

NOTES

Synthesis and Properties of Fluorinated Polyamides Based on 2,7-Bis(4-amino-2-trifluoromethylphenoxy)naphthalene

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Wholly aromatic polyamides (aramids) are characterized as highly thermally stable polymers with a favorable balance of other physical and chemical properties.^{1,2} However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms due to their high melting or glass transition temperature and their limited solubility in common organic solvents. Therefore, a great deal of effort has been expended to try to improve the processing characteristics of the relatively intractable polymers. Attempts to increase the solubility of polyamides have been made through the introduction of flexible units into the polymer backbone or bulky pendant groups along the main chain.^{3–11} We have demonstrated that polyamides containing bis(phenoxy)naphthalene unit such as those from 2,7- or 1,5-bis(4-aminophenoxy)naphthalene showed enhanced solubility and comparable thermal stability as compared to conventional aramids.^{12,13} However, some of these modified polyamides such as that derived from 2,7-bis(4-aminophenoxy)naphthalene (BAPON) and rigid terephthalic acid were crystalline and insoluble in organic solvents. It is known that the introduction of ether linkages into the polymer backbone imparts processability and solubility to polymers without much loss of thermal stability, and the incorporation of fluorine-containing substituents is also known to enhance the solubility of aromatic polymers such as polyimides.^{14,15} Very recently, we have demonstrated that the polyimides derived from 2,7-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (3F-BAPON) were characterized by high solubility, good film-forming capability, high optical transparency, excellent thermal stability, and low dielectric constants.¹⁶ In connection with our interest in preparing easily pro-

cessable high-performance polymers bearing naphthyl units, the present study deals with the synthesis and basic characterization of novel fluorinated polyamides derived from 3F-BAPON and various aromatic dicarboxylic acids. For a comparative study, a series of analogous polyamides based on the non-fluorinated diamine BAPON were also prepared and characterized. It was hoped that the attachment of bulky trifluoromethyl (CF₃) groups would decrease polymer interchain interactions and generally disturb the coplanarity of aromatic units to reduce packing efficiency and crystallinity, thus leading to enhanced solubility.



EXPERIMENTAL

Materials

According to a well-established procedure,^{12–16} BAPON (mp = 172–173 °C) and 3F-BAPON (mp = 160–161 °C) were prepared by the aromatic nucleophilic substitution reaction of 2,7-dihydroxynaphthalene with *p*-chloronitrobenzene and 2-chloro-5-nitrobenzotrifluoride, respectively, in the presence of potassium carbonate, and subsequent reduction of the intermediate dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst. The synthetic details and characterization

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data of the new diamine 3F-BAPON were described in a previous publication.¹⁶ The aromatic dicarboxylic acids such as terephthalic acid (**Ia**; Fluka), isophthalic acid (**Ib**; Fluka), 4,4'-biphenyldicarboxylic acid (**Ic**; TCI), 4,4'-oxydibenzoic acid (**Id**; TCI), 1,4-naphthalenedicarboxylic acid (**Ie**; Wako), 2,6-naphthalenedicarboxylic acid (**If**; TCI), 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**Ig**; Chriskev), 4,4'-sulfonyldibenzoic acid (**Ih**; New Japan Chemical Co.), were used as received. *N*-Methyl-2-pyrrolidone (NMP) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP; Fluka) was purified by distillation under reduced pressure. Commercially obtained anhydrous calcium chloride (CaCl₂; Wako) was dried under vacuum at 180 °C for 8 h.

General Procedure of Polyamide Synthesis

The synthesis of polyamide **IId** is described as a representative example of preparation methodology. A 50 mL round bottom flask was charged with 0.7176 g (1.5 mmol) of 3F-BAPON, 0.3873 g (1.5 mmol) of 4,4'-oxydibenzoic acid **Id**, 0.3 g of calcium chloride, 1.5 mL of triphenyl phosphite (TPP), 0.8 mL of pyridine (Py), and 4 mL of NMP. The mixture was heated to 120 °C and stirred for 3 h. As the polycondensation proceeded, the reaction mixture became viscous gradually. The resultant viscous polymer solution was precipitated into 300 mL of stirred methanol giving rise to a tough, fiber-like polymer precipitate. The product was washed thoroughly by methanol and hot water, collected by filtration, and dried. The inherent viscosity of this polyamide **IId** was 1.23 dL g⁻¹, measured at 30 °C with polymer solution concentration of 0.5 g dL⁻¹ in *N,N*-dimethylacetamide (DMAc) containing 5 wt% LiCl dissolved.

Preparation of Polyamide Films

The polyamide films were cast from their solutions in DMAc (*ca.* 10% solid) in an oven set at 90 °C. The films were then released from the glass surface and dried under vacuum at 160 °C for 10 h. The obtained films showed about 0.05 mm in thickness and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Measurements

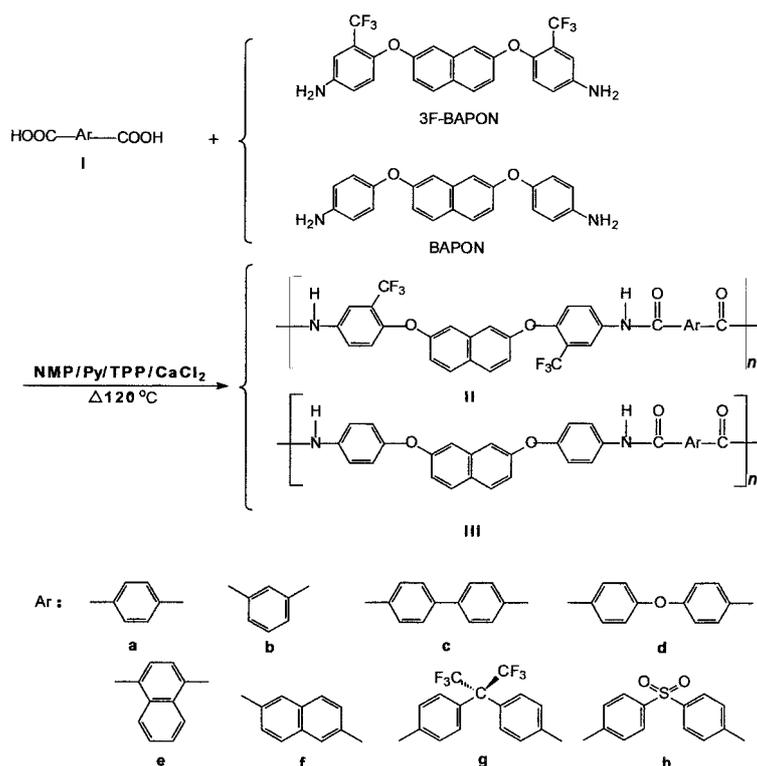
Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared (FT-IR) spectrometer. The inherent viscosities of the polyamides were measured with a Cannon-Fenske viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements

were performed at room temperature (about 25 °C) on a Shimadzu XRD 6000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized Cu-K α radiation. Gel permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μ m Styragel HR-2 and HR-4 columns (7.8 mm I.D. \times 300 mm) connected in series were used with tetrahydrofuran (THF) as the eluent and were calibrated with narrow polystyrene standards. An Instron universal tester model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the polyamide film samples. A gauge length of 2 cm and a crosshead speed of 5 mm min⁻¹ were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.05 mm thick), and an average of at least five individual determinations was used. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 7–10 mg film samples heated in flowing nitrogen or air (flow rate 30 cm³ min⁻¹) at a heating rate of 20 °C min⁻¹. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C min⁻¹ in flowing nitrogen (20 cm³ min⁻¹). Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 50 °C to 300 °C at a scan rate of 10 °C min⁻¹ using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s) were taken as the onset temperature of probe displacement on the TMA traces.

RESULTS AND DISCUSSION

Synthesis of Polyamides

According to the phosphorylation technique described by Yamazaki and co-workers,^{17,18} a series of new aromatic polyamides **IIa–h** containing the CF₃ groups were synthesized from 3F-BAPON with various aromatic dicarboxylic acids **Ia–h** (Scheme 1). For comparison, another series of polyamides **IIIa–h** based on the nonfluorinated diamine BAPON were also prepared by the same technique. As shown in Table I, the inherent viscosities of the resultant **II** and **III** series polyamides were in the range of 0.40–1.46 dL g⁻¹ and 0.48–0.76 dL g⁻¹, respectively. The weight-average molecular weights (M_w) and number-average molecular weights (M_n) of some polyamides were recorded in the range of 43000–97000 and 30000–79000, re-

**Table I.** synthesis conditions, inherent viscosity, and film quality of polyamides

Polymer code	Amount of reagents used ^a				η_{inh}^b (dL g ⁻¹)	Film quality ^c
	NMP (mL)	Pyridine (mL)	TPP (mL)	CaCl ₂ (g)		
IIa	2.5	0.6	1.5	0.25	0.54	F
IIb	2.5	0.5	1.5	0.20	0.47	F
IIc	2.5	0.6	1.5	0.25	0.54	F
IId	3 + 1	0.8	1.5	0.30	1.23	F
IIe	2.5	0.6	1.5	0.20	0.61	F
IIf	3 + 1	0.8	1.5	0.30	1.46	F
IIg	2.5	0.6	1.5	0.25	0.40	F
IIh	2.5	0.6	1.5	0.25	0.41	F
IIIa	2.5 + 4	0.6	1.5	0.25 + 0.30	0.64	— ^d
IIIb	2.5	0.6	1.5	0.25	0.48	F
IIIc	4 + 4	0.8	1.5	0.40 + 0.30	—	—
IIId	3 + 2	0.8	1.5	0.25 + 0.10	0.69	B
IIIe	2.5	0.8	1.5	0.25	0.76	F
IIIf	4	0.6	1.5	0.40	0.70	—
IIIg	2.5	0.6	1.5	0.25	0.76	F
IIIh	2.5	0.6	1.5	0.25	0.75	F

^aThe polymerization was carried out with 1.5 mmol of each monomer at 120 °C for 3 h. ^bInherent viscosity of the polyamides measured in DMAc-5 wt% LiCl at a concentration of 0.5 g dL⁻¹ at 30 °C.

^cFilms were cast by slow evaporation of solutions in DMAc. B: brittle film (cracked upon creasing); F: flexible film. ^dInsoluble in all the available organic solvents.

spectively, relative to polystyrene standards (Table II). In some cases of the **III** series polyamides such as **IIIa**, **IIIc**, and **IIIf**, precipitation occurred during the polymerization due to insolubility of the polymers, and adding more solvent or salt in order to carry out the reaction in a homogeneous phase has met with failure

in obtaining clear and viscous polymer solutions. A powdery product was obtained when these polymer solutions were precipitated into methanol. The insolubility for these polyamides may be attributed to their high level of crystallinity. No attempts were made to cast the powdery products into polymer films. For

Table II. Inherent viscosity and molecular weights of some fluorinated polyamides

Polyimide	η_{inh}^a (dL g ⁻¹)	\overline{M}_w^b	\overline{M}_n^b	$\overline{M}_w/\overline{M}_n$
IIa	0.54	66000	41500	1.59
IIb	0.47	66500	43500	1.53
IIc	0.54	59000	36500	1.62
IId	1.23	97000	79000	1.23
IIg	0.40	58000	38500	1.51
IIh	0.41	43000	30000	1.43

^aMeasured at a concentration of 0.5 g dL⁻¹ in DMAc-5 wt% LiCl at 30 °C. ^bMeasured by GPC in THF, relative to polystyrene standards.

the polyamides with good solubility, the polymerization proceeded homogeneously throughout the reaction and gave a clear and viscous polymer solution. A tough, stringy precipitate could be obtained when slowly pouring the resulting polymer solutions into stirred methanol. Most of the soluble polyamides could be fabricated into strong and flexible films *via* solution casting, indicating that these polyamides had medium to high molecular weights. The chemical structures of these polyamides were confirmed by FT-IR and NMR spectroscopy. They exhibited characteristic IR absorption bands of the amide group around 3300 (N–H stretching), 1650 (C=O stretching), and 1530 cm⁻¹ (N–H bending), along with the characteristic absorption band of aryl ether stretching near 1220 cm⁻¹. The polyamides derived from 3F-BAPON revealed an additional strong absorption around 1140 cm⁻¹ due to the C–F stretching vibrations. As a typical example, the structure of polyamide **IIa** was confirmed by solution NMR in DMSO-*d*₆ (Figure 1). The formation of the amide group was confirmed by the resonance signals of amide protons at δ 10.7 in the ¹H NMR spectrum and amide carbons at δ 165.0 in the ¹³C NMR spectrum.

Properties of Polyamides

As can be seen from the typical WAXD patterns shown in Figure 2, the BAPON polyamides (**III** series) derived from rigid diacids such as **IIIa**, **IIIc**, and **IIIf** showed some diffraction signals of medium to high intensity assignable to a semicrystalline polymer. In contrast, the corresponding CF₃-substituted **II** series analogues displayed a nearly completely amorphous pattern. The incorporation of bulky CF₃ side groups produces a wider separation of polymer chains, a weakening of intermolecular hydrogen bonding, and a lowering of chain packing efficiency with a gain of free volume, thus resulting in a decrease in crystallinity.

The qualitative solubility properties of polyamides are reported in Table III. All the 3F-BAPON-based polyamides (**IIa–h**) exhibited good solubility. How-

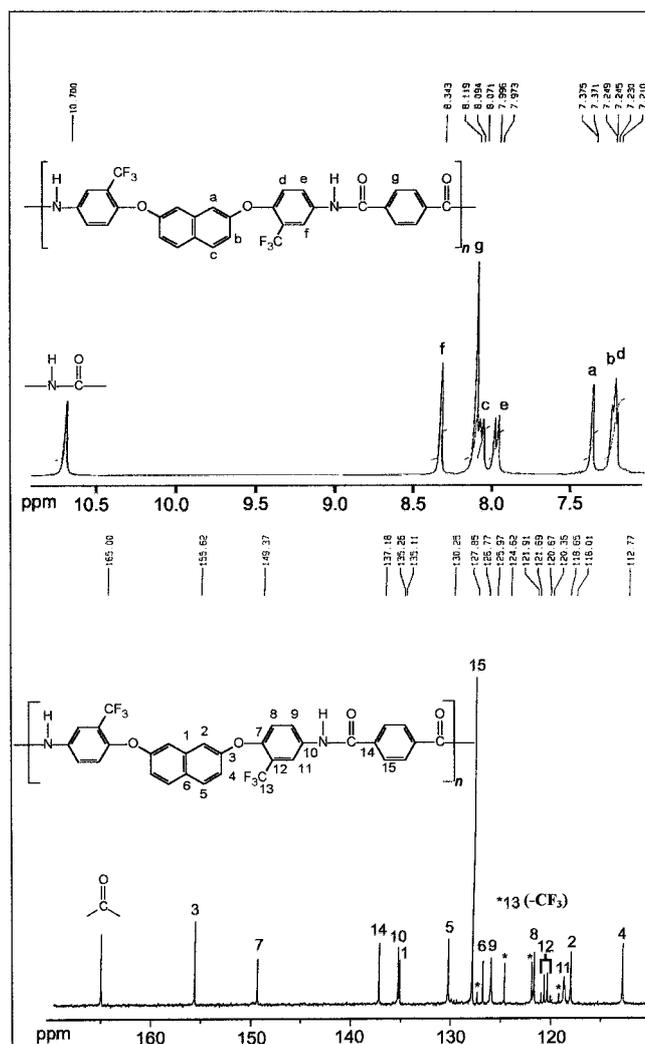


Figure 1. The ¹H NMR and ¹³C NMR spectra of polyamide **IIa** in DMSO-*d*₆.

ever, the **III** series polyamides derived from rigid dicarboxylic acids, such as **Ia**, **Ic**, and **If**, generally showed a lower solubility due to a high level of crystallinity. Almost all of them were insoluble in any of the solvents tested. Polyamides **IId** and **IIIe** also revealed a less solubility, although their WAXD patterns did not show an obvious crystalline halo. Poor solubility for polyamides **IId** and **IIIe** indicates either strong intermolecular interactions or good packing capability. The amorphous **III** series polyamides exhibited a higher solubility; they were soluble in most polar aprotic solvents. Obviously, the solubility of the **II** series polyamides was higher than that of the **III** series polyamides. It is evident that the introduction of the CF₃ units improves the solubility of polyamides. The reason is similar to that cited above. All the soluble polyamides could be processed to flexible, creasable films by casting from solutions in DMAc. Their tensile strengths, elongations to break, and initial moduli were in the range of 60–94 MPa, 7–18%, 1.8–2.3 GPa,

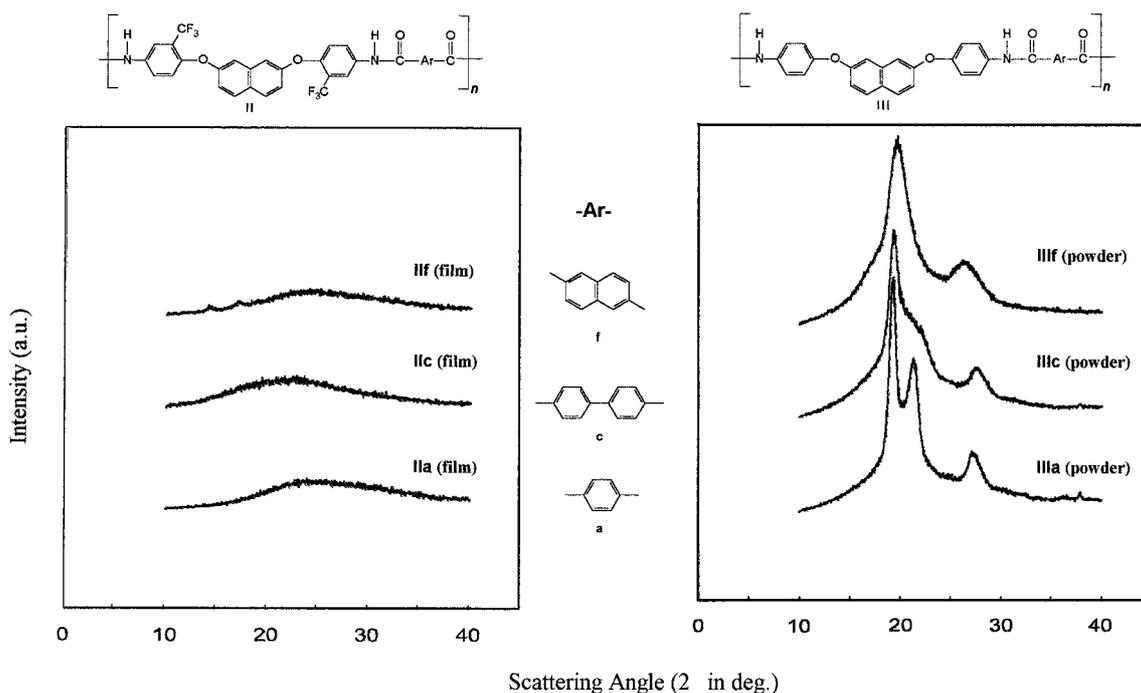


Figure 2. Wide-angle X-ray diffractograms of some typical polyamides.

Table III. Solubility behavior of polyamides

Polymer code	Solubility ^a					
	NMP	DMAc	DMSO	DMF	<i>m</i> -cresol	THF
IIa	+	+	+	+	+	+
IIb	+	+	+	+	+	+
IIc	+	+	+	+	+	+
IId	+	+	+	+	+	+
IIe	+	+	+	+	+h	+h
IIf	+	+	+	+	-	-
IIg	+	+	+	+	+	+
IIh	+	+	+	+	+	+
IIIa	+	-	-	-	-	-
IIIb	+	+	+	-	-	-
IIIc	-	-	-	-	-	-
IIId	+	-	-	-	-	-
IIIe	+h	+h	-	-	-	-
IIIf	+	-	-	-	-	-
IIIg	+	+	+	+	+	+
IIIh	+	+	+	+	-	-

^aQualitative solubility tested with 10 mg of sample in 1 mL of the solvent. +: soluble at room temperature; +h: soluble on heating; -: insoluble even on heating.

respectively. In general, the **II** series polyamides behaved as strong and tough materials.

The thermal behavior data of the polyamides determined by DSC, TMA, and TGA are reported in Table IV. All the 3F-BAPON-based polyamides (**IIa–h**), showed clear glass transitions on their DSC curves between 227 °C and 257 °C, generally following the increasing order of chain rigidity, steric hindrance, and polarity of the diacid residues. The lowest T_g of 227 °C was observed for polyamide **IIb** derived from

isophthalic acid (**IIb**). The highest T_g value (257 °C) of polyamide **IIf** is believed to be due to the increased structural rigidity caused by the naphthalene-2,6-diyl units. For the **III** series polyamides, the semicrystalline **IIIa**, **IIIc**, and **IIIf** showed melting endotherms centered in the range of 443–463 °C but no well-defined T_g 's on the DSC traces. The structurally less rigid polyamides **IIIb**, **IIId**, and **IIIe** also showed clear melting endotherms around 376–392 °C in the first DSC heating scan. By contrast, none of the **II** series polyamides showed any well-defined melting endotherms on the DSC traces because of their amorphous characteristics. The softening temperatures (T_s 's) of the polymer film samples were measured with TMA by the penetration method. In most cases, the T_s values obtained by TMA are comparable to the T_g values observed by the DSC measurements. The 3F-BAPON-based polyamides **IIe** and **IIg** exhibited slightly lower T_g or T_s values as compared to the corresponding BAPON-based **IIIe** and **IIIg** because of decreased interchain interactions caused by the CF_3 groups. However, in some cases, such as **IIb**, **IId**, and **IIh**, the introduction of the pendent CF_3 groups resulted in very small changes in the T_g and T_s values, as compared with those of the corresponding polyamides **IIIb**, **IIId**, and **IIh**. Thus, the increased rotational barrier of the CF_3 group may overcome the effect of decreased intermolecular interactions introduced with the pendent group. The decomposition temperatures at a 10% weight loss determined from the original TGA curves are listed in Table IV. All polymers exhibited

Table IV. Thermal behavior data of polyamides^a

Polymer code	T_g^b (°C)	T_s^c (°C)	$T_d(°C)^g$		Char yield ^h (%)
			In N ₂	In air	
IIa	232	236	470	450	61
IIb	227	225	483	457	60
IIc	242	243	465	446	62
IId	237	233	484	474	58
IIe	234	232	460	449	59
IIf	257	257	497	485	63
IIg	235	238	487	461	53
IIh	252	243	482	466	59
IIIa	— ^c (455) ^d	— ^f	486	470	71
IIIb	227 (376)	224	518	521	57
IIIc	— (463)	—	512	487	70
IIId	234 (392)	238	492	483	68
IIIe	250 (382)	251	490	502	70
IIIf	— (443)	—	491	520	71
IIIg	245	247	527	532	59
IIIh	248	247	508	522	67

^aAll the samples were heated at 250 °C for 30 min prior to DSC, TMA, and TGA experiments. ^bMidpoint temperature of baseline shift on the DSC heating trace at a heating rate of 20 min⁻¹. For polymer series **II**, T_g was taken from the first DSC heating trace; for polymer series **III**, T_g was taken from the second DSC heating scan after quick cooling from 400 °C at a programmed rate of 200 °C min⁻¹. ^cNo discernible transition. ^dValues in the parentheses were the peak top temperatures of melting endotherms observed on the first DSC heating traces. ^eSoftening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C min⁻¹. ^fNo available specimen. ^gDecomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C min⁻¹. ^hResidual wt% at 800 °C in nitrogen.

a moderately high thermal stability with insignificant weight loss up to temperatures of approximately 400 °C in both air and nitrogen atmospheres, and the anaerobic char yield at 800 °C for all polymers was in the range of 53–71 wt%. Obviously, the **II** series polyamides started to lose weight at a lower temperature in comparison with the **III** series analogues. This is contrary to that observed for the 3F-BAPON polyimides reported previously¹⁶ and may be a consequence of decreased chain–chain hydrogen bonding in the series **II** polyamides caused by the bulky CF₃ group. Although a slight detriment in thermal stability caused by the introduction of the CF₃ groups, most of the **II** series polyamides showed some better properties for practical use such as good solubility and mechanical properties, as compared to the **III** series counterparts.

CONCLUSIONS

New soluble ether-bridged aromatic polyamides with trifluoromethyl substituents were successfully

synthesized by the direct polycondensation of the diamine 2,7-bis(4-amino-2-trifluoromethylphenoxy)-naphthalene and various aromatic dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents. The introductions of the bulky trifluoromethyl group were to disrupt any regularity in chain packing while increasing the spacing or fractional free volume between the polymer chains. All the polyamides were noncrystalline and could be cast to transparent and tough films. The introduction of trifluoromethyl groups along the polymer backbone significantly increases the solubility in common solvents but with a slight decrease in thermal stability.

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