

Thermostable Soluble Aromatic Poly(amide-imide)s Having Hexafluoroisopropylidene and Ether Links in the Main Chain

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Abstract: An imide-containing dicarboxylic acid, 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]hexafluoropropane (**I**), was prepared by the condensation of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and trimellitic anhydride. A series of new hexafluoroisopropylidene-containing poly(amide-imide)s having inherent viscosities of 0.64-1.44 dL/g were prepared by the direct polycondensation of diimide-diacid **I** with various long-chain aromatic diamines using triphenyl phosphite and pyridine as condensing agents in *N*-methyl-2-pyrrolidone in the presence of calcium chloride. Most of the resulting poly(amide-imide)s were noncrystalline and showed good solubility in polar organic solvents. Almost all polymers afforded transparent, flexible, and tough films. The 10 % weight loss temperatures of these polymers were all above 499 °C, and the glass transition temperatures were in the range of 203-277 °C.

Keywords: Hexafluoroisopropylidene, Diimide-diacids, Trimellitic anhydride, Triphenyl phosphite, Poly(amide-imide)s.

Introduction

Aromatic polyimides have earned a reputation as high performance materials based on their excellent thermal stability, chemical resistance, and outstanding mechanical properties [1]. However, poor handling and intractable characteristics have been major problems due to high glass transition temperatures and insolubility. To extend the utility of such high performance materials, it has been a long-desired goal to synthesize soluble polymers without sacrificing their thermomechanical properties. It is well-known that the synthesis of poly(amide-imide)s (PAIs) can offer a compromise between excellent thermal stability and processability.

PAIs can be synthesized readily by general synthetic methods similar to those used for both aromatic polyamides and polyimides [2]. In 1989, we established an efficient and convenient approach [3] for the synthesis of PAIs by the direct polycondensation of imide-preformed dicarboxylic acids

with aromatic diamines according to the Yamazaki-Higashi phosphorylation technique [4]. The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in the laboratory preparation of PAIs as well as polyamides. Thus, several series of novel PAIs have been readily synthesized by this straightforward technique in this laboratory [5]. Furthermore, this synthetic approach to PAIs can offer us the option of introducing specific diamine residues between the amide or imide groups into the polymer backbone and may provide an easy method of controlling the physical properties of PAIs.

According to earlier papers [5], it was repeatedly observed that a key factor in obtaining high molecular weight PAIs in the phosphorylation reaction is the maintenance of a homogeneous, smoothly stirred reaction solution throughout the reaction using as high a reactant concentration as possible. The solubility of the polymer in the reaction medium

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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 bistrimellitimidates with diamines by means of the phosphorylation technique. In general, at least one more flexible diamine component should be inserted into either amide or imide segment in the PAI repeating unit in order to obtain satisfactory results.

The hexafluoroisopropylidene (6F) group has been popularly incorporated in the polymer backbones of various thermally stable polymer systems [6-17]. 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. Recently, we have demonstrated that PAIs prepared from the bistrimellitimide (**I**) condensed from trimellitic anhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane showed good processability together with high thermal stability [5(c)]. As a continuation of our efforts to screen new and easily tractable PAIs, the present article deals with the synthesis and basic characterization of a series of fluorinated PAIs derived from the diimide-diacid **I** with various "multiring" flexible aromatic diamines. The properties of these polymers, such as solubility, film-forming ability, tensile property of thin films, crystallinity, thermal stability, and glass transition, are discussed.

Experimental

1. Materials

2,2-Bis[4-(4-trimellitimidophenoxy)phenyl]hexafluoropropane (**I**) (mp. 337 °C by DSC) was prepared by a procedure described previously [5(c)] from trimellitic anhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane. Some diamines, such as α,α' -bis(4-aminophenyl)-1,4-diisopropylbenzene (**IIa**; TCI), α,α' -bis(4-aminophenyl)-1,3-diisopropylbenzene (**IIb**; TCI), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**IIc**; Chriskev), 1,4-bis(4-aminophenoxy)benzene (**IIg**; TCI), bis[4-(4-aminophenoxy)phenyl] sulfone (**IIm**; Chriskev), and bis[4-(3-aminophenoxy)phenyl] sulfone (**IIn**; Chriskev), were used without purification. Other diamines, such as α,α' -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**IIc**), α,α' -bis[4-(4-aminophenoxy)phenyl]-1,3-diisopropylbenzene (**IIb**), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**IIf**), 2-methyl-1,4-bis(4-aminophenoxy)benzene

(**IIh**), 2,5-bis(4-aminophenoxy)biphenyl (**IIi**), 4,4'-bis(4-aminophenoxy)biphenyl (**IIj**), 3,3',5,5'-tetramethyl-4,4'-bis(4-aminophenoxy)biphenyl (**IIk**), and 2,2'-bis(4-aminophenoxy)biphenyl (**III**), were prepared according to a well-developed method by the nucleophilic substitution reaction of *p*-chloronitrobenzene and the corresponding bisphenols, such as α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene, α,α' -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, methylhydroquinone, phenylhydroquinone, 4,4'-biphenol, 3,3',5,5'-tetramethyl-4,4'-biphenol, and 2,2'-bisphenol, followed by catalytic hydrazine reduction.

Commercially obtained anhydrous calcium chloride (CaCl_2) was dried under a vacuum at 180 °C for 10 hrs. *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; TCI) was purified by distillation under reduced pressure.

2. Polymerization

A typical example for the preparation of PAI **IIId** is described as follows. A mixture of 0.655 g (1.25 mmol) of diamine **IIId**, 1.083 g (1.25 mmol) of diimide-diacid **I**, 0.8 g of calcium chloride, 0.8 mL of TPP, 1.2 mL of pyridine, and 5.5 mL of NMP was heated with stirring at 100 °C. An additional 2.5 mL of NMP was added as the solution became too viscous such that the magnetic stirrer could no longer work. After 3 hrs of stirring at 100 °C, the resulting polymer solution was slowly poured into 500 mL of stirred 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 was 1.34 dL/g, as measured in DMAc-5% LiCl at a concentration of 0.5 g/dL at 30 °C.

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

3. Preparation of PAI films

A polymer solution of approximately 10 wt% was made by dissolving about 1 g of the PAI sample in 10 mL of hot DMAc. The solution was filtered into a 9-cm glass culture dish, which was placed in a 90 °C oven overnight to evaporate the solvent. The semi-dried PAI film was stripped off from the glass substrate and further dried in a vacuum oven at 160 °C for 8 hrs. The obtained films were about 80 μm in thickness and were used for X-ray diffraction measurements, tensile tests, and thermal analysis.

4. 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 concentration using a Cannon-Fenske viscometer. Thermogravimetric analysis (TGA) data were obtained on a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 thermal analyzer. Measurements were performed with 10 ± 2 mg samples heated in flowing nitrogen or air ($50 \text{ cm}^3/\text{min}$) at a heating rate of $20 \text{ }^\circ\text{C}/\text{min}$. 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 ($30 \text{ cm}^3/\text{min}$) at a heating rate of $20 \text{ }^\circ\text{C}/\text{min}$. 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 rate was $4^\circ/\text{min}$. 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 crosshead speed of 5 cm/min were used for this study. Measurements were performed at room temperature (about $25 \text{ }^\circ\text{C}$) with film specimens (0.5 cm wide, 6 cm long, and about 0.08 mm thick) and an average of at least five individual determinations was used.

Results and Discussion

1. Polymer synthesis

The phosphorylation technique, developed by Yamazaki and co-workers [4], was used to prepare PAI **IIIa-n** from diimide-diacid **I** with diamines **IIa-n**. Structures and codes of the polymers are shown in Scheme 1. No attempts were made to maximize molecular weights. Using the reaction conditions listed in Table I, high molecular weight polymers were generally obtained. Viscosities of the polymerization mixtures were normally very high and the nature of the precipitated polymers implied high molecular weight products. Except for polymer **IIIj**, all the reaction solutions were homogeneous throughout the reaction and afforded stringy, fiber-like polymer precipitates when the resulting polymer solutions were slowly poured into stirred methanol. As shown in Table I, the resulting polymers had inherent viscosities higher than 0.64 dL/g and up to 1.44 dL/g. All the PAIs except **IIIg** and **IIIj** could be solution-cast into good-quality, creasable films.

Structural characterization was conducted with the aid of IR spectroscopy and elemental analysis.

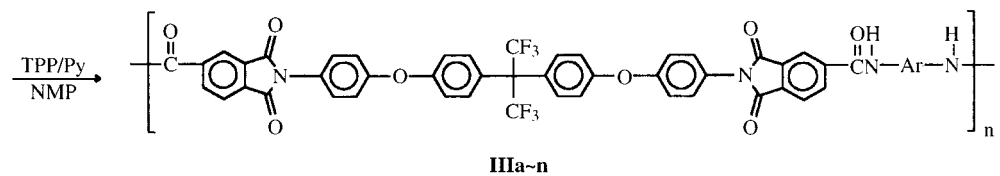
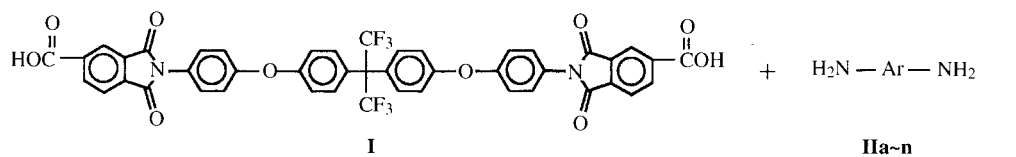
A typical FTIR spectrum of the representative PAI **IIIb** is shown in Figure 1(b). Key structural features were verified based on characteristic absorption bands for imide rings observed around 1780, 1720 (imide C=O), 1390 (C-N), 1100, and 720 cm^{-1} (imide ring deformation) and those for amide groups appearing at 3350 cm^{-1} (N-H) and 1680 cm^{-1} (amide 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 those calculated for the proposed repeating units. This may be explained by the hydroscopic nature of the samples caused by the amide groups of these PAIs. The moisture intake was in the 1.4-4.6 % range, calculated from the weight change of the vacuum-dried polymer samples after they were exposed in air at room temperature.

2. Polymer properties

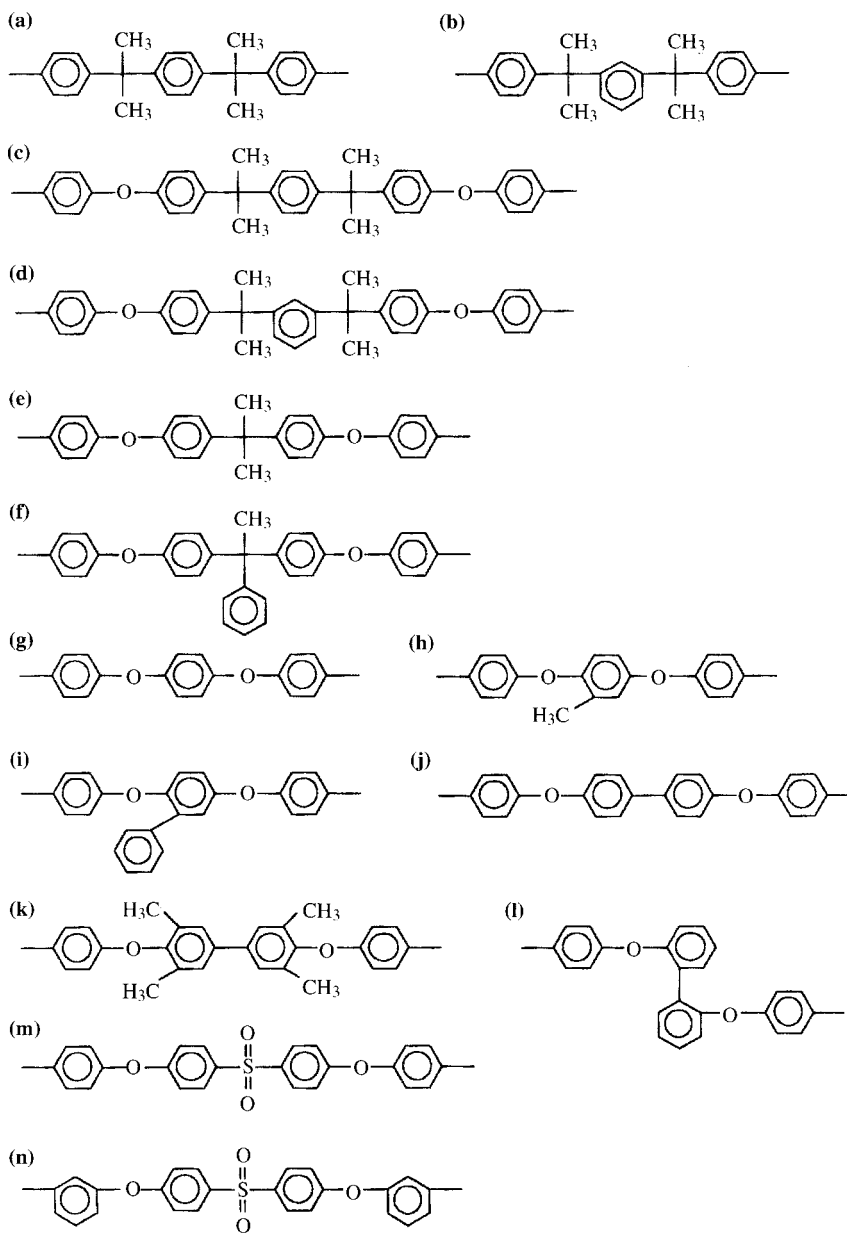
The solubility behavior of these PAIs was qualitatively tested in various solvents. Table III summarizes the results. Except for **IIIg** and **IIIj**, almost all PAIs were soluble in all the tested organic solvents. PAI **IIIj** was insoluble in all the tested solvents and dissolved only in concentrated sulfuric acid. The poor solubility of **IIIj** may be attributed to its semicrystalline nature, as indicated by its wide-angle X-ray diffraction pattern. PAI **IIIg** also showed a lower solubility, although it is amorphous in nature as evidenced by the X-ray diffraction pattern. The lower solubility of **IIIg** is probably due to its higher molecular weight, as indicated by its higher inherent viscosity value. The high solubility of most of these PAIs is apparently due in part to the presence of a bulky 6F group in the polymer backbone, which results in increased chain packing distances and decreased interchain interactions. One of the factors contributing to the excellent solubility was the characteristic amorphous nature caused by the introduction of the 6F structure and flexible diamine residues.

X-ray diffraction patterns confirmed that all PAIs except **IIIj** were amorphous. Typical patterns of some PAIs are shown in Figure 2. Transparent, tough, and flexible films could be obtained by casting their DMAc solutions. The tensile properties of the PAI films are summarized in Table IV. These films had tensile strengths of 46-96 MPa, elongations at break of 6-14 %, and initial moduli of 1.3-2.0 GPa.

DSC and TGA analyses were used to evaluate the thermal properties of all PAIs. Figure 3 illustrates typical TGA curves of PAI **IIIb**. The temperatures of 10 % weight loss in nitrogen and air atmospheres were determined from the original TGA



— Ar —



Scheme 1

Table I. Synthesis of poly(amide-imide)s^(a).

Polymer	Initial amount of NMP (mL)	Additional amount of NMP (mL)	CaCl ₂ (g)	$\eta_{inh}^{(b)}$ (dL/g)	Remark ^(c)
IIIa	5.5		0.6	0.66	Stringy
IIIb	5.5		0.6	0.64	Stringy
IIIc	6.5	2	0.8	0.96	Stringy
III d	5.5	2.5	0.8	1.34	Stringy
IIIe	6	5.5	0.8	1.27	Stringy
III f	5.5	2.5	0.8	1.39	Stringy
III g	7.5	2.5	0.8	1.44	Stringy
III h	5.5	2	0.8	1.01	Stringy
III i	5.5	1.5	0.8	1.08	Stringy
III j	7.5		0.8	—	Powder
III k	6	2	0.8	1.42	Stringy
III l	8	2	0.8	0.90	Stringy
III m	5.5	8	0.8	1.29	Stringy
III n	6.5	1	0.8	1.18	Stringy

(a) Polymerization was carried out with 1.25 mmol of each monomer, 0.8 mL of triphenyl phosphite, 1.2 mL of pyridine at 100 °C for 3 h.

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

(c) Appearance of the polymer product precipitated in methanol.

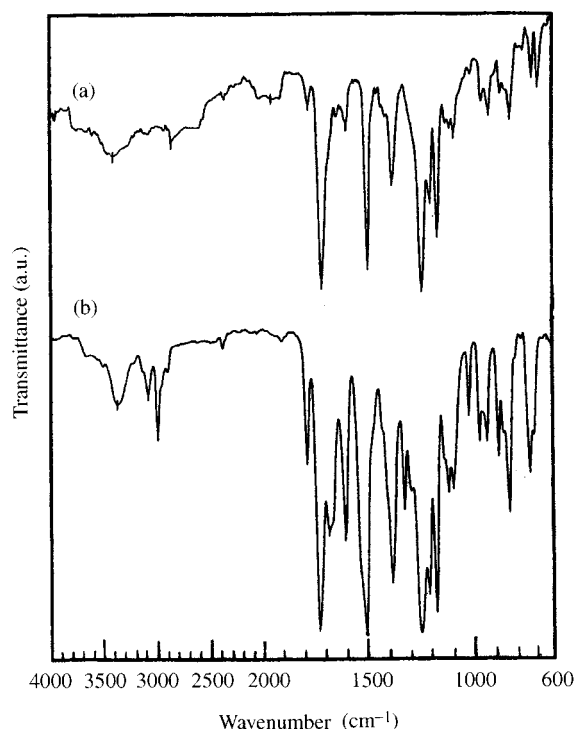


Figure 1. IR spectrum of (a) diimide-diacid **II** and (b) poly(amide-imide) **IIIb**.

curves and are included in Table V. All polymers exhibited good thermal stability with no significant weight loss up to temperatures of approximately 450 °C in both air and nitrogen atmospheres, and the temperatures at 10% weight loss were all higher than

499 °C. The anaerobic char yield at 800 °C for all polymers was in the range of 45-59 wt%.

Table V also summarizes the T_g data of the PAIs. Quenching from an elevated temperature of ~400 °C to room temperature yields predominantly amorphous samples so that, in almost all cases, the T_g s could be easily read in the subsequent DSC heating traces. DSC observed no discernible T_g for the semicrystalline PAI **IIIj**. The other PAIs showed well-defined glass transitions between 203 and 277 °C, generally following the decreasing order of chain flexibility. If one compares some isomeric pairs such as **IIIa/IIIb**, **IIIc/III d**, and **III m/III n**, the difference in T_g is strikingly clear. The meta orientation is effective in decreasing the T_g . The introduction of pendent phenyl groups, such as **III f** and **III i**, inhibits close chain packing and increases the polymer fractional free volume that increases polymer rotational and flexural mobility, thus also leading to a decrease in T_g .

Conclusions

Diimide-diacid 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]hexafluoropropane was used as a PAI building block. A series of new PAIs having moderate to high inherent viscosities were successfully prepared by direct polycondensation of the diimide-diacid with various long-chain aromatic diamines by means of triphenyl phosphite and pyridine. These PAIs generally showed high thermal stability and

Table II. Elemental analysis of poly(amide-imide)s.

Polymer	Formula (Molecular weight)		Elemental analysis(%)			Moisture intake ^(a) (%)
			C	H	N	
IIIa	(C ₆₉ H ₃₆ N ₄ O ₈ F ₆) _n (1163.06) _n	Calcd.	70.52	4.12	4.77	1.8
		Found	69.30	4.32	4.66	
IIIb	(C ₆₉ H ₃₆ N ₄ O ₈ F ₆) _n (1163.06) _n	Calcd.	70.52	4.12	4.77	2.6
		Found	68.75	4.25	4.64	
IIIc	(C ₈₁ H ₅₆ N ₄ O ₁₀ F ₆) _n (1359.35) _n	Calcd.	71.57	4.15	4.12	1.5
		Found	70.51	4.33	4.02	
IIId	(C ₈₁ H ₅₆ N ₄ O ₁₀ F ₆) _n (1359.35) _n	Calcd.	71.57	4.15	4.12	1.4
		Found	70.59	4.29	4.33	
IIIe	(C ₇₂ H ₄₆ N ₄ O ₁₀ F ₆) _n (1241.17) _n	Calcd.	69.68	3.74	4.51	1.5
		Found	68.67	3.92	4.45	
IIIf	(C ₇₇ H ₄₈ N ₄ O ₁₀ F ₆) _n (1303.24) _n	Calcd.	70.97	3.71	4.30	1.4
		Found	69.97	4.08	4.24	
IIIg	(C ₆₃ H ₃₆ N ₄ O ₁₀ F ₆) _n (1122.99) _n	Calcd.	67.38	3.23	4.79	1.4
		Found	66.44	3.42	4.92	
IIIh	(C ₆₄ H ₃₈ N ₄ O ₁₀ F ₆) _n (1137.02) _n	Calcd.	67.61	3.37	4.71	2.0
		Found	66.29	3.54	4.83	
IIIi	(C ₆₉ H ₄₀ N ₄ O ₁₀ F ₆) _n (1199.09) _n	Calcd.	69.12	3.36	4.67	3.3
		Found	66.93	4.00	4.52	
IIIj	(C ₆₉ H ₄₀ N ₄ O ₁₀ F ₆) _n (1199.09) _n	Calcd.	69.12	3.36	4.67	4.6
		Found	66.06	3.52	4.59	
IIIk	(C ₇₃ H ₄₄ N ₄ O ₁₀ F ₆) _n (1251.16) _n	Calcd.	69.85	3.85	4.46	2.5
		Found	68.12	4.02	4.25	
IIIl	(C ₆₉ H ₄₀ N ₄ O ₁₀ F ₆) _n (1199.09) _n	Calcd.	69.12	3.36	4.67	1.9
		Found	67.83	3.69	4.59	
III m	(C ₆₉ H ₄₀ N ₄ O ₁₂ SF ₆) _n (1263.15) _n	Calcd.	65.61	3.19	4.44	1.9
		Found	64.41	3.55	4.35	
III n	(C ₆₉ H ₄₀ N ₄ O ₁₂ SF ₆) _n (1263.15) _n	Calcd.	65.61	3.19	4.44	1.4
		Found	64.73	3.33	4.28	

(a) Moisture intake (%) = $(W - W_0)/W_0 \times 100\%$, W = weight of polymer sample after standing at room temperature for at least 3 days, W₀ = weight of polymer sample after dried in a vacuum at 100 °C for 10 h.

Table III. Solubility of poly(amide-imide)s^(a)

Polymer	Solvents ^(b)							
	DMAc	DMAc +5%-LiCl	NMP	DMF	DMSO	Py	<i>m</i> -Cresol	Conc. H ₂ SO ₄
IIIa	+	+	+	+	+	+	+	+
IIIb	+	+	+	+	+	+	+	+
IIIc	+	+	+	+	+-	+	+	+
IIId	+	+	+	+	+-	+	+	+
IIIe	+	+	+	+	+	+	+	+
IIIf	+	+	+	+	+-	+	+	+
IIIg	-	+	+	-	-	-	-	+
IIIh	+	+	+	+	+	+	+	+
IIIi	+	+	+	+	+	+	+	+
IIIj	-	+-	-	-	-	-	-	+
IIIk	+	+	+	+	+-	+	+	+
IIIl	+	+	+	+	+	+-	+	+
III m	+	+	+	+	+	+	+	+
III n	+	+	+	+	+	+	+	+

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

(b) DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; NMP: *N*-methyl-2-pyrrolidone; Py: pyridine.

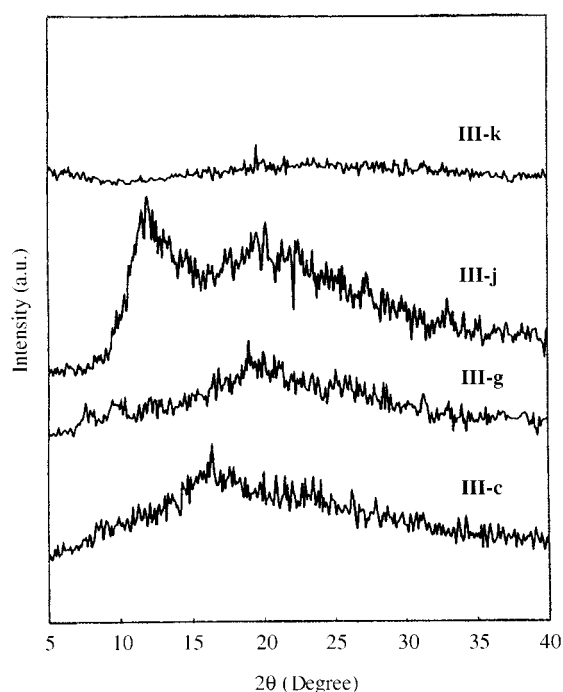
excellent solubility, and the solution cast films exhibited good tensile properties. Thus, the present

PAIs are considered as new candidates for processable high-performance polymeric materials.

Table IV. Tensile properties of poly(amide-imide)s.^(a)

Polymer	Yield strength (MPa)	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
IIIa	85	91	13	2.0
IIIb	—	46	6	1.7
IIIc	57	53	9	1.9
III-d	—	72	14	1.5
IIIe	—	93	9	2.0
III-f	—	79	9	1.3
III-h	—	93	9	1.6
III-i	—	71	7	1.5
III-k	—	79	9	1.7
III-m	—	64	11	1.7
III-n	—	96	9	1.8

(a) Films were cast from slow evaporation of the polymer solutions in DMAc.

**Figure 2.** Wide-angle X-ray diffractograms of poly(amide-imide)s.

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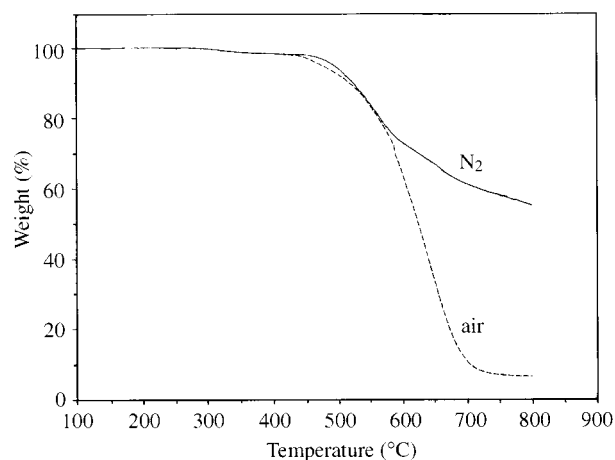
Table V. Thermal properties of poly(amide-imide)s.

Polymer	T _g ^(a) (°C)	Decomposition temperature ^(b) (°C)		Char yield ^(c) (wt%)
		in N ₂	in air	
IIIa	236	502	507	55
IIIb	213	511	499	45
IIIc	217	520	503	51
III-d	203	543	528	59
IIIe	241	548	542	49
III-f	211	542	536	55
III-g	241	558	511	52
III-h	213	521	533	48
III-i	209	556	534	47
III-j	—	544	523	53
III-k	277	521	501	47
III-l	233	544	538	49
III-m	268	547	529	49
III-n	227	544	520	50

(a) Baseline shifts on the second heating DSC traces at a heating rate of 10 °C/min in nitrogen.

(b) Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

(c) Residual weight % at 800 °C in nitrogen.

**Figure 3.** TGA curves of poly(amide-imide) IIIb at a heating rate of 20 °C/min.

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