 cm⁻¹ [C-O-C str.].

¹H NMR (DMSO-*d*₆): δ 7.92 (d, H_d, 4H), 7.28 (d, H_a, 4H), 7.01 (d, H_c, 4H), 6.98 ppm (d, H_b, 4H).

¹³C NMR (DMSO-*d*₆): δ 166.77 (C=O), 161.01 (C⁶), 152.96 (C⁷), 146.38 (C³), 131.67 (C⁹), 128.31 (C⁴), 125.20 (C¹⁰), 119.36 (C⁸), 117.17 (C⁵), 41.38 (C²), 30.58 ppm (C¹).

Anal. Calcd for C₂₉H₂₄O₆ (468.51): C, 73.34%; H, 5.16%. Found: C, 73.97%; H, 5.21%.



2.4 4,4'-[Hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (3-F)

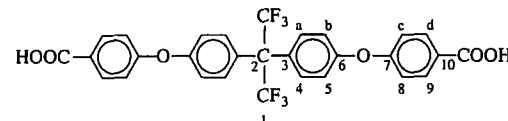
Dicarboxylic acid 3-F was synthesized from alkaline hydrolysis of its corresponding dinitrile 2-F in an analogous procedure as described above. Yield 93.8%, m.p. 318 °C (lit. [8] 319 °C).

IR (KBr): 2500-3500 cm⁻¹ [O-H str.], 1692 cm⁻¹ [C=O str.], 1420-1600 cm⁻¹ [arom. C=C str.], 1251 cm⁻¹ [C-O-C str.], 1209 cm⁻¹ [C-F str.].

¹H NMR (DMSO-*d*₆): δ 8.01 (d, H_d, 4H), 7.44 (d, H_a, 4H), 7.21 (d, H_c, 4H), 7.19 ppm (d, H_b, 4H).

¹³C NMR (DMSO-*d*₆): δ 166.68 (C=O), 159.58 (C⁶), 156.45 (C⁷), 131.80 (C⁴), 131.75 (C⁹), 127.59 (C³), 126.31 (C¹⁰), 124.42 (C¹, quartet, with ¹J_{CF} = -288.2 Hz), 119.05 (C⁵), 118.49 (C⁸), 63.78 ppm (C², multiplet, with ²J_{CF} = 20.9 Hz).

Anal. Calcd for C₂₉H₁₈O₆F₆ (576.45): C, 60.42%; H, 3.15%; Found: C, 59.30%; H, 3.16%.



3. Polymer syntheses

A typical polymerization procedure for the preparation of polyamide 5_a is as follows. A mixture of 0.5885 g (1.25 mmol) of dicarboxylic acid 3, 0.2503 g (1.25 mmol) of 4,4'-diaminodiphenyl ether (4_a), 0.3 g of calcium chloride, 0.9 mL of triphenyl phosphite (TPP), 2.5 mL of NMP was heated with stirring at 110 °C for 3 hrs. As the polycondensation proceeded for about 1 hr, the reaction mixture became viscous gradually. The resultant polymer solution was trickled into 400 mL of methanol giving rise to a stringy precipitate which was washed

thoroughly with methanol and hot water, collected by filtration and dried. The yield was 0.78 g (99%), the inherent viscosity of the polymer was 1.02 g/dL as measured in DMAc containing 5 wt % LiCl at a concentration of 0.5 g/dL at 30 °C.

All other polyamides were synthesized by an analogous procedure.

4. Preparation of polyamide films

A polymer solution was made by dissolving about 0.8 g of the polyamide in 8 mL of hot DMAc. The solution was poured into a 9 cm diameter glass culture dish, which was placed in a 90 °C oven for 12 hrs to remove the solvent. Then, the obtained semi-dried polymer film was stripped from the glass substrate and further dried *in vacuo* at 100 °C for 8 hrs.

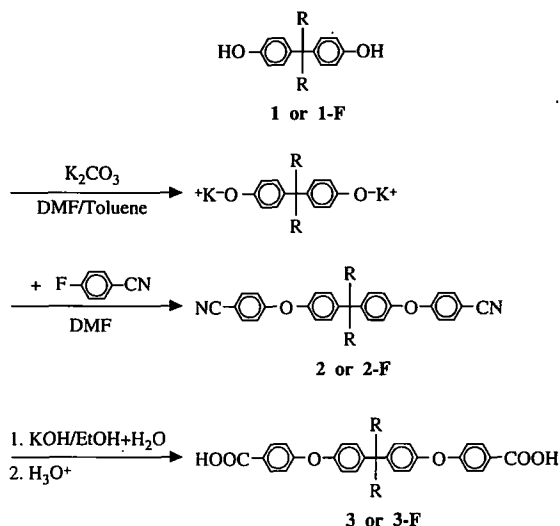
5. Measurements

Infrared spectra were obtained on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Jeol EX-400 NMR spectrometer with tetramethylsilane (TMS) as an internal standard and perdeuterated dimethyl sulfoxide (DMSO-*d*₆) as an external standard, respectively. The inherent viscosities were measured with a Canon-Fenske viscometer at 30 °C. Differential scanning calorimetry (DSC) was performed on a Sinku Riko DSC-7000 coupled to a Sinku Riko TA-7000 thermal controller under a nitrogen atmosphere (30 cm³/min) at a heating rate of 20 °C/min. Thermogravimetric (TG) data were obtained on a Rigaku Thermoflex TG-8110 coupled to a Rigaku TAS-100 thermal analysis station. Measurements were performed with 10 ± 2 mg samples heated under a nitrogen atmosphere or air (50 cm³/min) at a heating rate 20 °/min. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered CuKα radiation (40 kV, 15 mA). The scanning rate was 2 °/min. An Instron Universal tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples. The measurements were performed at room temperature using solution-cast film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick). Specimens of 2 cm gauge length were clamped between the jaws of the instrument and elongated at a constant rate of 5 cm/min. Reported data are averages of at least five replica tests.

Results and Discussion

1. Monomer synthesis

As shown in Scheme 1, 4,4'-[isopropylidenebis



1, 2, 3 : R = -CH₃

1-F, 2-F, 3-F : R = -CF₃

Scheme 1. Preparation of dicarboxylic acids

(1,4-phenylene)dioxy]-dibenzonitrile (2) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)-dioxy]-dibenzonitrile (2-F) were prepared through the nucleophilic fluoro-displacement of *p*-fluorobenzonitrile with the bisphenoxide ion of the corresponding bisphenols, bisphenol A (1) and bisphenol AF (1-F), in the presence of a base such as K₂CO₃. The yield of dinitriles 2 and 2-F after purification were 73.5% and 78.8%, respectively. These dinitriles were converted into the dicarboxylic acids, 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (3) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (3-F), by alkaline hydrolysis and subsequent acidification. The yield of the dicarboxylic acids 3 and 3-F were 90.2% and 97.8% (on the basis of dinitrile), respectively. The purity was high enough for the preparation of polymers with high molecular weights. The structures of dinitriles and dicarboxylic acids were determined by elemental analysis and FTIR, ¹H NMR and ¹³C NMR spectroscopy. The most important evidence can be seen from their IR and ¹³C NMR spectra. Figure 1 shows the FTIR spectra of dinitrile 2-F and diacid 3-F. The cyano group in 2 gives a sharp absorption at 2232 cm⁻¹. When 2-F was hydrolyzed to 3-F, the characteristic band of the C≡N group disappeared, carbonyl stretching absorption occurred at 1692 cm⁻¹, and the broad O-H absorption appeared in the region from 2500 to 3500 cm⁻¹. The ¹³C NMR spectra of 2-F and 3-F are given in Figure 2. The most obvious features of the spectra are the shifts of the

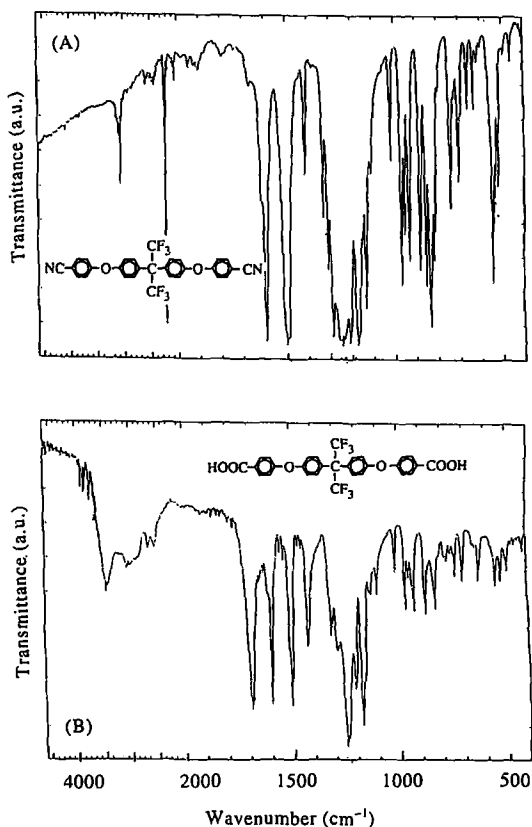


Figure 1. IR spectra of (A) dinitrile 2-F and (B) dicarboxylic acid 3-F.

resonance signals for the carbon of the cyano group and its adjacent carbon C¹⁰. The C¹⁰ of 2-F is shielded by the anisotropic field induced by the π electrons of the cyano group, and hence C¹⁰ has resonates at higher field than the other aromatic carbons. After the cyano group was converted to a carboxyl group, the resonance signal of C¹⁰ moved to lower field (from 106.92 to 126.31 ppm) due to the lack of anisotropic shielding, the original signal at 118.51 ppm assigned to cyano carbon disappeared, and the resonance of carbonyl carbon occurred the farthest downfield (166.68 ppm). Furthermore, the splitting of the ¹³C signals caused by couplings between carbon and fluorine also could be observed in these spectra. The magnitudes of the one-bond and two-bond carbon-fluorine couplings ¹J_{CF} and ²J_{CF} in these fluorocompounds are -228.2 and 20.9 Hz, respectively.

2. Polymer synthesis

As outlined in Scheme 2, two series of aromatic polyamides 5_{a-k} and 5_{a-k}-F were directly prepared by a Yamazaki phosphorylation polycondensation technique [20] from dicarboxylic acids 3 and 3-F with eleven structurally different diamines

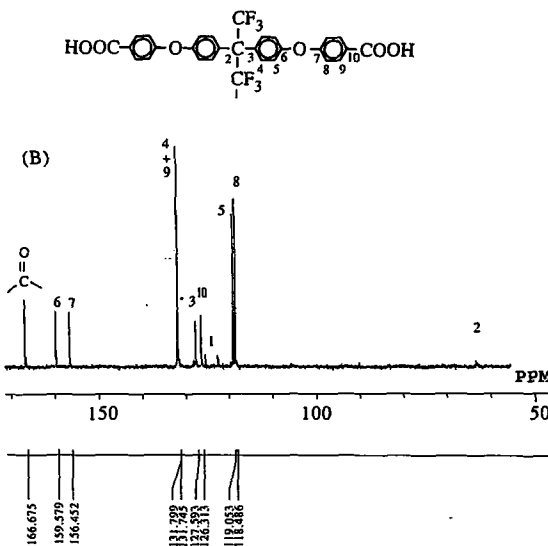
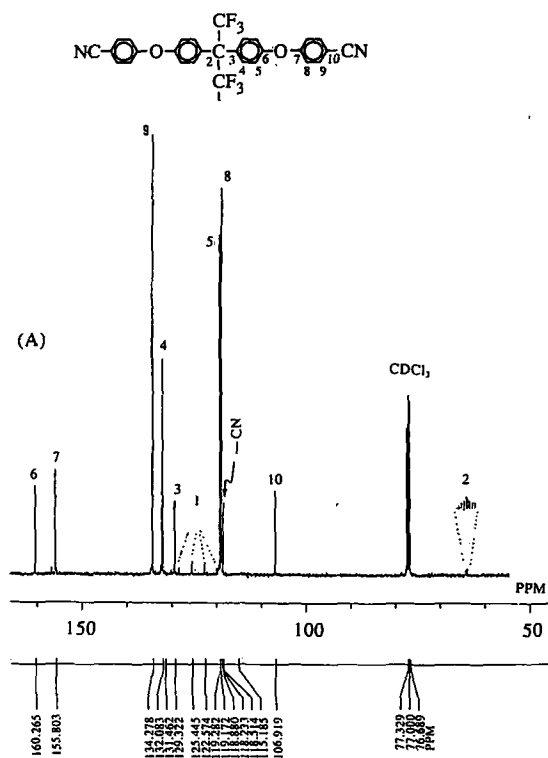
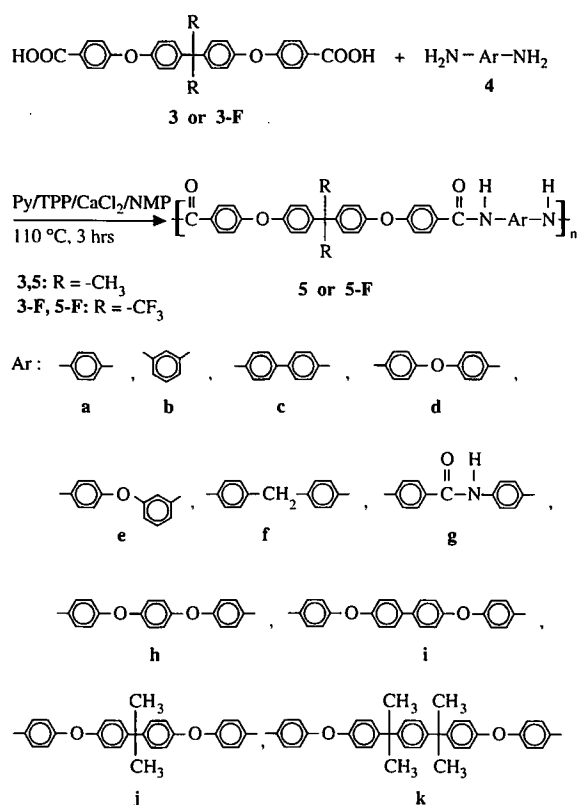


Figure 2. ¹³C NMR spectra of (A) dinitrile 2-F as measured in CDCl₃ and (B) dicarboxylic acid 3-F as measured in DMSO-d₆.

4_{a-k} using triphenyl-phosphite and pyridine as condensing agents in the NMP solution containing dissolved CaCl₂ at 110 °C for 3 hrs. The inherent viscosities of 5_{a-k} and 5_{a-k}-F were in the range of 0.92-1.29 dL/g and 0.60-0.92 dL/g, respectively.



Scheme 2. Preparation of polyamides.

Except for 5_c, all other polyamides were soluble in NMP or DMAc and afforded free-standing films by means of solution-casting. The films made from polyamides 5_a, 5_c-F and 5_g-F cracked upon creasing, possibly due to the presence of a high level of

Table I. The inherent viscosities and film quality of polyamides.

Polymer code	$\eta_{inh}^{(a)}$ (dL/g)	Film ^(b) quality	Polymer code	$\eta_{inh}^{(a)}$ (dL/g)	Film ^(b) quality
5 _a	1.24	B ^(c)	5 _a -F	0.83	F
5 _b	1.07	F	5 _b -F	0.60	F
5 _c	1.21	- ^(d)	5 _c -F	0.92	B
5 _d	1.02	F	5 _d -F	0.82	F
5 _e	1.07	F	5 _e -F	0.70	F
5 _f	0.96	F	5 _f -F	0.80	F
5 _g	1.29	F	5 _g -F	0.92	B ^(c)
5 _h	1.28	F	5 _h -F	0.90	F
5 _i	0.92	F	5 _i -F	0.85	F
5 _j	1.17	F	5 _j -F	0.88	F
5 _k	1.09	F	5 _k -F	0.80	F

(a) Measured in DMAc-5% LiCl on 0.5 g/dL at 30 °C.

(b) Films were cast by slow evaporation of polymer solutions in DMAc; B: brittle; F: flexible.

(c) Cast from NMP.

(d) Insoluble in DMAc and NMP.

crystallinity. Other polyamide films were transparent, flexible and tough. The inherent viscosities and film quality of all of the polyamides are summarized in Table I.

The structure of the polyamides was confirmed by IR spectroscopy. Some characteristic absorptions can be observed in the IR spectra, such as N-H stretching at 3300 cm⁻¹, carbonyl stretching at 1650 cm⁻¹, and aryl ether stretching at 1250 cm⁻¹.

3. Properties of polymers

The solubility of polyamides was tested qualitatively, and the results are presented in Table II. Most of the polyamides were easily soluble at room temperature in polar aprotic solvents such as NMP, DMAc and DMF. The polyamides derived from rigid diamines such as *p*-phenylenediamine (4_a), benzi-*dine* (4_c) and 4,4'-diaminobenzanilide (4_g) showed less solubility. This may be due to the higher level of crystallinity associated with these polymers. In general, the solubility of hexafluoroisopropylidene-containing polyamides was higher than that of isopropylidene-bearing polyamides. For example, polymers 5_a-F and 5_c-F showed apparently improved solubility as compared to the corresponding polymers 5_a and 5_c, and most of the 5-F series polyamides were soluble in less polar THF. Due to the

Table II. Solubility of polyamides^(a).

Polymer code	Solvent ^(b)					
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF
5 _a	+	-	-	-	-	-
5 _b	+	+	+	+	+	-
5 _c	S	-	S	S	-	-
5 _d	+	+	+	+	+	-
5 _e	+	+	+	+	+	-
5 _f	+	+	+	+	+	-
5 _g	+h	+	-	-	-	-
5 _h	+	+	+	+	+	-
5 _i	+	+	+	S	-	-
5 _j	+	+	+	S	+	+
5 _k	+	+	+	S	+	+
5 _a -F	+	+	+	+	+	-
5 _b -F	+	+	+	+	+	+
5 _c -F	+	+	+	-	-	-
5 _d -F	+	+	+	+	+	+
5 _e -F	+	+	+	+	+	+
5 _f -F	+	+	+	+	+	+
5 _g -F	+	-	-	+	+	+
5 _h -F	+	+	+	+	+	+
5 _i -F	+	+	+	+h	-	-
5 _j -F	+	+	+	+	+	+
5 _k -F	+	+	+	+h	+	+

(a) +: soluble at room temperature; +h: soluble on heating; S: swelling; -: insoluble.

(b) NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethyl-acetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethylsulfoxide; THF: tetrahydrofuran.

more bulky $-CF_3$ group, the packing of polymeric chains in tight structures through hydrogen bonding between amide groups is probably disturbed, and consequently the solvent molecules can penetrate easily to solubilize the chains.

Most of the polyamides possess outstanding film-forming properties. Transparent flexible films have been obtained by casting polymer solutions from DMAC or NMP onto glass substrates, followed by heating to remove the solvent. All the flexible films were subjected to tensile testing, and their tensile properties are listed in Table III. The yield strength, tensile strength, elongation to break, and initial modulus of the polyamide films were in the range of 57-73 MPa, 55-82 MPa, 4-110%, and 1.08-1.84 GPa, respectively. Most of the films showed yield points on their stress-strain curves and moderate to high elongation-to-break, indicative of high ductility.

X-ray diffractograms of some representative polyamides of the 5 series are shown in Figure 3. Polyamide 5_c was measured in a powder form due to the fact that it could not be cast into a polymer film with enough self-supporting strength. All other polyamides were measured as films. The scattering curve for polyamide 5_c showed the highest degree of crystallinity and exhibited a strong reflection peak around $2\theta = 20^\circ$. The brittle film of 5_a also revealed a moderately crystalline pattern. All other

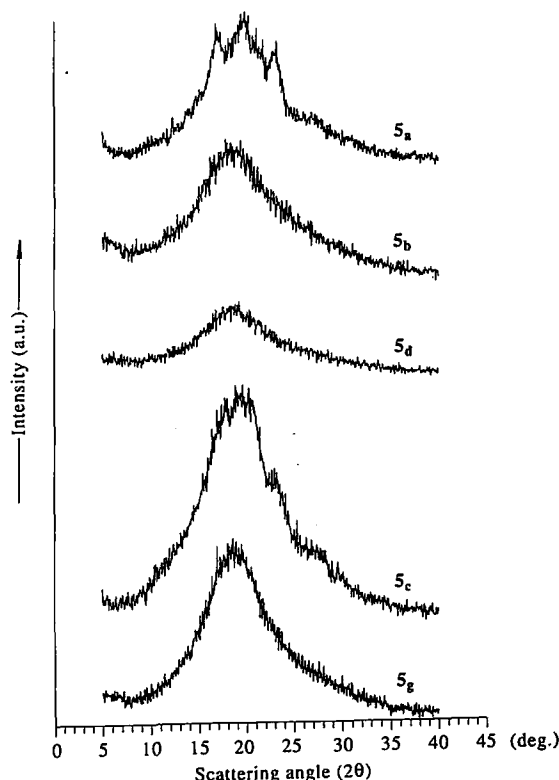


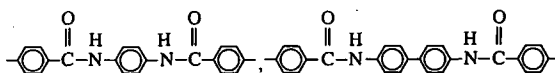
Figure 3. Wide angle X-ray diffractograms of some polyamides of 5 series.

Table III. Tensile properties of polyamide films^(a).

Polymer code	Strength at yield (MPa)	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
5_a	—	—	—	—
5_b	73	60	40	1.36
5_c	—	—	—	—
5_d	59	55	31	1.29
5_e	69	66	17	1.84
5_f	62	65	81	1.08
5_g	—	73	45	1.36
5_h	67	82	110	1.53
5_i	65	77	99	1.59
5_j	66	64	70	1.49
5_k	57	58	29	1.39
5_a-F	60	55	15	1.56
5_b-F	—	53	4	1.62
5_c-F	—	—	—	—
5_d-F	59	58	46	1.41
5_e-F	68	57	25	1.59
5_f-F	66	60	28	1.49
5_g-F	—	—	—	—
5_h-F	63	59	45	1.37
5_i-F	62	63	92	1.32
5_j-F	63	56	78	1.38
5_k-F	66	58	94	1.40

(a) No available sample could be obtained from polymer 5_c . The films of 5_a , 5_a-F and 5_g-F were too brittle to test.

polyamides of this series exhibited less crystalline or noncrystalline diffraction patterns similar to those shown from 5_b , 5_d , and 5_g . The higher crystallinity of polyamides 5_a and 5_c , compared to the other polyamides of the same series can be explained mainly by the presence of the following rigid planner amide segments in the polymer main chains:



which led to a better packing of polymer chains.

Figure 4 gives X-ray diffractograms of some polyamides of 5-F series. In general, the incorporation of hexafluoroisopropylidene groups into the polyamide backbones led to a decreased crystallinity. Among this series of polyamides, only the cast film of 5_c-F displayed a rougher X-ray diffraction pattern.

Although the cast film of polyamide 5_g-F was brittle, it did not display a susceptible crystalline diffraction pattern. The reason was not investigated in detail; however, it should be associated with its chain packing density.

The thermal stability of polyamides were de-

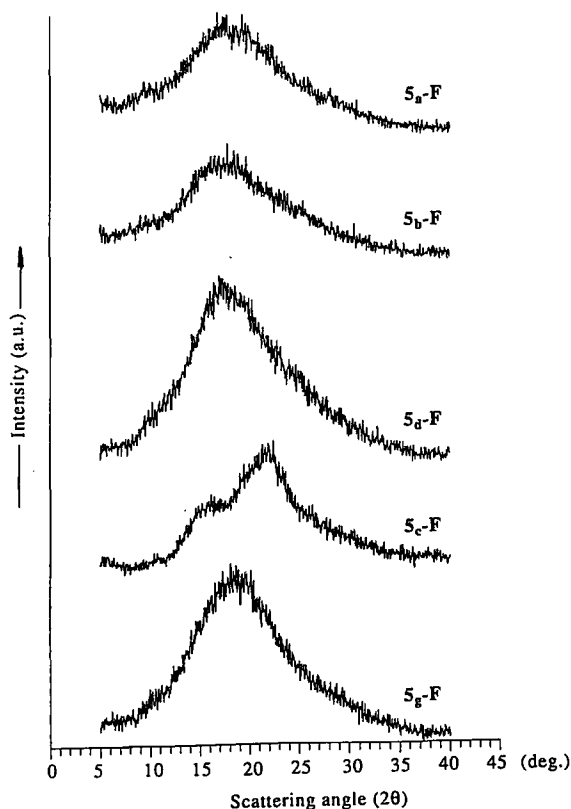


Figure 4. Wide angle X-ray diffractograms of some polyamides of 5-F series.

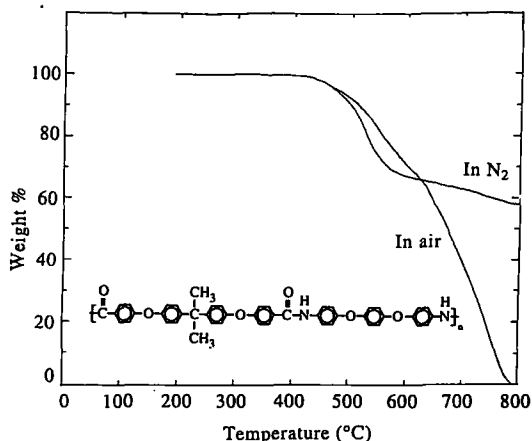


Figure 5. TG thermograms of polyamide 5_b at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$.

terminated by thermogravimetry (TG). Figure 5 shows typical TG thermograms of a representative isopropylidene-bearing polyamide 5_b in both air and nitrogen atmospheres. From these TG thermograms, it may be deduced that the polymer is highly thermostable, since no significant weight loss occurred

before $450\text{ }^\circ\text{C}$. In nitrogen, about 58 % weight residue remained even at $800\text{ }^\circ\text{C}$, in contrast to the complete weight loss of the polymer when compared in air below this temperature. However, presumably due to some oxidative crosslinking of aliphatic segments, the rate of thermal degradation in air was slightly lower than in nitrogen before $600\text{ }^\circ\text{C}$. All other polyamides of the isopropylidene-bearing series showed a similar thermal behavior, and the 10 % weight loss temperatures of these polymers, as shown in Table IV, were recorded in the range of $480\text{--}515\text{ }^\circ\text{C}$ in air and $468\text{--}502\text{ }^\circ\text{C}$ in nitrogen.

The typical TG curves of a representative hexafluoroisopropylidene-containing polyamide 5_i-F are illustrated in Figure 6. This polymer showed a similar TG behavior before $550\text{ }^\circ\text{C}$ in both air and nitrogen atmospheres. Extensive degradation occurred at temperatures higher than $450\text{ }^\circ\text{C}$. There was 62 % residual char left at $800\text{ }^\circ\text{C}$ in nitrogen. In air, the oxidative degradation continued above $550\text{ }^\circ\text{C}$, and the polymer decomposed completely at about $725\text{ }^\circ\text{C}$. All other polyamides of the hexafluoroisopropylidene-containing series showed a similar thermal behavior to that of polyamide 5_i-F . The data reported in Table IV show that the 10 % weight loss temperatures of this series polyamides were recorded between $495\text{--}528\text{ }^\circ\text{C}$ in air and $499\text{--}523\text{ }^\circ\text{C}$ in nitrogen. As expected, the hexafluoroisopropylidene containing polyamides are more stable than the isopropylidene containing polyamides of a comparable structure, because of the high C-F and C-CF₃ bond strengths.

The glass transition temperatures (T_g) of these polyamides were evaluated by differential scanning calorimetry (DSC). The polyamide samples were quenched from elevated temperatures at approximately $400\text{ }^\circ\text{C}$ to room temperature to form predominantly amorphous samples, and thus, distinct glass transitions generally could be observed on the subsequent heating DSC traces. Temperature at the middle of baseline shift on the second DSC heating trace was defined as T_g , and the T_g values of these polyamides are presented in Table IV. The 5_{a-k} polyamides showed glass transitions in the range of $175\text{--}239\text{ }^\circ\text{C}$, and the 5_{a-k}-F polyamides in the range of $172\text{--}267\text{ }^\circ\text{C}$. In most cases, the fluoropolyamides exhibited T_g s higher than those of corresponding -CH₃ containing polymers. This effect can be attributable to the increase of structural hindrance due to the bulky -CF₃ units [21, 22]. Polyamides 5_a , 5_c , 5_g , 5_a-F , 5_c-F , and 5_g-F derived from rigid diamines such as 4_a , 4_c , and 4_g exhibited sharp melting endotherm peaks in the first heating DSC traces. This implied that these polyamides possessed more crystalline regions. It can also be noticed that there is a large window between the T_g and the decomposition

Table IV. Thermal behavior data of polyamides.

Polymer code	T _g ^(a) (°C)	Decomposition in N ₂ (°C)	Temperature ^(c) in air (°C)	Char yield ^(d) (wt%)
S _a	220 (340) ^(b)	485	488	62.7
S _b	204	484	503	55.4
S _c	235 (403)	482	502	59.9
S _d	210	501	510	61.7
S _e	192	502	513	63.5
S _f	200	501	515	65.0
S _g	239 (375)	468	480	60.6
S _h	175	502	514	58.1
S _i	200	492	514	67.0
S _j	185	499	511	55.7
S _k	177	496	512	53.2
S _{a-F}	225 (428)	519	501	58.4
S _{b-F}	200	507	505	56.2
S _{c-F}	265 (404)	523	507	57.9
S _{d-F}	206	515	528	60.7
S _{e-F}	187	515	514	60.0
S _{f-F}	188	505	500	55.5
S _{g-F}	267 (362)	499	495	57.0
S _{h-F}	184	509	509	57.8
S _{i-F}	230	521	517	62.3
S _{j-F}	185	508	508	58.3
S _{k-F}	172	502	504	57.1

(a) Midpoint of baseline shift in the second heating DSC trace, with a heating rate of 10 °C/min under a nitrogen atmosphere.

(b) Values in the parentheses are the peak temperatures of sharp endotherms in the first DSC heating trace.

(c) Temperatures at which 10 % weight loss were recorded by TG at a heating rate of 20 °C/min.

(d) Residual weight % at 800 °C under a nitrogen atmosphere.

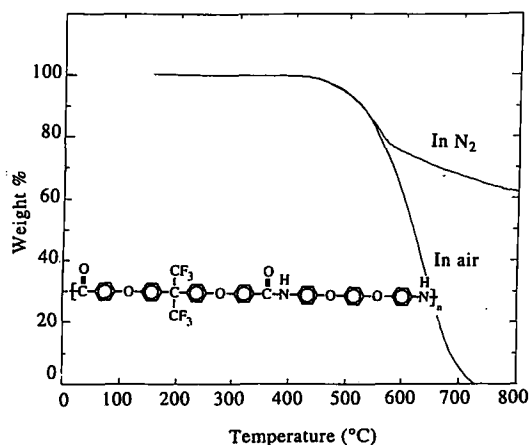


Figure 6. TG thermograms of polyamide S_{1-F} at a heating rate of 20 °C/min.

temperature for all the polyamides, which could be advantageous in the processing of these polymers.

Conclusions

A series of polyamides containing hexafluoroisopropylidene bridges in the main chain have been

prepared and compared with related polymers which have isopropylidene groups. Almost all of the prepared polyamides can be easily processed from solution due to their excellent solubility in several polar solvents. Flexible films with high toughness have been obtained by casting polymer solutions onto glass substrates. They show a high thermal stability and a large window between decomposition and glass transition temperature. All these properties make these polymers potential candidates for high-performance polymeric materials. Moreover, fluorine containing polyamides generally exhibit higher solubility, lower crystallinity, and higher thermostability and glass transition temperatures.

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