Synthesis and Properties of Organosoluble Poly(amide-imide-imide)s Based on Tetraimide-Dicarboxylic Acid Condensed from 4,4'-(Hexafluoroisopropylidene)diphthalic Anhydride, 1,4-Bis(4-aminophenoxy)benzene, and Trimellitic Anhydride, and Various Aromatic Diamines

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(Received November 1, 2001; Accepted January 9, 2002)

ABSTRACT: A novel tetraimide-dicarboxylic acid (**I**) was synthesized starting from the ring-opening addition of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 1,4-bis(4-aminophenoxy)benzene (TPEQ), and trimellitic anhydride (TMA) at a 1:2:2 molar ratio in *N*-methyl-2-pyrrolidone (NMP), followed by azeotropic condensation to the diacid **I**. A series of poly(amide-imide-imide)s (PAIIs) with inherent viscosities of 1.0–1.3 dL g⁻¹ was prepared from the diacid **I** with various aromatic diamines by direct polycondensation. Most of the PAIIs were readily soluble in a variety of amide polar solvents, and even in less polar *m*-cresol and pyridine. Solvent-cast films had a tensile strength ranging from 80 to 101 MPa, elongation at break from 10 to 17%, and initial modulus from 2.0 to 2.4 GPa, and all of them exhibited clear yield points on their stress-strain curves. The glass transition temperature of these PAIIs was recorded at 260–289°C. They had 10% weight loss at a temperature above 520°C in air or nitrogen atmosphere.

KEY WORDS Tetraimide-Dicarboxylic Acid / Organosoluble / Poly(amide-imide-imide)s / Direct Polycondensation /

Aromatic polyimides are well-known as high performance polymeric materials due to their excellent thermal stability, electric insulation property, and chemical resistance.^{1–7} Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. However, the applications are limited due to their high softening or melting temperatures and their insoluble nature in most organic solvents. To overcome these drawbacks, the modifications of polyimide structure are often be used, for example the introduction of flexible linkages, non-symmetrical structure, or bulky substituents into polymer backbones.^{8–13} The other method is by using copolymerization to synthesize copolymers to improve processability, such as poly(amide-imide) (PAI).^{14,15}

Aromatic PAIs possess desirable characteristics with merits of both polyamides and polyimides such as high thermal stability and good mechanical properties as well as easy processability. These polymers can be synthesized from various aromatic monomers containing dianhydride, diamine, dicarboxylic acid, amino acid, or anhydride-acid by polycondensation. PAIs usually have been synthesized through several main routes. The first route goes through the amide-imide-forming reaction, by which trimellitic anhydride (TMA) reacts either with diisocyanate to produce PAI^{16–19} or with thionyl chloride to synthesize TMA-chloride before the

latter and diamine can produce PAI.²⁰ The second route goes through the imide-forming reaction, with amide-containing monomer serving as a medium; for example, amide-containing diamine is polycondensed with dianhydride to provide the poly(amide amic acid), which is then dehydrated to obtain PAI.^{21,22} The third route goes through the amide-forming reaction from imide-containing monomers such as dicarboxylic acids or diamines. Imide-containing dicarboxylic acids usually come from the thermal imidization of diamines and TMA,^{23–25} from the condensation of dicarboxylic anhydride and amino acids,^{26–28} or from the dehydration of aromatic amino acids and TMA.^{29–31} Then, these resultant imide-containing dicarboxylic acids react with aromatic diamines to synthesize aromatic PAIs by polycondensation.

In our laboratory, the dicarboxylic acid, 1,4-bis(4-trimellitimidophenoxy)benzene, was prepared from TMA and 1,4-bis(4-aminophenoxy)benzene (trivially termed triphenyl ether hydroquinone diamine, referred to as TPEQ). A series of aromatic PAIs was synthesized from the dicarboxylic acid and various aromatic diamines.³² However, these polymers showed limited solubility and poor tensile properties. Thus, this research describes the synthesis of novel PAIIs to modify their tensile properties and process. 6FDA, TPEQ, and TMA were used to prepare a new-type tetraimide-dicarboxylic acid (TIDA), which then reacted with vari-

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ous aromatic diamines to form PAIIs (**IV_{a–m}**) by direct polycondensation. Various properties of the resultant PAIIs, specifically, their solubility, tensile properties, and thermal stability, will be investigated and compared with those of corresponding PAIs.

EXPERIMENTAL

Materials

p-Phenylenediamine (**III_a**; from Tokyo Chemical Industry, TCI) and *m*-phenylenediamine (**III_b**; from TCI) were vacuum-distilled before use. Other diamines including 2,4-diaminotoluene (**III_c**; from TCI), 4,4'-oxydianiline (**III_d**; from TCI), 4,4'-methylenedianiline (**III_e**; from TCI), 4,4'-thiodianiline (**III_f**; from TCI), 1,4-bis(4-aminophenoxy)benzene (TPEQ) (**III_g**; from TCI), 1,3-bis(4-aminophenoxy)benzene (**III_h**; from Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**III_j**; from Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**III_k**; from TCI), bis[4-(4-aminophenoxy)phenyl]sulfone (**III_l**; from Chriskev), and bis[4-(3-aminophenoxy)phenyl]sulfone (**III_m**; from Chriskev) were used as received. According to a reported method,³³ 1,2-bis(4-aminophenoxy)benzene (**III_i**) was prepared by the nucleophilic substitution reactions of the corresponding aromatic diol and *p*-chloronitrobenzene followed by catalytic hydrazine reduction. Trimellitic anhydride (TMA; from Wako) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA; from Chriskev) were used without further purification. The calcium chloride (CaCl₂; from Wako) was dried under vacuum at 180°C for 10 h. *N,N*-Dimethylacetamide (DMAc; from Fluka), *N*-methyl-2-pyrrolidone (NMP; from Fluka) and pyridine (Py; from Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP; from TCI) was used as received.

Synthesis of Tetraimide-Dicarboxylic Acid (**I**)

4.78 g (16 mmol) of TPEQ was first dissolved in 40 mL of NMP. After the monomer was completely dissolved, 3.55 g (8 mmol) of 6FDA and 3.07 g (16 mmol) of TMA were added to it in one portion. The mixture was stirred at room temperature for 2 h. About 10 mL of toluene was then added, and the mixture was heated at the reflux for about 3 h until about 0.6 mL of water was distilled off azeotropically *via* a Dean–Stark trap. After complete removal of water, the residual toluene was then distilled off under reduced pressure. After cooling, the obtained partial solution was trickled into water and the precipitated product was collected by filtration, washed several times with water, and dried in a

vacuum to give sawlow-powder diacid **I**; mp 342–344°C (by DSC).

IR $\nu_{\max}$ (KBr): 3500–2500 (carboxylic acid, –OH), 1782 (symmetric imide C=O stretching), 1724 (acid C=O stretching and asymmetric imide C=O stretching), 1382 (imide, imide ring vibration, axial), 1118 (imide, imide ring vibration, transverse), and 723 cm^{–1} (imide, imide ring vibration, out of plane). ¹H NMR [dimethyl sulfoxide (DMSO)-*d*₆]: δ = 8.42, 8.41 (H_b), 8.31 (H_a), 8.19, 8.17 (H_i), 8.08, 8.07 (H_c), 7.98, 7.96 (H_h), 7.76 (H_g), 7.49, 7.47, 7.45 (H_d+H_{d'}), 7.21, 7.20, 7.17, 7.16 (H_e+H_{e'}+H_f+H_{f'}). ¹³C NMR (DMSO-*d*₆): δ = 168.42, 168.40, 168.26, 168.13 (C², C^{2'}, C^{2''}, C^{2'''}), 167.86 (C¹), 159.10, 158.96 (C¹², C^{12'}), 153.93, 153.88 (C¹³, C^{13'}), 138.99 (C¹⁷), 138.14 (C⁶), 137.44 (C¹⁵), 137.08 (C³), 136.54 (C⁸), 134.63 (C¹⁸), 134.23 (C²⁰), 133.65 (C⁵), 130.76, 130.64 (C¹⁰, C^{10'}), 128.10, 128.02 (C⁹, C^{9'}), 125.86 (C¹⁹), 125.26 (C⁴), 125.09 (C¹⁶), 124.85 (C⁷), 122.70, 122.65 (C¹¹, C^{11'}), 119.47 (C¹⁴, C^{14'}), 129.19, 126.29, 123.39, 120.49 (C²¹, quartet, with ¹J_{CF} = 290 Hz), 65.37 (C²², multiplet, with ²J_{CF} = 25 Hz).

C₇₃H₃₈N₄O₁₆F₆(1341.11) Calcd. C 65.38 H 2.86 N 4.18
Found C 65.28 H 2.83 N 4.15

Synthesis of Diimide-Dicarboxylic Acid (**II**)

2.34 g (8 mmol) of TPEQ was first dissolved in 16 mL of DMAc, and then 3.07 g (16 mmol) of TMA was added. After the mixture was completely dissolved, toluene was then added, and the mixture was heated at the reflux for about 3 h until water was distilled off azeotropically. The residual toluene was then distilled off under reduced pressure. After cooling, the obtained solution was trickled into methanol and the precipitated product was collected by filtration, and then recrystallized from DMF solvent. The purified product was dried under vacuum to obtain powder; mp 398–400°C (by DSC).

C₃₆H₂₀N₂O₁₀(640.56) Calcd. C 67.50 H 3.15 N 4.37
Found C 67.46 H 3.13 N 4.34

Synthesis of Poly(amide-imide-imide)s

A typical example of polycondensation is described as follows. A mixture of 1.34 g (1 mmol) of tetraimide-dicarboxylic acid **I**, 0.20 g (1 mmol) of 4,4'-oxydianiline (**III_d**), 0.2 g of CaCl₂, 1.8 mL of Py, 0.6 mL of TPP, and 7.3 mL of NMP was heated while being stirred at 100°C for 3 h. The viscosity of reaction solutions increased after 1 h, and an additional 2.0 mL of NMP was added to the reaction mixture. At the

Scheme 1. Preparation of tetraimide-diacid **I**.

end of the reaction, the obtained viscous polymer solution was trickled into 400 mL of stirred methanol. The yellow-stringy polymer was washed thoroughly with hot water and methanol, collected by filtration and dried in a vacuum. The yield was 1.50 g. The inherent viscosity of **IV_d** in DMAc at a 0.5 g dL⁻¹ concentration at 30°C was 1.3 dL g⁻¹. All other poly(amide-imide-imide)s were synthesized in a similar procedure.

Preparation of the Poly(amide-imide-imide) Films

A polymer solution of approximately 10% was made by the dissolving of poly(amide-imide-imide) in DMAc. The solution was poured into a glass culture dish 9 cm in diameter that was placed in a 90°C oven overnight to remove the solvent. Then, the obtained semidried polymer film was stripped from the glass substrate and further dried in vacuum at 160°C for 6 h. The obtained films were about 0.05 mm thick.

Measurements

Elemental analyses were performed on a Perkin–Elmer Model 2400 C, H, N analyzer. IR spectra were recorded on a Horiba Fourier-Transform Infrared Spectrometer FT-IR-720. ¹H and ¹³C NMR spectra were determined on a JEOL EX-200 FT-NMR spectrometer. The inherent viscosities were measured with a Cannon–Fenske viscometer at 30°C. Differential scanning calorimeter (DSC) traces were measured on TA Instruments DSC 2010 in flowing nitrogen (40 cm³ min⁻¹) at a heating rate of 15°C min⁻¹. Thermogravimetry analysis (TGA) was conducted with a TA

Instruments TGA 2050, and experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (100 cm³ min⁻¹) at a heating rate of 20°C 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 polymer film. A gauge of 2 cm and a strain rate of 5 cm 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 adopted.

RESULTS AND DISCUSSION

Monomer Synthesis

TIDA **I** was prepared starting from the ring-opening addition of TPEQ, 6FDA, and TMA in a 2:1:2 molar ratio at room temperature in amide-type solvent (such as DMAc or NMP), followed by the intramolecular cyclodehydration of the intermediate tetraamide-hexacarboxylic acid (**I'**), as shown in Scheme 1. For the synthesis of imide-containing dicarboxylic acid, pure diimide-dicarboxylic acid **II** was easily obtained, because the aromatic amine groups of TPEQ hardly reacted with the carboxylic acid group of TMA in pure solvent. For the synthesis of TIDA **I**, the addition of TPEQ, 6FDA, and TMA might not form the structure of intermediate **I'** completely in the initial period, and some other diacids were produced. However, the exchange reaction of amic acid was carried out during a long time of stir,³⁴ and the product with the low-

Figure 1. FT-IR spectra of tetraimide-diacid **I** and poly(amide-imide-imide) **IV_b**.

est free energy was prepared. From the molar ratio of monomers, **I'** is a more stable structure among intermediates. Therefore, a higher purity of TIDA **I** was obtained after the cyclodehydration of **I'**. The FT-IR characteristic absorptions of TIDA **I** are shown in Figure 1. As TIDA **I** was prepared, the characteristic absorption bands of the imide ring were observed at 1782, 1724, 1382, 1118, and 723 cm^{-1} , and those of the acid group of TIDA **I** appeared at 2500–3500 cm^{-1} . The structures of TIDA **I** were also confirmed by ^1H and ^{13}C NMR spectroscopy.

In the ^1H NMR spectrum (Figure 2) of **I**, the protons of TMA and 6FDA moieties resonated at 8.42, 8.41 (H_b), 8.31 (H_a), 8.08, 8.07 (H_c) ppm and 8.19, 8.17 (H_i), 7.98, 7.96 (H_h), 7.76 (H_g) ppm, respectively. Different linkages caused the $\text{H}_{d,e,f}$ and $\text{H}_{d',e',f'}$ of **I** to shift at different positions, and their signals appeared at higher field than the rest protons in that it was less affected by other groups. The relative shifts of monomer **I** were similar to these of model compound **II**. The protons in TPEQ segment of two monomers appeared at similar shift range, but their splitting patterns were different. From the integrals of protons, it is testified that the proposed structures of TIDA **I** had formed with high purity. The ^{13}C NMR spectrum of **I** shows 33 signals (Figure 3), including 5 signals of carbonyl, 23 signals of carbon of benzene, and 5 signals of aliphatic carbon. With their different environments, the carbonyls of imide ring ($\text{C}^{2,2',2'',2'''}$) displayed four different signals (168.42, 168.40, 168.26, and 168.13 ppm). It will give off 24 signals for aromatic carbon of benzene according to the structure of **I**, but only 23 signals for carbon of benzene were found in the spectrum due to

Figure 2. ^1H NMR spectra of diacids **I** and **II** in $\text{DMSO-}d_6$.

the overlap shifts of C^{14} and $\text{C}^{14'}$. The chemical shifts of C^{9-14} were slightly different with those of $\text{C}^{9'-14'}$ because of different linkages. The splitting of the ^{13}C signals caused by couplings between carbon and fluorine also could be observed in this spectrum. The magnitudes of the one-bond and two-bond carbon-fluorine couplings $^1J_{\text{CF}}$ and $^2J_{\text{CF}}$ were 290 Hz and 25 Hz, respectively. Compared with those of the model compound **II**, the relative shift positions of C^{1-14} in **I** were very similar to those in **II**. Therefore, TIDA **I** was confirmed in agreement with predictive structure.

Polymer Synthesis

A series of PAIs **IV_{a-m}** was synthesized from **I** and various diamines by means of direct polycondensation with TPP/Py as the condensing agent in NMP in the presence of CaCl_2 (Scheme 2). Polymerization can also proceed directly using the resultant solution of diacid synthesis. The synthesis conditions and results of the preparation of PAIs are summarized in Table I. All the reactions went on smoothly in homogeneous solutions under conditions listed in Table I. The solubility of the polymer and the state of stirring affected the in-

Scheme 2. Synthesis of poly(amide-imide-imide)s.

herent viscosity of the resulting PAIIs significantly. In all cases, higher molecular weights of these polymers could be obtained by using a higher initial reactant concentration and adding a proper amount of supplemental NMP into the viscous reaction medium before the formation of swollen gel. Besides, an advantage of PAII synthesis from large molecular weight **I** is that a large product can be obtained by using a small amount of TPP. In other words, when the same amount of TPP is used, the same mole of a polymer in this study and in other reports is formed, but the weight of the polymer in this study is larger. Therefore, new-type PAIIs could significantly reduce the synthetic cost and were thus helpful in industrializing direct polycondensation.

The inherent viscosities of the **IV** series polymers were 1.0–1.3 dL g⁻¹. All of the PAIIs could be solution cast into transparent and tough films, indicating a high molecular weight. The composition and structures of these PAIIs were characterized by their IR spectra and elemental analyses. A typical IR spectrum is shown in Figure 1. The FT-IR spectrum of polymer **IV_b** exhibited characteristic absorption bands for the imide ring at 1781, 1724 (asymmetrical and symmetri-

cal C=O stretching vibration), 1379 (C–N stretching vibration), 1116, and 723 cm⁻¹ (imide ring deformation). The absorptions of amide groups appeared at 3380 (N–H stretch) and 1680 cm⁻¹ (C=O stretch). The results of the elemental analysis of all the PAIIs are listed in Table I. In all cases, however, the carbon values were found to be lower than the calculated ones for the proposed structures. This is possibly caused by the hygroscopic nature of the amide groups of these polymers. The uptakes of water were in the range of 1.23–2.35%, which could be calculated from the weight change of the vacuum-dried polymer samples after they were exposed in the air at room temperature for 1 h. When the found values were corrected by eliminating the amount of absorbed water, the correction values were in good agreement with the calculated ones.

Properties of Polymer

The qualitative solubility of PAIIs in various solvents is listed in Table II. Concentration for the solubility tests is 0.05 g mL⁻¹. Compared with the **IV** series and traditional TMA/TPEQ series PAIs **V**, the **IV** series polymers clearly exhibited a better solubility. In

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

Polymer	Solvent used		η_{inh}^b dL g ⁻¹	Formula M_w		Elemental analysis ^c /%			Moisture uptake ^d %
	NMP mL	Supplemental NMP mL				C	H	N	
IV_a	5.8	3	1.0 ^e	(C ₇₉ H ₄₂ N ₆ O ₁₄ F ₆) _n (1413.22) _n	Calcd	67.14	3.00	5.95	1.58
					Found	66.08	3.12	5.78	
					Corrected	67.12	3.07	5.87	
IV_b	6.3	2	1.0	(C ₇₉ H ₄₂ N ₆ O ₁₄ F ₆) _n (1413.22) _n	Calcd	67.14	3.00	5.95	1.82
					Found	65.92	3.14	5.80	
					Corrected	67.12	3.08	5.91	
IV_c	5.8	3	1.0	(C ₈₀ H ₄₄ N ₆ O ₁₄ F ₆) _n (1427.25) _n	Calcd	67.32	3.11	5.89	2.35
					Found	65.74	3.22	5.73	
					Corrected	67.28	3.14	5.86	
IV_d	7.3	2	1.3	(C ₈₅ H ₄₆ N ₆ O ₁₅ F ₆) _n (1505.32) _n	Calcd	67.82	3.08	5.58	1.75
					Found	66.63	3.17	5.38	
					Corrected	67.80	3.11	5.47	
IV_e	8.0	8	1.0	(C ₈₆ H ₄₈ N ₆ O ₁₄ F ₆) _n (1503.35) _n	Calcd	68.71	3.22	5.59	2.31
					Found	67.12	3.34	5.46	
					Corrected	68.67	3.26	5.59	
IV_f	7.2	2	1.3	(C ₈₅ H ₄₆ N ₆ O ₁₄ F ₆ S) _n (1521.38) _n	Calcd	67.11	3.05	5.52	1.71
					Found	65.96	3.13	5.39	
					Corrected	67.09	3.08	5.48	
IV_g	6.5	6	1.0 ^e	(C ₉₁ H ₅₀ N ₆ O ₁₆ F ₆) _n (1597.42) _n	Calcd	68.42	3.15	5.26	1.34
					Found	67.50	3.28	5.09	
					Corrected	68.40	3.23	5.16	
IV_h	7.6	5	1.2	(C ₉₁ H ₅₀ N ₆ O ₁₆ F ₆) _n (1597.42) _n	Calcd	68.42	3.15	5.26	1.52
					Found	67.38	3.22	5.10	
					Corrected	68.40	3.17	5.18	
IV_i	6.3	4	1.1	(C ₉₁ H ₅₀ N ₆ O ₁₆ F ₆) _n (1597.42) _n	Calcd	68.42	3.15	5.26	1.78
					Found	67.20	3.23	5.18	
					Corrected	68.39	3.17	5.27	
IV_j	7.6	6	1.3	(C ₁₀₀ H ₆₀ N ₆ O ₁₆ F ₆) _n (1715.60) _n	Calcd	70.01	3.53	4.90	1.67
					Found	68.84	3.63	4.80	
					Corrected	69.99	3.57	4.88	
IV_k	7.1	5	1.2	(C ₁₀₀ H ₅₄ N ₆ O ₁₆ F ₁₂) _n (1823.54) _n	Calcd	65.87	2.98	4.61	1.23
					Found	65.06	3.10	4.48	
					Corrected	65.86	3.06	4.54	
IV_l	6.5	7	1.1	(C ₉₇ H ₅₄ N ₆ O ₁₈ F ₆ S) _n (1737.58) _n	Calcd	67.05	3.13	4.84	2.10
					Found	65.64	3.26	4.69	
					Corrected	67.02	3.19	4.79	
IV_m	7.3	2	1.2	(C ₉₇ H ₅₄ N ₆ O ₁₈ F ₆ S) _n (1737.58) _n	Calcd	67.05	3.13	4.84	1.85
					Found	65.81	3.19	4.66	
					Corrected	67.03	3.13	4.75	

^aPolymerization was carried out with 1 mmol of each monomer in NMP, 1.5–1.9 mL of pyridine. 0.2–0.4 g of CaCl₂ and 0.6 mL of triphenyl phosphite at 100°C for 3 h. ^bMeasured at a polymer concentration of 0.5 g dL⁻¹ in DMAc at 30°C. ^cFor C and N: Corrected value = found value × (100% + moisture uptake%). For H: Corrected value = found value × (100% – moisture uptake%). ^dMoisture uptake (%) = $(W - W_0)/W_0 \times 100\%$; W = weight of polymer sample after standing at room temperature, and W_0 = weight of polymer sample after dried in vacuum at 100°C for 10 h. ^eMeasured at a polymer concentration of 0.5 g dL⁻¹ in NMP +5%LiCl at 30°C.

series **V**, only **V_{d,h}** were partially soluble in NMP. On the contrary, the solubility of most PAIs **IV** was significantly improved, and **IV_{d,f,g,h}** were soluble in the tested solvents. **IV_a** including rigid *p*-phenylene in diamine showed a limited solubility but was still soluble in NMP. The good solubility of these polymers **IV** might be due to the presence of the flexible ether and bulky hexafluoropropane groups in TIDA **I**, which dis-

turbed the co-planarity of aromatic units to reduce the packing efficiency and the crystallinity.

All the polymers could afford good-quality, creasable films by casting from DMAc or NMP solution. The tensile properties are summarized in Table III. All of the films necked under tension, indicating a ductile nature. These films had strengths at yield of 84–109 MPa, strengths at break of 80–101 MPa, elongations at break

Figure 3. ^{13}C NMR spectra of diacids **I** and **II** in $\text{DMSO}-d_6$.

of 10–17%, and initial moduli of 2.0–2.4 GPa. On comparing tensile properties of polymers **IV** with their analogous PAI **V**, series **IV** polymers exhibited higher strengths at break as a result of a higher proportion of the imide group in the main chain. Most of the polymers **V** couldn't be cast into films or formed brittle films, but all the PAIs **IV** showed a good film-forming ability. Therefore, the tensile properties of PAIs **V** could be modified as well as PAIs **IV** by copolymerization.

The thermal properties of all the PAIs were evaluated by TGA and DSC. The results of all polymers are summarized in Table IV. DSC measurements were conducted at a heating rate of $15^\circ\text{C min}^{-1}$ in nitrogen. Quenching from the elevated temperature (approximately 400°C) to room temperature in air gave predominantly amorphous samples so that the glass transition temperatures (T_g) of PAIs could be easily measured in the second heating traces of DSC. The T_g values of these PAIs were in the range 260 – 289°C , depending on the structure of the diamine component and following with the increasing stiffness of the polymer backbones. For isomers, **IV**_{a,g,l}, whose diamine struc-

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

Polymer	Solvent ^b					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py
IV _a	+	—	—	—	—	—
IV _b	+	+	+	+	+	+
IV _c	+	+	+	+	+	+
IV _d	+	+	+	+	±	S
IV _e	+	+	+	+	+	±
IV _f	+	+	+	+	+	+
IV _g	+	+	+	+	+	+
IV _h	+	+	+	+	+	+
IV _i	+	+	+	+	+	+
IV _j	+	+	+	+	+	+
IV _k	+	+	+	+	+	+
IV _l	+	+	+	+	+	+
IV _m	+	+	+	+	+	+
V _d	±	—	—	—	—	—
V _f	—	—	—	—	—	—
V _g	—	—	—	—	—	—
V _h	±	—	—	—	—	—

^aSolubility: measured at a polymer concentration of 0.05 g mL^{-1} . +, soluble at room temperature; ±, partially soluble; S, swelling; —, insoluble. ^bNMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine.

Table III. Tensile properties of poly(amide-imide-imide) films^a

Polymer	Strength at yield	Strength at break	Elongation to break	Initial modulus
	MPa	MPa	%	GPa
IV _a ^b	97	90	11	2.1
IV _b	98	93	14	2.3
IV _c	109	101	17	2.4
IV _d	94	90	14	2.2
IV _e	86	83	10	2.2
IV _f	87	85	12	2.0
IV _g	103	99	13	2.2
IV _h	97	90	12	2.0
IV _i	95	81	10	2.0
IV _j	84	80	12	2.1
IV _k	90	83	13	2.1
IV _l	99	95	17	2.3
IV _m	97	93	15	2.1
V _b	86	83	24	2.1
V _c	89	83	45	2.3
V _k	—	62	9	1.5
V _l	—	54	4	1.9

^aFilms were cast from polymer solutions of DMAc. ^bFilm was cast from polymer solution of NMP + 0.5% LiCl.

tures were all *para*-oriented, showed higher T_g values than did **IV**_{b,h,m}, derived from *meta*-oriented diamines. **IV**_j had structures analogous to **IV**_k, but substituent magnitude of $-\text{CF}_3$ was much larger than $-\text{CH}_3$, leading to higher T_g value. When comparing PAIs **IV** with

Table IV. Thermal data of poly(amide-imide-imide)s

Polymer	DSC $T_g^a / ^\circ\text{C}$	TGA		
		Decomposition temperature ^b / $^\circ\text{C}$		wt% Residual at 800 $^\circ\text{C}$ in N_2
		In air	In nitrogen	
IV_a	289	528	527	50
IV_b	281	533	538	56
IV_c	280	537	549	53
IV_d	274	532	545	51
IV_e	281	535	550	50
IV_f	280	537	554	50
IV_g	268	536	546	56
IV_h	260	543	550	57
IV_i	266	545	555	59
IV_j	261	520	539	52
IV_k	266	526	545	55
IV_l	277	530	544	54
IV_m	260	531	546	55
<hr/>				
V_c	292	515	526	58
V_e	— ^c	501	529	48
V_f	—	507	541	48
V_l	269	525	521	49

^aFrom second heating traces of DSC measurements conducted with a heating rate of $15^\circ\text{C min}^{-1}$ in nitrogen. ^bTemperature at which a 10% weight loss was recorded by TG at a heating rate of $20^\circ\text{C min}^{-1}$. ^cNo T_g was observed in DSC trace.

PAIs **IV**, the **IV** series displayed lower T_g values than the corresponding **V**. This was attributed to the flexible ether and hindered hexafluoroisopropylidene linkages of TIDA **I**, which disturbed the co-planarity of aromatic units to reduce the packing efficiency.

The thermal stability of the PAIs was examined by TGA measurements. The temperatures at 10% weight loss (T_{10}) and their char yields at 800°C in nitrogen atmosphere were determined from the original thermograms. The T_{10} values of polymers **IV** were in the range of 527 – 555°C in nitrogen and 520 – 545°C in air, respectively. The fluorine-containing **IV_k** had a slightly better thermal stability than its nonfluoro analogous **IV_j** did because the C–F bond of the CF_3 group is stronger than that of the CH_3 group. When compared with the **V** series, series **IV** had a char yield close to series **V** did, but the **IV** series exhibited higher T_{10} values under nitrogen and air atmospheres as a result of a higher proportion of the thermostable imide group in the main chain. Figure 4 shows typical TGA curves of PAII **IV_e** and PAI **V_e**. The thermogravimetric traces indicated that polymers **IV** possessed a high thermal stability with no significant weight loss up to approximately 450°C and had a char yield above 50%.

CONCLUSIONS

Unlike traditional diimide-diamide or imide-amide PAIs, a series of novel PAIs with alternating four imide

Figure 4. TGA curves of polymers **IV_e** and **V_e** at a heating rate of $20^\circ\text{C min}^{-1}$.

and two amide groups was synthesized. The polymers showed excellent solubility in a variety of amide-type solvents and even in less polar solvents. These polymers were characterized by good film-forming ability, a wide temperature range between T_g and decomposition temperature, and excellent thermal stability as well as good tensile properties, demonstrating a good combination of properties and processability. Thus, they were considered as new candidates for processable high-performance polymeric materials.

Acknowledgment. The authors are grateful to the National Science Council of the Republic of China for the support of this work (Grant NSC 90-2216-E-036-016).

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