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New soluble aromatic polyamides containing ether linkages and laterally attached *p*-terphenyls

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Abstract

Two series of new polyamides containing flexible ether linkages and laterally attached side rods (**3a-i** and **4a-i**) were synthesized from 2′,5′-bis(4-aminophenoxy)-[1,1′;4′,1″]terphenyl (**1a**) and 2′,5′-bis(4-amino-2-trifluoromethylphenoxy)-[1,1′;4′,1″]terphenyl (**1b**), respectively, with various aromatic dicarboxylic acids by the direct phosphorylation polycondensation. The polymers were produced with high yields and moderate to high inherent viscosities (0.41–0.97 dl/g) that corresponded to weight-average molecular weights (by size exclusion chromatography) of 47,000–65,000. Except for some polyamides that derived from rigid diacids, the obtained polyamides were readily soluble in aprotic polar solvents, such as *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc), and could afford flexible and tough films via solvent casting. The polymer films cast from DMAc solutions possessed tensile strengths of 85–106 MPa and initial moduli of 1.82–2.96 GPa. These polyamides showed glass-transition temperatures (T_g) in the range of 206–263 °C (by DSC) and softening temperatures (T_s) in the range of 211–253 °C (by TMA). Decomposition temperatures (T_d) for 10% weight loss all occurred above 400 °C (by TGA) in both nitrogen and air atmospheres. The polyamides **4a-i** derived from trifluoromethyl-substituted diamine **1b** generally showed a higher solubility, T_g and T_s but lower thermal stability as compared to the analogous polyamides **3a-i** based on diamine **1a**.

Keywords: Trifluoromethyl; Polyamides; *p*-Terphenyl

1. Introduction

Wholly aromatic polyamides (aramids) have been well known for their high temperature stability, excellent mechanical strength and good chemical resistance, which qualify them as high-performance polymeric materials [1,2]. Fibers obtained from anisotropic solutions of these high-performance materials have been used in applications where high thermal stability and mechanical strength are required. However, most aramids suffer poor processability due to limited solubility in common organic solvents and high glass-transition (T_g) and softening (T_s) temperatures. Therefore, considerable effort has been made to increase the processability and solubility of aramids by structural modification. Soluble or thermoplastic aramids may open applications in films, separation membranes, coatings, polymer blends, and composites. One of the most common approaches to increasing solubility and lowering T_g and T_s is the introduction of flexible bonds in the polymer backbone and/or bulky pendent groups along the main chain [3–16]. In this respect, it is known that the incorporation of bulky pendent groups such as *tert*-butyl [9,10], adamantly [11], and norbornane [12] units provides enhanced solubility because this approach results in a separation of chains, a weakening of hydrogen bonding, and a decrease of packing efficiency with a gain of free volume. Bulky side groups also give rise to

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restricted segmental mobility, so that the overall observable effect is a remaining high T_g and an enhancement in solubility at the same time. However, the introduction of these pendent groups generally decreases thermal and thermo-oxidative stability due to their aliphatic nature. According to these research trends, the present work deals with the synthesis of novel polyamides containing both ether and thermally stable bulky pendent groups such as CF_3 and phenyl groups along the polymer backbones. Our strategy was based on the phosphorylation polyamidations of diamines 2′,5′-bis(4-aminophenoxy)-[1,1′; 4′,1″]terphenyl (**1a**) and 2′,5′-bis(4-amino-2-trifluoromethylphenoxy)-[1,1′;4′,1″]terphenyl (**1b**) with various aromatic dicarboxylic acids. The basic properties of these new polyamides, such as solubility, film-forming capability, mechanical properties, crystallinity, and thermal properties, are discussed. A major object was to study the effect of the laterally attached *p*-terphenyls and the CF_3 substituents on the properties of the polymers.

2. Experimental

2.1. Reagents and solvents

Triphenyl phosphite (TPP) (from Fluka) was purified by distillation under reduced pressure. *N*-Methyl-2-pyrrolidone (NMP) and pyridine (Py) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. Commercially obtained anhydrous calcium chloride ($CaCl_2$) (from Wako) was dried under vaccum at 180 °C for 8 h. [1,1′;4′,1″]Terphenyl-2′,5′-diol was prepared from the reduction of 2,5-diphenyl-*p*-benzoquinone by means of zinc powder in refluxing acetic acid [17]. According to well-developed methods [18–20], diamines **1a** (m.p. 250–251 °C) and **1b** (m.p. 222–223 °C) were synthesized by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene and 2-chloro-5-nitrobenzotrifluoride, respectively, with [1,1′;4′,1″]terphenyl-2′,5′-diol in the presence of potassium carbonate, followed by catalytic reduction of the intermediate dinitro compounds using hydrazine monohydrate as the reducing agent and palladium on charcoal as the catalyst. The synthetic details and characterization data of these two diamines have been described in a previous publication [21]. The commercially available aromatic dicarboxylic acids such as terephthalic acid (**2a**; from Fluka), isophthalic acid (**2b**; from Fluka), 5-*tert*-butylisophthalic acid (**2c**; from Aldrich), 4,4′-biphenyldicarboxylic acid (**2d**; from TCI), 2,6-naphthalenedicarboxylic acid (**2e**; from TCI), 1,4-naphthalenedicarboxylic acid (**2f**; from Wako), 4,4′-dicarboxyphenyl ether (**2g**; from TCI), 4,4′-dicarboxyphenyl sulfone (**2h**; from New Japan Chemical Co.), and 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**2i**; from Chriskev) were used as received.

2.2. Polymer synthesis

The phosphorylation polycondensation method was used to prepare the polyamides presented in this work. A typical synthetic procedure for polyamide **4b** is described as follows. A mixture of 0.5805 g (1.0 mmol) of diamine **1b**, 0.1661 g (1.0 mmol) of isophthalic acid (**2b**), 0.2 g of $CaCl_2$, 1.2 ml of TPP, 0.5 ml of pyridine, and 2 ml of NMP was heated with stirring at 120 °C for 3 h. The reaction mixture became viscous gradually as polycondensation proceeded. The resulting viscous polymer solution was poured slowly into 300 ml of stirred methanol giving rise to a tough, fiber-like white polymer precipitate. The product was collected by filtration, thoroughly washed by methanol and hot water, and dried. The inherent viscosity of the polyamide (**4b**) was 0.50 dl/g, as measured at a concentration of 0.5 g/dl in DMAc containing 5 wt% LiCl at 30 °C.

IR (film): 3294 (N–H stretching), 1668 (C=O stretching), 1227 (C–O stretching), and 1134 cm^{-1} (C–F stretching). ELEM. ANAL. Calcd. for $(C_{40}H_{24}N_2O_4F_6)_n$ $(710.63)_n$: C, 67.61%; H, 3.40%; N, 3.94%; Found: C, 66.07%; H, 3.43%; N, 3.56%.

2.3. Film preparation

A polymer solution of approximately 10 wt% was made by dissolving about 0.8 g of the polyamide in 8 ml of hot DMAc. The clear solution was poured into a 9-cm diameter glass culture dish, which was placed in a 90 °C oven for 12 h to evaporate the solvent. Then, the semi-dried polyamide film was stripped off from the glass surface and further dried in vacuo at 160 °C for 24 h. The obtained films showed about 0.08 mm in thick and were used for X-ray diffraction measurements, solubility tests, tensile tests, and thermal analyses.

2.4. Characterization methods

Infrared (IR) spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analysis was made on a Heraeus VarioEL-III elemental analyzer. The inherent viscosities of the polyamides were determined with a Cannon-Fenske viscometer at 30 °C. Size exclusion chromatography (SEC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5-μm styragel HR-2 and HR-4 columns (7.8 mm inside diameter × 300 mm) connected in series were used with tetrahydrofuran (THF) as the eluent and were calibrated with narrow polystyrene standards. The measurements were carried out at 35 °C with a flow rate of 1.0 ml/min. An Instron universal tester (model 4400R) 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 were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.08 mm thick), and an average of at least three replicas was used. Wide-angle X-ray diffraction measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer (operating at 40 kV and 30 mA) with graphite-monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å). The scanning rate was 2 °C/min over a range of $2\theta = 10$–40 °C. Thermogravimetric analysis (TGA) was conducted with a Perkin–Elmer Pyris 1 TGA. Experiments were carried out on approximately 6-8 mg of samples in flowing nitrogen or air (flow rate 20 cm^3/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a Perkin–Elmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. Glass-transition temperatures (T_g's) were read at the middle of the transition in the heat capacity and were taken from the heating DSC traces. Thermomechanical analysis (TMA) was conducted with a Perkin–Elmer TMA 7 instrument. The TMA experiments were conducted from 40 to 300 °C at a scan rate of 10 °C/min using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s's) were taken as the onset temperature of probe displacement on the TMA traces. The samples were heated at 250 °C for 1 h prior to all thermal analysis experiments.

3. Results and discussion

3.1. Polymer synthesis

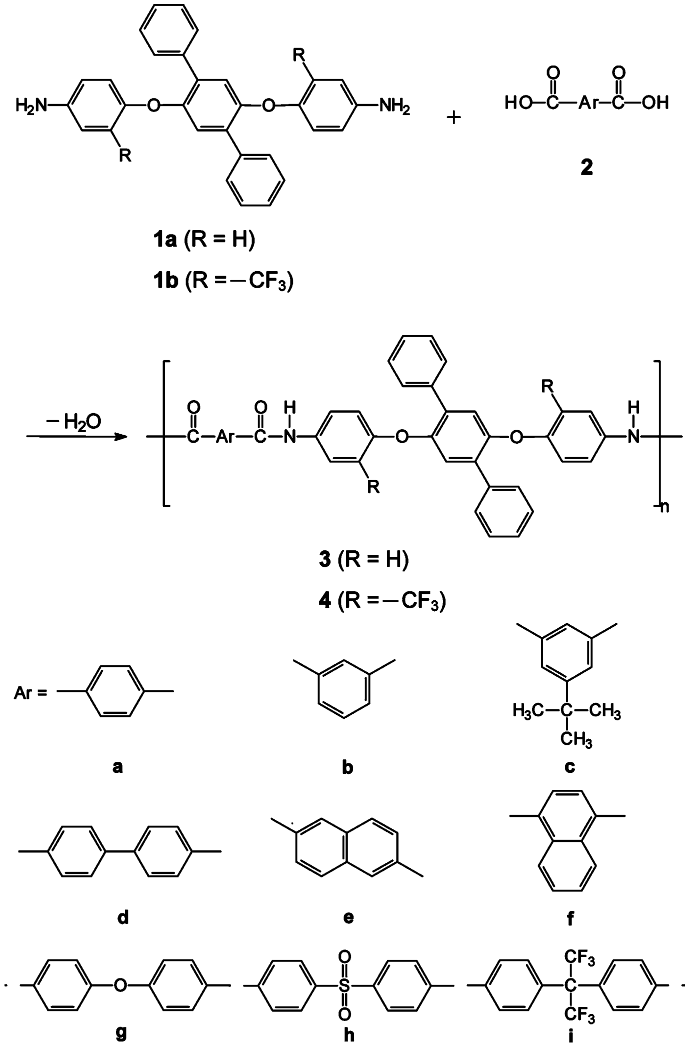
Direct polycondensation of a dicarboxylic acid with a diamine using triphenyl phosphite and pyridine as condensing agent to form amide bonds is an efficient way in the synthesis of polymers [22]. Two series of aromatic polyamides, **3a-i** and **4a-i,** were synthesized using the phosphorylation polyamidation procedure from dicarboxylic acids **2a-i** with diamines **1a** and **1b,** respectively. Structures and codes of the polymers prepared are shown in Scheme 1. Except for **3e** and **3f**, all other polyamidations proceeded in homogeneous, transparent and viscous solutions throughout the reaction, and the polyamides were isolated as stringy fibers or powders in quantitative yields. In some cases, using a higher initial reactant concentration and adding more solvent to the highly viscous reaction medium before the occurrence of precipitation or the formation of the swollen gel could yield polymers with higher molecular weights. As shown in Table 1, inherent viscosities for **3a-3i** ranged from 0.36 to 0.82 dl/g, and for **4a-4i** were between 0.48 and 0.97 dl/g in DMAc-5 wt% LiCl, indicating medium to high molecular weight polyamides. SEC analysis revealed that the weight-average (M_w) and number-average (M_n) molecular weights of the THF-soluble polyamides are in the ranges of 47,000–65,000 and 27,000–39,000, respectively. Most of the polyamides prepared could be solvent-cast into flexible, high-strength films. Structural features of these polyamides were verified by FTIR spectroscopy. They exhibited characteristic absorption bands of the amide group around 3300 (N–H stretching) and 1670 cm^{-1} (C=O stretching), together with strong absorptions of C–F stretching near 1130 cm^{-1} for the **4** series polyamides. The representative IR spectra for the thin films of polyamides **3b** and **4b** are illustrated in Fig. 1.

3.2. Polymer characterization

The crystallinity of all the polymers was evaluated by wide-angle X-ray diffraction (WAXD) studies. The WAXD patterns of the **3** and **4** series polyamides are shown in Fig. 2. The **3** series polyamides derived from rigid diacids such as **2a**, **2d,** **2e**, and **2f** showed some diffraction signals of medium to high intensity assignable to a semi-crystalline polymer. In contrast, all the CF$_3$-substituted **4** series polyamides except **4a** displayed a nearly completely amorphous pattern. On comparing the WAXD patterns of the analogous pairs of **3d/4d**, **3e/4e**, and **3f/4f**, an obvious effect of the introduction of the pendent CF$_3$ groups on decreasing the crystallinity of these polyamides was observed. The incorporation of bulky CF$_3$ groups further decreases the regularity of polymer chains, a weakening of intermolecular hydrogen bonding, and chain packing efficiency, thus resulting in a decrease in crystallinity.

The solubility behavior of polyamides was tested qualitatively, and the results are summarized in Table 2. The polyamides derived from rigid dicarboxylic acids, such as **3a**, **3d**, **3e**, **3f**, and **4a,** revealed a lower solubility due to the semi-crystalline nature as shown by their WAXD patterns. Almost all of them were insoluble in any of the solvents tested. The other amorphous polyamides generally showed an excellent solubility in polar aprotic solvents. Obviously, the **4** series polyamides exhibited an enhanced solubility as compared to the **3** series analogs. It is evident that the introduction of the CF$_3$ substituents resulted in increased chain packing distances and decreased intermolecular interactions, leading to higher solubility.

The tensile properties of the flexible polyamide films are reported in Table 3. They had tensile strengths of 89–114 MPa, elongations to break of 7–16%, and initial moduli of 1.82–2.96 GPa, which qualify them as strong and tough materials. In general, the polymer films



Scheme 1. Synthesis of polyamides.

obtained from the **4** series revealed a relatively lower tensile strength than those of their corresponding **3** counterparts. This can be attributed to the presence of CF_3 substituents, which may result in decreased chain–chain interactions, e.g., hydrogen bonding.

DSC, TMA, and TGA were used to evaluate thermal properties of all polymers. The thermal behavior data of the polyamides are summarized in Table 4. To avoid the effects of the moisture absorbed by the samples and the residual solvent in the film samples, we heated the samples at 250 °C for 1 h prior to thermal analysis. Glass-transition temperature (T_g) of these polyamides was obtained from the middlepoint temperature of baseline shift on the DSC heating trace (heating rate = 20 °C/min). Except for **3d** and **3e**, all other polyamides showed a clear T_g in the range of 206–263 °C on their DSC curves, generally following the increasing order of chain rigidity. No discernible T_g's were observed for polyamides **3d** and **3e** by DSC, probably due to their high level of crystallinity. When the two sets of polyamides are compared, the **4** series polyamides generally showed relatively higher T_g values. This might be a consequence of higher restriction of mobility in diamine **1b**, which has CF_3 groups hindering rotation at the ether sites. The T_s values of these polymer film samples were measured with TMA by the penetration method. They were obtained from the onset temperature of the probe displacement on the TMA trace. Typical TMA thermograms for polymers **3g** and **4g** are illustrated in Fig. 3. Polyamides **4a-4i** exhibited T_s values between 212 and 253 °C. The T_s values for

Table 1
Synthesis conditions, inherent viscosities, and average molecular weights of polyamides

Polymer	Amounts of reagents used[a]				η_{inh} (dl/g)[b]	GPC data of polyamides[c]		
	NMP (ml)	Py (ml)	TPP (ml)	$CaCl_2$ (g)		M_n	M_w	M_w/M_n
3a	2.5 + 1[d]	0.6	1.5	0.25	0.63	–[e]	–	–
3b	1.5	0.5	1.5	0.2	0.41	–	–	–
3c	2	0.5	1.5	0.2	0.36	–	–	–
3d	3	0.8	1.5	0.3	0.65	–	–	–
3e	3 + 2	0.8	1.5	0.3	0.82	–	–	–
3f	3 + 1	0.8	1.5	0.3	0.47	–	–	–
3g	3	0.8	1.5	0.3	0.61	–	–	–
3h	3	0.8	1.5	0.3	0.45	–	–	–
3I	3	0.8	1.5	0.3	0.45	27000	47000	1.74
4a	2 + 1	0.5	1.0	0.2	0.92	39000	65000	1.67
4b	2	0.5	1.0	0.25	0.50	30000	52000	1.78
4c	1.5	0.5	1.0	0.15	0.48	31000	57000	1.86
4d	2.5 + 1	0.6	1.0	0.15	0.97	37000	61000	1.65
4e	2.5	0.6	1.0	0.25	0.79	33000	64000	1.93
4f	2.5	0.6	1.0	0.25	0.61	33000	63000	1.87
4g	2.5	0.6	1.0	0.25	0.54	32000	61000	1.91
4h	2.5	0.6	1.0	0.25	0.58	30000	54000	1.79
4i	2	0.5	1.0	0.2	0.61	29000	61000	2.14

[a] Monomer scale: 1.5 mmol for the **3** series and 1 mmol for the **4** series polymers. Reaction temperature = 110 °C; time = 3 h; NMP = *N*-methyl-2-pyrrolidone; Py = pyridine; TPP = triphenyl phosphite.

[b] Measured in DMAc containing 5 wt% LiCl at 30 °C on 0.5 g/dl.

[c] Molecular weights relative to polystyrene standards in THF by GPC.

[d] "2.5 + 1" means that an initial amount of 2 ml of NMP was used and an additional 1 ml of NMP was added when the reaction solution was too viscous to stir.

[e] Insoluble in THF.

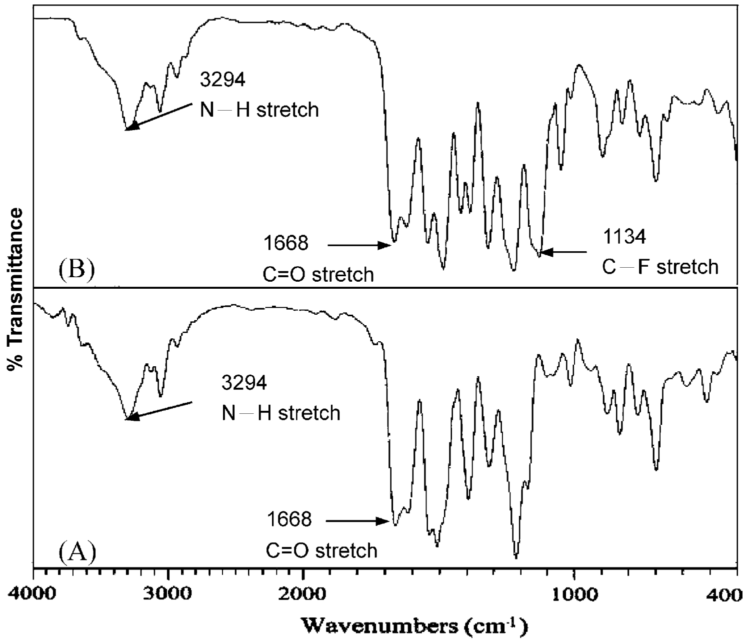


Fig. 1. (A) The FTIR spectrum of polyamide **3b** and (B) the FTIR spectrum of polyamide **4b.**

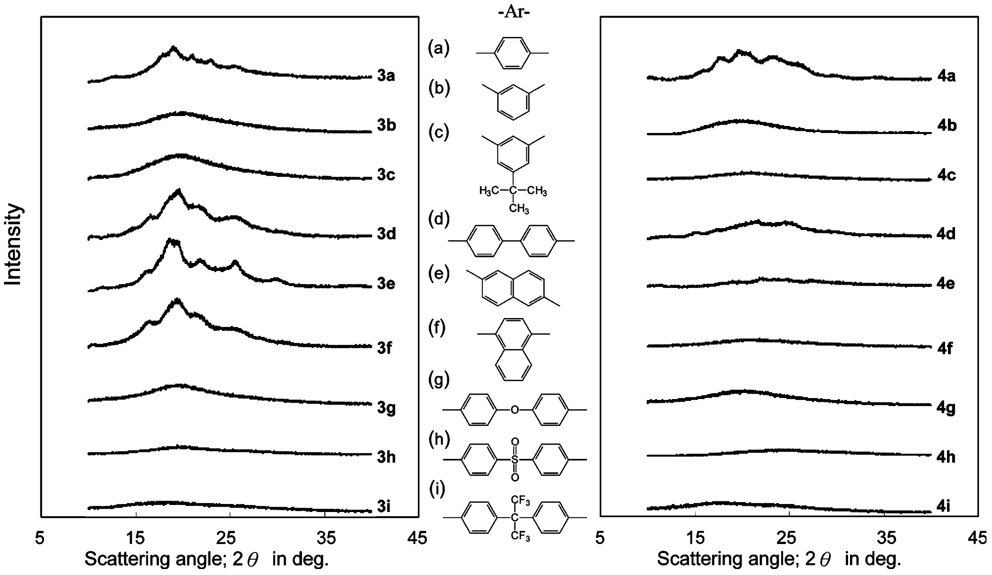


Fig. 2. WAXD patterns of polyamides.

Table 2
Solubility behavior of polyamides

Polyamide	Solvent[a]					
	NMP	DMA	DMF	DMSO	m-Cresol	THF
3a	–	–	–	–	–	–
3b	+	+	+	+h	+h	–
3c	+	+	+	+	+h	–
3d	–	–	–	–	–	–
3e	–	–	–	–	–	–
3f	–	–	–	–	–	–
3g	+	+	+	+	+h	–
3h	+	+	+h	–	+h	–
3i	+	+	+	+	+	+
4a	+	–	–	–	+h	+
4b	+	+	+	+h	+	+
4c	+	+	+	+	+	+
4d	+	+h	+	–	+	+
4e	+	+	+h	–	–	+h
4f	+	+	+	+	+	+
4g	+	+	+	+	+	+
4h	+	+	+	+	+	+
4i	+	+	+	+h	+	+

+: soluble at room temperature; +h: soluble on heating at 100 °C; –: insoluble even on heating. NMP: *N*-methyl-2-pyrrolidone; NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

[a] Qualitative solubility tested with 10 mg of sample in 1 ml of the solvent.

the **3** series polymers that could afford freestanding films were between 196 and 236 °C. In most cases, the T_s values obtained by the TMA technique are comparable to the T_g values measured by the DSC experiments. The same T_s trend was observed where the CF_3-substituted **4** polyamides generally had higher T_s's than the **3** series polyamides. Thus, the effect of increased rotational barrier caused by the CF_3 groups may overcome the effect of decreased intermolecular interactions introduced with these pendent groups.

The thermal and thermo-oxidative stability of the polyamides was studied by TGA. The decomposition

Table 3
Tensile properties of polyamide films[a]

Polymer code	Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)
3b	109	9	2.24
3g	114	14	2.09
3h	106	16	2.02
3i	105	10	2.19
4b	85	7	2.03
4c	91	9	1.92
4f	92	10	1.82
4g	100	14	2.10
4h	89	12	2.08
4i	96	13	2.10

[a] Films were cast from slow evaporation of polymer solutions in DMAc. The cast films were dried under vacuum at 160 °C for 24 h prior to the tensile test.

Table 4
Thermal properties of polyamides[a]

Polymer code	T_g[b] (°C)	T_s[c] (°C)	$T_{5\%\mathrm{wt\,loss}}$[d] (°C)		$T_{10\%\mathrm{wt\,loss}}$[d] (°C)		Char yield[e] (%)
			In N_2	In air	In N_2	In air	
3a	218	212	439	426	469	476	67
3b	206	196	476	436	524	491	70
3c	216	211	394	383	484	466	57
3d	–[f]	–[g]	508	475	560	506	67
3e	–	–	483	471	510	500	68
3f	238	–	465	445	508	502	64
3g	216	214	480	439	532	482	66
3h	229	225	449	432	495	472	63
3i	231	236	464	441	506	489	66
4a	228	212	408	406	446	433	58
4b	220	218	416	415	456	455	53
4c	228	215	416	409	459	446	55
4d	263	253	426	425	476	474	60
4e	249	249	392	394	449	449	61
4f	226	225	405	394	451	436	59
4g	224	221	417	409	463	449	59
4h	251	251	391	396	455	448	56
4i	248	229	414	408	464	460	5

[a] All the polyamide samples were heated at 250 °C for 1 h prior to DSC, TMA, and TGA experiments.

[b] Midpoint temperature of baseline shift on the DSC heating trace.

[c] Softening temperature measured by TMA at a heating rate of 10 °C/min.

[d] Recorded by TGA at heating rate of 20 °C/min.

[e] Residual weight % at 800 °C in nitrogen.

[f] No discernible transition.

[g] No available sample.

temperatures of at 5% and 10% weight loss in nitrogen and air atmospheres determined from the original thermograms are included in Table 4. All polymers exhibited good 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 52-70 wt%. Typical TGA curves in nitrogen and air atmospheres of the representative polymers **3d** and **4d** are shown in Fig. 4. As can be seen from Fig. 4 and Table 4, all the **4** series polyamides showed slightly lower thermal and thermo-oxidative stability compared to the corresponding **3** counterparts. This might be explained by the fact that the presence of CF_3 groups brought about chain separation, thus decreasing the interchain interactions between amide groups.

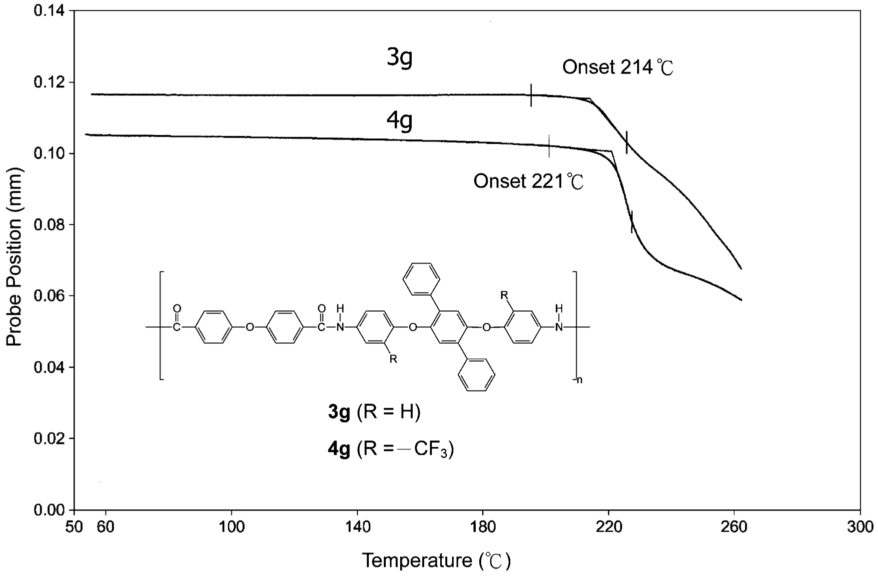


Fig. 3. TMA thermograms of polyamides **3g** and **4g** at a heating rate of 10 °C/min.

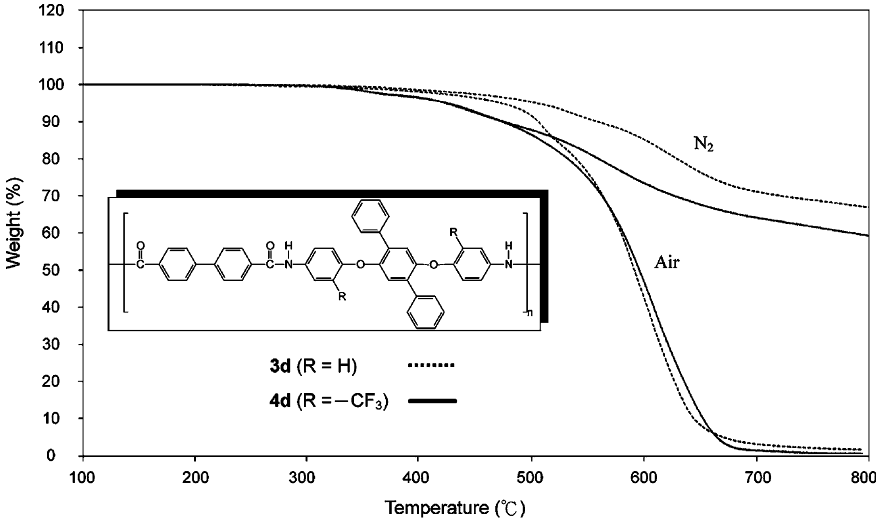


Fig. 4. TGA curves of polyamides **3d** and **4d** at a heating rate of 20 °C/min.

4. Conclusions

Two series of novel polyamides with ether and laterally attached *p*-terphenyl groups have been successfully synthesized from the polycondensation reactions of diamines **1a** and **1b** with various aromatic dicarboxylic acids by using triphenyl phosphite and pyridine as condensing agents. The fluorinated polyamides derived from **1b** showed decreased crystallinity and improved solubility in organic solvents but decreased thermal stability when compared to homologous polyamides from **1a**. It was also found that the introduction of CF_3 groups increased rotational barriers and formed more rigid segments that enhance T_g and T_s values.

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References

[1] Cassidy PE. Thermally stable polymers. New York: Dekker; 1980.

[2] Yang HH. Aromatic high-strength fibers. New York: Wiley; 1989. p. 66–289.

[3] Imai Y. High Perform Polym 1995;7:337.

[4] Imai Y. React Funct Polym 1996;30:3.

[5] Maglio G, Palumbo R, Vignola MC. Macromol Chem Phys 1995;196:775.

[6] Hsiao SH, Chang CF. Macromol Chem Phys 1996; 34:1433.

[7] Hsiao SH, Yu CH. J Polym Res 1996;3:247.

[8] Chern YT, Lin KS, Kao SC. J Appl Polym Sci 1998; 68:315.

[9] Hsiao SH, Yang CP, Yang HW. Macromol Chem Phys 1999;200:1528.

[10] Espeso JF, Ferrero E, de la Campa JG, Lozano AE, de Abajo J. J Polym Sci Part A Polym Chem 2001;39:475.

[11] Espeso JF, de la Campa JG, Lozano AE, de Abajo J. J Polym Sci Part A Polym Chem 2000;38:1014.

[12] Hsiao SH, Huang TL. J Polym Sci Part A Polym Chem 2002;40:947.

[13] Liou GS, Hsiao SH. J Polym Sci Part A Polym Chem 2002;40:1781.

[14] Liou GS, Hsiao SH. J Polym Sci Part A Polym Chem 2002;40:2564.

[15] Liou GS, Hsiao SH, Ishida M, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem 2002;40:2810.

[16] Wu SC, Shu CF. J Polym Sci Part A Polym Chem 2003;41:1160.

[17] Zhao L, He CB, Lu ZH, Chung CL. J Polym Sci Part A Polym Chem 2001;39:1288.

[18] Hsiao SH, Yang CP, Lin CK. J Polym Res 1995;2:1.

[19] Tamai S, Yamaguchi A, Ohta M. Polymer 1996;37: 3686.

[20] Hsiao SH, Yang CP, Chung CL. J Polym Sci Part A Polym Chem 2003;41:2001.

[21] Hsiao SH, Chang YH. J Polym Sci Part A Polym Chem 2004;42:1255.

[22] Yamazaki N, Matsumoto M, Higashi F. J Polym Sci Polym Chem Ed 1975;13:1373.