

New Poly(amide-imide) Syntheses. 24. Synthesis and Properties of Fluorinated Poly(amide-imide)s Based on 2,2-Bis[4-(trimellitimidophenoxy)phenyl]hexafluoropropane and Various Aromatic Diamines

CHIN-PING YANG, SHENG-HUEI HSIAO, HSIU-CHUN HSIAO

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, Section 3, Taipei 104, Taiwan, Republic of China

Received 10 April 1998; accepted 3 July 1998

ABSTRACT: An imide ring-performed dicarboxylic acid bearing one hexafluoroisopropylidene and two ether linkages between aromatic rings, 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]hexafluoropropane (**II**), was prepared from the condensation of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and trimellitic anhydride. A novel series of poly(amide-imide)s having inherent viscosities of $0.72 \sim 1.86 \text{ dL g}^{-1}$ was prepared by the triphenyl phosphite-activated polycondensation from the diimide-diacid (**II**) with various aromatic diamines in a medium consisting of *N*-methyl-2-pyrrolidone, pyridine, and calcium chloride. Several of the resulting polymers were soluble in polar amide solvents, and their solutions could be cast into transparent, thin, flexible films having good tensile properties and high thermal stability. The 10% weight loss temperatures were all above 495°C in air or nitrogen atmosphere, and the glass transition temperatures were in the range of 237°–276°C. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 823–831, 1999

Key words: hexafluoroisopropylidene; poly(amide-imide)s; triphenyl phosphite; trimellitic anhydride

INTRODUCTION

Aromatic poly(amide-imide)s (PAIs) are useful high-performance materials that exhibit better processing characteristics when compared with polyimides of analogous structures.¹ A notable example is Torlon® (Amoco Chemicals Co.), a commercial PAI obtained from trimellitic anhydride chloride and 4,4'-methylenedianiline.² PAIs are usually prepared by low-temperature polycondensation of an aromatic diamine with the acyl chloride of trimellitic anhydride (TMA)^{3,4} or with acyl chlorides of aromatic dicarboxylic acids bear-

ing performed imide rings.^{5,6} Alternatively, PAIs may also be obtained by the polycondensation of diisocyanates with TMA^{7,8} or with diimido-dicarboxylic acids derived from TMA.^{9,10} In previous publications,^{11–15} we described a more convenient approach to synthesize high molecular weight PAIs based on the triphenyl phosphite (TPP) and pyridine (Py) promoted polycondensation¹⁶ of diamines with imide ring-performed dicarboxylic acids. This route provides significant advantages in manufacturing operations when compared with conventional acyl chloride or isocyanate methods. Recently, a new simplified route to synthesize high molecular weight PAIs by a “one-pot” procedure based on the TPP/Py-activated direct polycondensation of aromatic diamines and 1,2,4-benzenetricarboxylic acid (or trimellitic acid) mono-

Correspondence to: C.-P. Yang.

Journal of Applied Polymer Science, Vol. 71, 823–831 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/050823-09

ethyl ester was proposed by Maglio and coworkers.^{17–19}

The TPP/Py-activated direct polycondensation of diamines with imide ring-containing diacids proved to be a very valuable means for the synthesis of PAIs. The feasibility of this straightforward synthesis method prompted us to use it in the preparation of many series of PAIs in the past decade.²⁰ One particular advantage of this synthetic procedure is that PAIs with regular, alternating (amide-amide)–(imide-imide) sequence can be easily tailored from TMA and various available aromatic diamines. A bistrimellitamide can be first prepared by the condensation of a diamine with TMA and then directly polycondensated with another diamine to form the PAIs. This can offer us the option of the incorporation of specific molecular architecture between amide or imide groups in the PAI backbone. The incorporation of such architecture may provide a method of controlling certain physical properties of the resulting PAIs.

According to earlier papers,²⁰ it was repeatedly observed that a key factor to obtain high molecular weight PAIs in the phosphorylation reaction is to maintain a homogeneous, smoothly stirred reaction solution throughout the reaction using a higher reactant concentration as possible. The solubility of the polymer in the reaction medium and the state of stirring affected the final inherent viscosity of the resulting PAIs significantly. Therefore, careful molecular design is necessary to attain high molecular weight PAIs from the polycondensation of bistrimellitimidides with diamines by means of TPP/Py. In general, at least one more flexible diamine component should be instead in either amide or imide segment in the PAI repeating unit to result in satisfactory results.

The hexafluoroisopropylidene (6F) group has been popularly incorporated in the polymer backbones of various thermally stable polymer systems.^{21–33} Frequently, the incorporation of 6F groups into a macromolecular backbone will improve the solubility and other properties, such as flame resistance, thermal stability, oxidation resistance, and environmental stability, whereas there is often a decrease in color, crystallinity, dielectric constant, and moisture absorption. In our continuing effort to develop easily processable aromatic PAIs, the present study deals with the syntheses and basic characterization of a series of fluorinated PAIs based on the bistrimellitamide condensed from TMA and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, a diamine con-

taining one 6F and two aryl ether linkages between the phenylene units. Some properties of the 6F-containing PAIs are compared with those of their corresponding nonfluorine-containing counterparts that were reported in a previous publication.^{20(e)}

EXPERIMENTAL

Materials

p-Phenylenediamine (**I_a**; Wako), *m*-phenylenediamine (**I_b**; TCI), 2,4-diaminotoluene (**I_c**; TCI), benzidine (**I_d**; TCI), 4,4'-oxydianiline (**I_e**; TCI), 3,4'-oxydianiline (**I_f**; Teijin Ltd., Tokyo), 4,4'-methylenediamine (**I_g**; TCI), 4,4'-thiodianiline (**I_h**; TCI), 1,4-bis(4-aminophenoxy)benzene (**I_i**; TCI), and 1,3-bis(4-aminophenoxy)benzene (**I_j**; Chriskev) were used without previous purification. 1,2-Bis(4-aminophenoxy)benzene (**I_k**), bis-[4-(4-aminophenoxy)phenyl] sulfone (**I_l**; Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**I_m**) was prepared according to a reported method³⁴ by the nucleophilic substitution reaction of *p*-chloronitrobenzene (TCI) and the corresponding bisphenols, such as 1,2-dihydroxybenzene, bis(4-hydroxyphenyl) sulfone, and 2,2-bis(4-hydroxyphenyl)hexafluoropropane, followed by catalytic hydrazine reduction.

Commercially obtained anhydrous calcium chloride was dried under vacuum at 180°C for 10 h. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and Py were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. TPP (TCI) was purified by distillation under reduced pressure.

Synthesis of 2,2-Bis[4-(4-trimellitimidophenoxy)phenyl]hexafluoropropane (II)

The diamine 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**I_m**) [8.67 g (0.01 mol)] and trimellitic anhydride [10.65 g (0.02 mol)] were dissolved in 45 mL dried NMP at 60°C. About 30 mL of toluene was added, and the mixture was heated at reflux until ~ 0.36 mL of water was distilled off azeotropically *via* a Dean–Stark trap. After cooling, the reaction solution was poured into distilled water, and the resulting solid product was collected by filtration and washed thoroughly with methanol.

This product was dried to give quantitative yield of pure diimido dicarboxylic acid **II**; m.p. 337°C.

Infrared (IR) (KBr): 3200–3700 cm^{-1} (carboxylic acid, —OH), 1700 cm^{-1} (carboxylic acid, C=O), 1782 cm^{-1} , 1722 cm^{-1} (imide, C=O), 1390 cm^{-1} (C—N), 728 cm^{-1} (imide ring deformation).

ANAL. Calcd for $\text{C}_{45}\text{H}_{24}\text{O}_{10}\text{N}_2\text{F}_6$ (866.68): C, 62.35%; H, 2.79%; N, 3.23%. Found: C, 62.22%; H, 2.91%, N, 3.05%.

Polymerization

A typical example for the preparation of PAI **III_b** is as follows. A mixture of 0.25 g (1.25 mol) of diamine **I_b** [0.963 g (1.25 mol)] of diimide-diacid **II**, 0.5 g of calcium chloride, 0.8 mL of TPP, 1.2 mL Py, and 5.5 mL of NMP was heated with stirring at 100°–110° for 3 h. The polymer solution was too viscous to stir after ~ 1 h and was diluted gradually with an additional 5 mL of NMP to maintain smooth stirring. The resulting polymer solution was slowly poured into 500 mL of methanol, giving rise to a stringy fiber-like precipitate that was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was quantitative, and the inherent viscosity of the polymer (**III_b**) was 1.0 dL g^{-1} , as measured at a concentration of 0.5 g dL^{-1} in DMAc–5% LiCl at 30°C.

All other PAIs were synthesized by an analogous procedure as described.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform IR (FTIR) spectrometer. Elemental analyses were run in a Perkin-Elmer model 2400 C, H, N analyzer. Inherent viscosities of all polymers were determined at 0.5 g dL^{-1} concentration using a Cannon-Fenske viscometer. Thermogravimetric (TG) data were obtained on a DuPont 951 TG analyzer coupled to a DuPont 2000 thermal analyzer. Measurements were performed with 10 ± 2 mg samples heated in flowing nitrogen or air ($50 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate of $20^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller in flowing nitrogen ($30 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate of $20^\circ\text{C min}^{-1}$. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, using Ni-filtered Cu-K_α radiation (40 kV, 20 mA), and the scanning

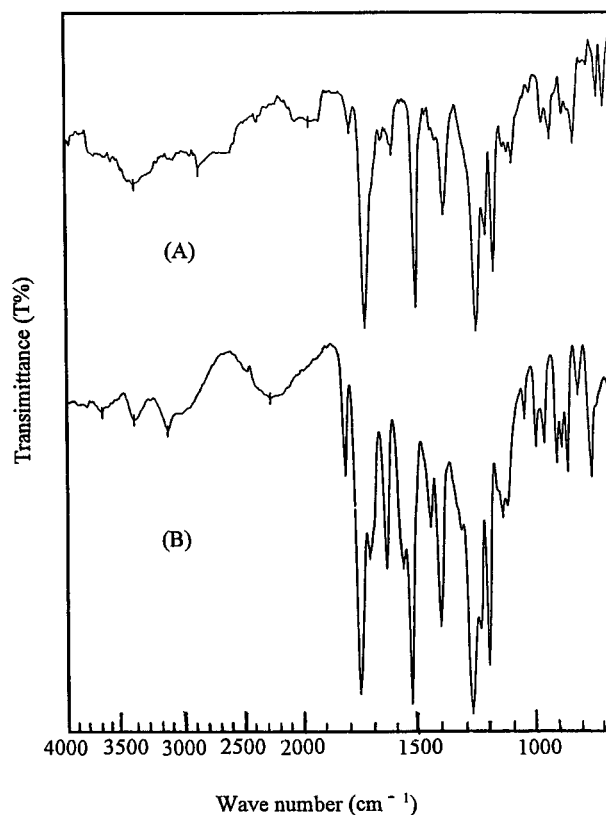


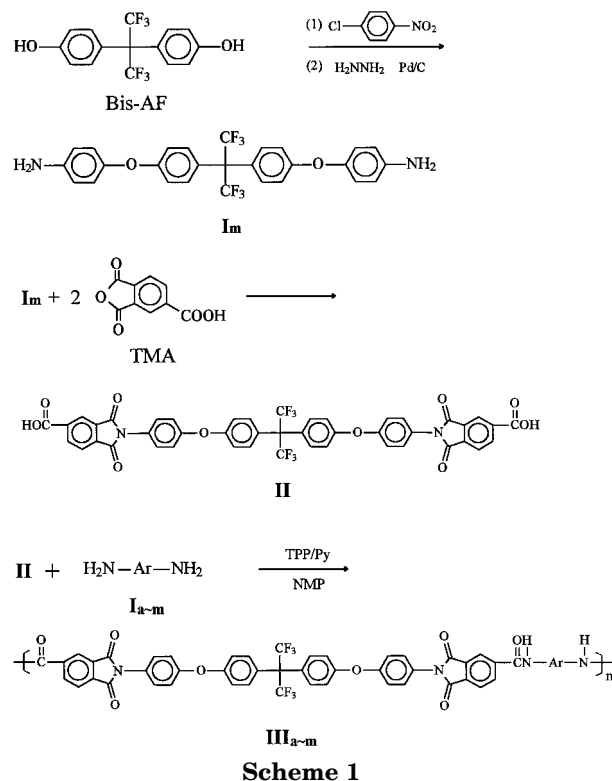
Figure 1 IR spectra of (A) diimide-diacid **II** and (B) PAI **III_b**.

rate was 4° min^{-1} . An Instron Universal tester model 1130, with a load cell of 5 kg, was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm min^{-1} were used for this study. Measurements were performed with film specimens of 0.5 cm wide, 6 cm long, and ~ 0.1 mm in thickness at room temperature (~ 25°C) and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Synthesis

The diimido dicarboxylic acid containing flexible 6F and ether linkages, 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]hexafluoropropane (**II**), was derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**I_m**) and TMA *via* a two-stage procedure that included ring-opening addition in polar solvents like NMP to give intermediate diamic acid, followed by cyclodehydration to the diimide-diacid **II** by means of toluene-water azeo-

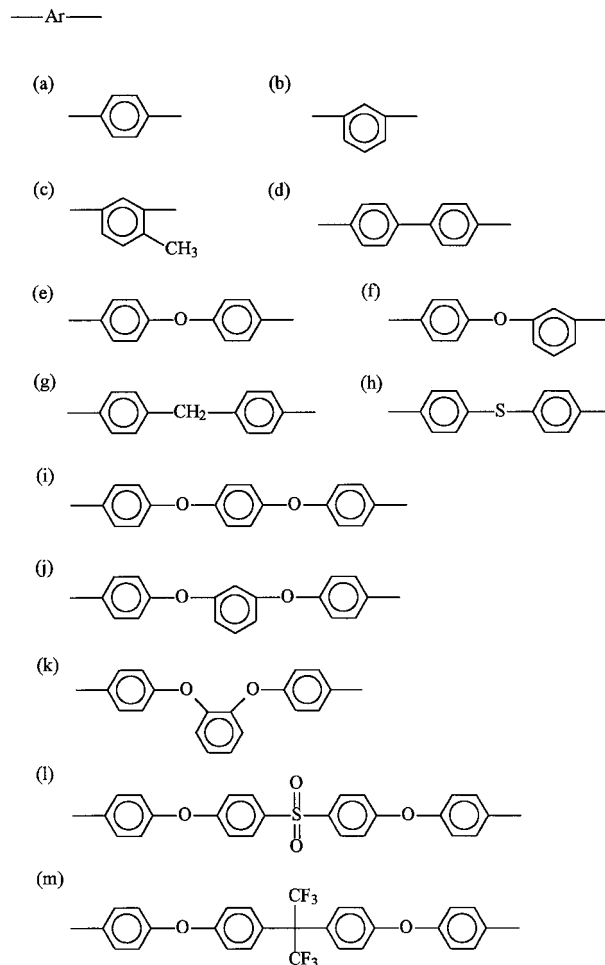


tropic distillation. The structure of **II** was confirmed by elemental analysis and IR spectroscopy. The FTIR spectrum of **II** is shown in Figure 1(A). The absorption bands appear between 2500–3500 (carboxyl —OH), 1780 (asymmetric imide C=O stretching), 1700–1720 (carboxyl C=O and symmetric imide C=O stretching), and 1390 cm^{-1} (C—N stretching) to establish the presence of the carboxyl group and imide rings in the structure of the monomer synthesized.

A series of new PAIs **III_{a-m}** were prepared by the direct polycondensation of dicarboxylic acid **II** with various aromatic diamines using TPP and Py as condensing agents in the NMP solution containing dissolved CaCl_2 (Scheme 1). Synthesis conditions and inherent viscosities of the resulting PAIs are summarized in Table I. Except for polymers **III_a** and **III_d**, which were derived from rigid diamines such as *p*-phenylenediamine and benzidine, all the reaction solutions were homogeneously transparent throughout the reaction and afforded stringy, fiber-like polymer precipitates when slowly pouring the resulting polymer solutions into stirred methanol. In most cases the initial amount of NMP was 5.5–7.0 mL, and additional 2.0–8.0 mL of NMP was added to the reaction solution after ~ 1 h to avoid the forma-

tion of a swollen gel. Except for **III_a** and **III_d**, inherent viscosities of these polymers stayed in the range of 0.90–1.86 dL g^{-1} , indicating the formation of high molecular weights.

Structural characterization was conducted with the aid of IR spectroscopy and elemental analysis. A typical FTIR spectrum of the representative PAI **III_b** is shown in Fig. 1(B). The characteristic absorptions for imide ring appear at 1780, 1725 (imide C=O), and 1390 cm^{-1} (C—N). Bands of amide groups appear at 3350 (N—H) and 1680 cm^{-1} (C=O). The results of elemental analyses of all the PAIs are listed in Table II. In all cases, however, the carbon values were found to be lower and the hydrogen values were found to be slightly higher than the calculated ones for the proposed repeating units. This can be explained by the hydroscopic nature of the samples caused by the amide groups of PAIs. The moisture uptake was in the 1.4–3.0% range, cal-



Scheme 1 (Continued)

Table I Synthesis of PAIs^a

Polymer	Initial NMP (mL)	Additional NMP (mL)	CaCl ₂ (g)	η_{inh}^b (dL g ⁻¹)	Remark ^c
III _a	12		0.8	0.72	Powdered
III _b	5.5	5	0.5	1.50	Stringy
III _c	5.5	2.5	0.4	1.38	Stringy
III _d	10		0.8	0.47 ^d	Powdered
III _e	6		0.4	1.00	Stringy
III _f	6	2.5	0.4	1.86	Stringy
III _g	5.5	4	0.7	1.51	Stringy
III _h	6	4	0.5	1.33	Stringy
III _i	7	2	0.4	1.05	Stringy
III _j	5.5	3.5	0.6	1.20	Stringy
III _k	5	2	0.4	1.56	Stringy
III _l	5.5	8	0.6	1.44	Stringy
III _m	6		0.4	0.90	Stringy

^a Polymerization was conducted with 1.25 mmol of each monomer, 0.8 mL of TPP, and 1.2 mL of Py at 100°C for 3 h.

^b Measured at a concentration of 0.5 g dL⁻¹ in DMAc-5% LiCl at 30°C, unless otherwise indicated.

^c Appearance of the polymer precipitate when pouring the resulting polymer solution in stirred methanol.

^d Measured in concentrated sulfuric acid.

Table II Elemental Analysis of PAIs

Polymer	Formula (Molecular Weight)		Elemental Analysis (%)			Moisture Uptake ^a (%)
			C	H	N	
III _a	(C ₅₁ H ₂₈ N ₄ O ₈ F ₆) _n (938.80) _n	Calcd.	65.23	3.01	5.97	2.4
		Found	63.71	3.38	5.74	
III _b	(C ₅₁ H ₂₈ N ₄ O ₈ F ₆) _n (938.80) _n	Calcd.	65.23	3.01	5.97	2.8
		Found	63.48	3.36	5.88	
III _c	(C ₅₂ H ₃₀ N ₄ O ₈ F ₆) _n (952.82) _n	Calcd.	65.53	3.18	5.88	3.0
		Found	63.60	3.46	5.69	
III _d	(C ₅₇ H ₃₂ N ₄ O ₈ F ₆) _n (1014.89) _n	Calcd.	67.44	3.18	5.52	2.1
		Found	66.08	3.73	5.37	
III _e	(C ₅₇ H ₃₂ N ₄ O ₉ F ₆) _n (1030.89) _n	Calcd.	66.14	3.13	5.43	2.2
		Found	64.71	3.40	5.20	
III _f	(C ₅₇ H ₃₂ N ₄ O ₉ F ₆) _n (1030.89) _n	Calcd.	66.14	3.13	5.43	1.4
		Found	65.20	3.37	5.20	
III _g	(C ₅₈ H ₃₄ N ₄ O ₈ F ₆) _n (1028.23) _n	Calcd.	67.71	3.33	5.45	2.3
		Found	66.30	3.57	5.36	
III _h	(C ₅₇ H ₃₂ N ₄ O ₈ F ₆ S) _n (1046.18) _n	Calcd.	65.39	3.08	5.35	2.5
		Found	63.80	3.37	5.27	
III _i	(C ₆₃ H ₃₆ N ₄ O ₁₀ F ₆) _n (1122.23) _n	Calcd.	67.37	3.23	4.99	1.4
		Found	66.44	3.42	4.92	
III _j	(C ₆₃ H ₃₆ N ₄ O ₁₀ F ₆) _n (1122.23) _n	Calcd.	67.37	3.23	4.99	2.1
		Found	65.98	3.38	4.87	
III _k	(C ₆₃ H ₃₆ N ₄ O ₁₀ F ₆) _n (1122.23) _n	Calcd.	67.37	3.23	4.99	1.8
		Found	66.16	3.39	4.89	
III _l	(C ₆₉ H ₄₀ N ₄ O ₁₂ F ₆) _n (1263.15) _n	Calcd.	65.61	3.19	4.44	1.9
		Found	64.41	3.55	4.35	
III _m	(C ₇₂ H ₄₀ N ₄ O ₁₀ F ₁₂) _n (1349.11) _n	Calcd.	64.10	3.19	4.15	2.4
		Found	62.59	3.21	4.05	

^a Moisture uptake (%) = $(W - W_0/W_0) \times 100\%$. W = weight of polymer sample after standing at room temperature for at least 3 days. W_0 = weight of polymer sample after dried in vacuum at 100°C for 10 h.

Table III Solubility of PAIs^a

Polymer	Solvents							
	DMAc	DMAc + 5% LiCl	NMP	DMF	DMSO ^b	Py	<i>m</i> -Cresol	H ₂ SO ₄
III_a	—	+	+—	—	—	—	—	+
III_b	+	+	+	+	+	+	+	+
III_c	+	+	+	+	+	+	+	+
III_d	—	+—	—	—	—	—	—	+
III_e	—	+	+	—	—	—	—	+
III_f	+	+	+	+	+	+	+—	+
III_g	+—	+	+	—	—	—	—	+
III_h	+	+	+	+—	+	—	+—	+
III_i	—	+	+	—	—	—	—	+
III_j	+	+	+	+	+	+—	+	+
III_k	+	+	+	+	+	+	+	+
III_l	+	+	+	+	—	+	+	+
III_m	+	+	+	+	+	—	+	+

^a Solubility: (+) soluble at room temperature, (+—) partially soluble or swelling, (—) insoluble.

^b DMSO, dimethylsulfoxide.

culated from the weight change of the vacuum-dried polymer samples after they were exposed in air at room temperature, although they exhibit the hydrophobic 6F groups. However, these values are lower than those of nonfluoro analogs reported in the previous paper.^{20(e)}

Properties of Polymers

The qualitative solubility of the PAIs in various organic solvents is listed in Table III. These solubilities vary with the structures of the diamines. If the diamine components are of asymmetric structures, e.g., *m*-phenylene (**I_b**), 2,4-tolylene (**I_c**), 3,4'-oxydiphenylene (**I_f**), 1,3-diphenoxyben-

zene (**I_j**), 1,2-diphenoxybenzene (**I_k**), and those containing the sulfonyl (**I_l**) or 6F (**I_m**), the PAIs show better solubility and are readily soluble in aprotic dipolar solvents, such as NMP, DMAc, DMF, and dimethylsulfoxide, and even in less polar *m*-cresol. If the aromatic rings of diamines are of symmetric disubstituted structures [e.g., those of *p*-phenylenediamine (**I_a**), benzidine (**I_d**), 4,4'-oxydianiline (**I_e**), 4,4'-methylenedianiline (**I_g**), and 1,4-bis(4-aminophenoxy)benzene (**I_i**)], they cannot easily dissolve in the polar solvents without a metal salt also dissolved. However, except for polymers **III_a** and **III_d**, they are all soluble in NMP. PAIs **III_a** and **III_d** can be

Table IV Tensile Properties of PAIs^a

Polymer	Yield Strength (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)
III_b	94	93	25	2.1
III_c	93	89	25	1.9
III_f	88	97	13	1.9
III_j	—	93	10	1.5
III_k	—	57	12	1.8
III_l	—	64	11	1.7
III_m	—	96	10	1.4

^a Films were cast from polymer solutions in DMAc.

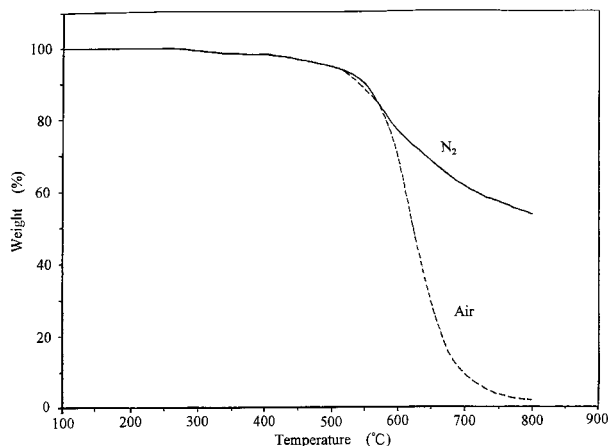


Figure 2 TG curves of PAI **III_b**, with a heating rate of $20^{\circ}\text{C min}^{-1}$.

dissolved only in concentrated sulfuric acid. The poor solubility of **III_a** and **III_d** may be due to their semicrystalline nature, as indicated by X-ray diffractograms. When comparing the solubilities of this series, polymers with their analogs that in differ only by replacement of the 6F group with the isopropylidene group,^{20(e)} their solubility behavior is similar.

Transparent, flexible, and tough films could be cast from the DMAc solutions of seven of the

obtained PAIs. The tensile properties of these flexible films are summarized in Table IV. They had a tensile strength of 57–97 MPa, elongation at a break of 10–25%, and an initial modulus of 1.4–2.1 GPa.

Thermal properties of all polymers were evaluated by DSC and TG analyses. Figure 2 shows typical TG curves of PAI **III_b**. Some TG data of all PAIs are listed in Table V. For comparison, the thermal behavior data of the corresponding counterparts containing isopropylidene instead of the 6F group are also presented. The decomposition temperature of 10% weight loss of these PAIs were recorded in the range of 512–564°C in nitrogen and 495–559°C in air. In almost all cases, the fluorine-containing PAIs had a relatively higher thermal stability than the nonfluorine-containing PAIs because of high C—F and C—CF₃ bond strengths.

Table V also summarizes the thermal transition data of the PAIs. Quenching from the elevated temperatures to room temperature yields predominately amorphous samples so that, in all cases, the glass transition temperatures (T_g s) could be easily read in the second heating traces of DSC. The T_g s of PAI **III_{a-m}** were in the range of 237°–276°C. In almost all cases, higher T_g values were recorded for the fluoro PAIs than those of

Table V Thermal Properties of PAIs

Polymer	T_g^a (°C)	Decomposition Temperature ^b (°C)		Wt % Residue at 800°C in N ₂
		In N ₂	In Air	
III_a	265 (257) ^c	522 (520)	495 (523)	55
III_b	275 (278)	516 (511)	508 (478)	55
III_c	273 (268)	544 (512)	559 (480)	61
III_d	276 (263)	562 (520)	523 (499)	58
III_e	269 (258)	553 (531)	523 (480)	62
III_f	259 (251)	562 (518)	552 (485)	60
III_g	260 (245)	548 (517)	522 (473)	58
III_h	275 (267)	512 (508)	538 (489)	50
III_i	250 (248)	564 (525)	536 (487)	63
III_j	238 (237)	548 (515)	547 (492)	57
III_k	237	559	505	57
III_l	271 (265)	547 (522)	533 (487)	49
III_m	244	536	524	58

^a Midpoint of baseline shift in the second heating DSC traces at a heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen.

^b Decomposition temperature at which 10% weight loss was recorded by TG at a heating rate of $20^{\circ}\text{C min}^{-1}$.

^c Data in parentheses are those of the homologous counterparts containing isopropylidene instead of hexafluoropropylidene.

the nonfluoro PAIs, which is similar to that observed in polyamides and polyimides.^{23,29,30} Apparently, the great volume and high polarity of the 6F group overcome the effects of chain separation and disruption of hydrogen bonding caused by the bulky 6F group.

CONCLUSIONS

The diimide-diacid 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]hexafluoropropane was used as a new PAI building block. A series of high molecular weight PAIs with alternating (amide-amide)-(imide-imide) sequence was successfully prepared by direct polycondensation of the diimide-diacid with aromatic diamines. The polymers derived from more flexible diamines showed excellent solubility and good film-forming ability, and their solution cast films exhibited good tensile properties. Most of the polymers were amorphous and showed T_g at 237°–276°C. All polymers showed good thermal stability, with 10 wt % loss temperatures being recorded above 495°C in nitrogen or in air. These fluorinated PAIs showed a higher thermal stability and a higher T_g , compared with the corresponding nonfluorinated analogs.

REFERENCES

1. Yang, H. H. *Aromatic High-Strength Fibers*; Wiley, New York, 1989.
2. Brillerbeck, C. J.; Henke, S. J. *Engineering Thermoplastic*; Marcel Dekker, New York, 1985.
3. Alvino W. M.; Ray, J. R. *J Polym Sci Polym Chem Ed* 1980, 19, 2551.
4. Imai, Y.; Maldar, N. N.; Kakimoyo, M. *J Polym Sci Part A: Polym Chem* 1985, 23, 2077.
5. Wrasidlo W.; Augl, J. M. *J Polym Sci A-1*, 1969, 10, 1377.
6. de Abajo, J.; Gabarda, J. P.; Fontan, J.; *Angew Makromol Chem* 1978, 71, 143.
7. Iwakura, Y.; Uno, K.; Chau, N. *Makromol Chem* 1975, 176, 351.
8. Kakimoto, M.; Akiyama, R.; Negi, Y. S.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1988, 26, 99.
9. Nieto, J. L.; de la Campa, J. G.; de Abajo, J. *Makromol Chem* 1982, 183, 557.
10. de la Campa, J. G.; de Abajo, J.; Nieto, J. L. *Makromol Chem* 1982, 183, 571.
11. Yang C.-P.; Hsiao, S.-H. *Makromol Chem* 1989, 190, 2119.
12. Hsiao S.-H.; Yang, C.-P. *J Polym Sci Part A: Polym Chem* 1990, 28, 1149.
13. Hsiao S.-H.; Yang, C.-P. *Makromol Chem* 1990, 191, 155.
14. Hsiao S. H.; Yang, C.-P. *J Polym Sci Part A: Polym Chem* 1990, 28, 2169.
15. Hsiao, S.-H.; Yang C.-P.; Wu, F.-Y. *Macromol Chem Phys* 1994, 195, 2531.
16. Yamazaki, N.; Matsumoto, M.; Higashi, F. *J Polym Sci Polym Chem Ed* 1975, 13, 1373.
17. Avella, N.; Maglio, G.; Palumbo, R.; Vignola, M. C. *Makromol Chem Rapid Commun* 1994, 15, 95.
18. Avella, N.; Maglio, G.; Palumbo, R. *J Polym Sci Part A: Polym Chem* 1996, 34, 1219.
19. Avella, N.; Maglio, G.; Palumbo, R.; Vignola, M. C. *Polymer* 1996, 37, 4615.
20. (a) Yang, C.-P.; Yen, Y.-Y. *J Polym Sci Part A: Polym Chem* 1992, 30, 1855; (b) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. *J Polym Sci Part A: Polym Chem* 1992, 30, 1865; (c) Yang, C.-P.; Cheng, J.-M.; Hsiao, S.-H. *Makromol Chem* 1992, 193, 445; (d) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. *Makromol Chem* 1992, 193, 1299; (e) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. *J Polym Sci Part A: Polym Chem* 1993, 31, 2995; (f) Yang C.-P.; Chen, W.-T. *Makromol Chem* 1993, 194, 3071; (g) Yang C.-P.; Chen, W.-T. *J Polym Sci Part A: Polym Chem* 1993, 31, 3081; (h) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. U.S. Pat. 5,268,487 1993; (i) Yang C.-P.; Chen, W.-T. *J Polym Sci Part A: Polym Chem* 1994, 32, 435; (j) Yang C.-P.; Chen, W.-T. *J Polym Sci Part A: Polym Chem* 1994, 32, 1101; (k) Hsiao, S.-H.; Yang, C.-P.; Wu, F.-Y. *J Polym Sci Part A: Polym Chem* 1994, 32, 1481; (l) Yang C.-P.; Lin, J.-H. *J Polym Sci Part A: Polym Chem* 1994, 32, 2653; (m) Hsiao, S.-H.; Yang, C.-P.; Wu, F.-Y. *Macromol Chem Phys* 1994, 195, 2531; (n) Yang, C.-P.; Hsiao, S.-H.; Chen, C.-D. *J Polym Res* 1994, 1, 43; (o) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. U.S. Pat. 5,414,070 1995; (p) Yang C.-P.; Lin, J.-H. *Macromol Chem Phys* 1995, 196, 2979; (q) Yang C.-P.; Lin, J.-H. *Macromol Chem Phys* 1995, 196, 3929; (r) Yang C.-P.; Lin, J.-H. *Polym Int* 1995, 38, 335; (s) Yang, C.-P.; Hsiao, S.-H.; Chou, W.-L. *J Polym Res* 1995, 2, 179; (t) Hsiao, S.-H.; Yang, C.-P.; Fan, J.-C. *Macromol Chem Phys* 1995, 196, 3053; (u) Yang, C.-P.; Hsiao, S.-H.; Tsai, M.-R. *J Polym Res* 1998, 5, 23.
21. Saegusa, Y.; Kuriki, M.; Kawai, A.; Nakamura, S. *J Polym Sci Part A: Polym Chem* 1990, 28, 3327.
22. Nagata, M. Tsutsumi, N.; Kiyotsukuri, T. *J Polym Sci Polym Chem Ed* 1988, 26, 235.
23. Negi, Y. S.; Suzuki, Y. I.; Kawamura, I.; Hagiwara, T.; Takahashi, Y.; Iijima, M.; Kakimoto, M. A.;

- Imai, Y. *J Polym Sci Part A: Polym Chem* 1992, 30, 2281.
24. Park, J. W.; Lee, M.; Liu, J. W.; Kim, S. D. Chang, J. Y.; Rhee, S. B. *Macromolecules* 1994, 27, 3459.
25. Wada, K.; Hager, W. S.; Neef, C. J.; Brewer, K. W.; Cassidy, P. E. *ACS Polym Prepr* 1990, 31, 350.
26. Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* 1991, 24, 5001.
27. Bruma, M.; Schulz, B.; Mercer, F. W. *Polymer* 1994, 35, 4209.
28. Bruma, M.; Mercer, F. W.; Fitch, J.; Cassidy, P. *J Appl Polym Sci* 1995, 56, 527.
29. Maglio, G.; Palumbo, R.; Vignola, M. C. *Macromol Chem Phys* 1995, 196, 2775.
30. Negi, Y. S.; Suzuki, Y.; Kawamura, I.; Kakimoto, M.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1996, 34, 1663.
31. Maruyama, Y.; Oishi, Y.; Kakimoto, M.; Imai, Y. *Macromolecules* 1988, 21, 2305.
32. Hsiao, S.-H.; Yu, C.-H. *J Polym Res* 1996, 3, 247.
33. Hsiao, S.-H.; Yu, C.-H. *Polymer J* 1997, 29, 944.
34. Yang C.-P.; Cherng, J. J. *J Polym Sci Part A: Polymer Chem* 1995, 33, 2209.