

Novel Organosoluble Poly(amide-imide-imide)s Synthesized from New Tetraimide-Dicarboxylic Acid by Condensation with 4,4'-Oxydiphthalic Anhydride, 1,4-Bis(4-amino-2-trifluoromethylphenoxy)benzene, Trimellitic Anhydride, and Various Aromatic Diamines

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ABSTRACT: A new monomer of tetraimide-dicarboxylic acid (**IV**) was synthesized by starting from ring-opening addition of 4,4'-oxydiphthalic anhydride, trimellitic anhydride, and 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene at a 1:2:2 molar ratio in *N*-methyl-2-pyrrolidone (NMP). From this new monomer, a series of novel organosoluble poly(amide-imide-imide)s with inherent viscosities of 0.7–0.96 dL/g were prepared by triphenyl phosphite activated polycondensation from the tetraimide-diacid with various aromatic diamines. All synthesized polymers were readily soluble in a variety of organic solvents such as NMP and *N,N*-dimethylacetamide, and most of them were soluble

even in less polar *m*-cresol and pyridine. These polymers afforded tough, transparent, and flexible films with tensile strengths ranging from 99 to 125 MPa, elongations at break from 12 to 19%, and initial moduli from 1.6 to 2.4 GPa. The thermal properties and stability were also good with glass-transition temperatures of 236–276°C and thermogravimetric analysis 10 wt % loss temperatures of 504–559°C in nitrogen and 499–544°C in air. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2854–2864, 2006

Key words: poly(amide-imide-imide)s; fluorinated; organosoluble; 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene

INTRODUCTION

Aromatic polyimides are well known as high-performance polymeric materials because of their excellent thermal stabilities, electric insulation properties, and chemical resistance.^{1–7} Polyimides are mainly used in the aerospace and electronic industries in the form of films and moldings. However, applications are still limited because of their high softening or melting temperatures and their insoluble nature in most organic solvents. To overcome these drawbacks, modifications of the polyimide structure are often used, for example, introducing flexible linkages, nonsymmetrical structures, or bulky substituents into the polymer backbones.^{8–13} In addition, various copolymers have been developed and reported, among them poly(amide-imide)s (PAIs),^{14,15} whose amide groups can improve the solubility. Aromatic PAIs possess the de-

sirable characteristics of both polyamides and polyimides, such as high thermal stability and good mechanical properties, as well as processability.

PAIs are usually synthesized through three main routes (routes a, b, and c). In principle, route a goes through the amide-imide forming reaction, in which trimellitic anhydride (TMA) reacts either with diisocyanate to produce PAI^{16–19} or with thionyl chloride to synthesize TMA-chloride, and then reacts with diamines to produce PAI.²⁰ Route b is through an imide-forming reaction from a medium of amide-containing monomer, for example, polycondensation of amide-containing diamine with dianhydride to obtain PAI.^{21,22} Route c is 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} Therefore, aromatic PAI can usually be synthesized by polycondensation of imide-containing monomers and aromatic diamines or dicarboxylic acids, whose structures can be varied in several ways to improve the polymers into which they are polymerized.

†The first author died August 17, 2005, at the age of 75. This article is now dedicated to the memory of Prof. Chin-Ping Yang, who cherished research and publications as his lifetime joys.

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In our previous studies³² we prepared the dicarboxylic acid 1,4-bis(4-trimellitimid-2-trifluoromethylphenoxy)benzene from TMA and 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (BAFPB). A series of PAIs (series VIII) was synthesized from the diacid and various aromatic diamines, and these polymers showed good physical properties. In extending our interest in introducing imide groups into PAIs, we designed and synthesized more novel poly(amide-imide-imide)s (PAIIs) based on large molecular weight tetraimide-dicarboxylic acid (TIDA). Various properties of the resultant PAIIs, such as the solubility, tensile properties, and thermal stability, were characterized and compared with those of corresponding PAIs.

EXPERIMENTAL

Materials

TMA (Wako) and 4,4'-oxydiphthalic anhydride (ODPA, Oxychem) were used without further purification. 2-Chloro-5-nitrobenzotrifluoride (Acros), hydroquinone (Showa), hydrazine monohydrate (TCI), and 10% palladium (Fluka) were acquired and used. The aromatic diamines in the study were the following: 4,4'-oxydianiline (**VI_a**, TCI), 4,4'-methylenedianiline (**VI_b**, TCI), 1,4-bis(4-aminophenoxy)benzene (**VI_c**, TCI), 1,3-bis(4-aminophenoxy)benzene (**VI_d**, Chriskev), 4,4'-bis(4-aminophenoxy)biphenyl (**VI_e**, Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**VI_f**, Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**VI_i**, TCI). BAFPB (**I**), 4,4'-bis(4-aminophenoxy)-3,3',5,5'-tetramethylbiphenyl (**VI_f**), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**VI_h**), and 'bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**VI_j**) were synthesized according to published methods.^{33–36} The solvents *N*-methyl-2-pyrrolidone (NMP, Fluka), pyridine (Py, Wako), and triphenyl phosphite (TPP, TCI) were used as received. Commercially available anhydrous calcium chloride (CaCl₂, Wako) was dried under a vacuum at 150°C for 6 h.

Synthesis of BAFPB

p-Hydroquinone (20 mmol) was first dissolved in 20 mL of *N,N*-dimethylacetamide (DMAc) in a 300-mL flask with stirring, and 2-chloro-5-nitrobenzotrifluoride (40.5 mmol) and potassium carbonate (35 mmol) were added to it in one portion. Then, the mixture was heated at 110°C for 12 h. The obtained mix was poured into methanol/water to attain a solid, which was collected, washed with water, and dried under a vacuum. The crude product was recrystallized from dimethylformamide (DMF)/methanol to produce fine crystals of 1,4-bis(4-nitro-2-trifluoromethylphenoxy)benzene

[9.3 g, yield 95%, differential scanning calorimetry (DSC) mp 221°C, lit.³⁷ mp 216°C]. To the suspension solution of the dinitro compound and 10% Pd/C (0.18 g) in ethanol (100 mL), hydrazine monohydrate (60 mmol) was added dropwise to the stirred mixture at 80°C. After complete addition, the mixture was heated at reflux temperature. The reaction solution was filtered hot to remove Pd/C, and the filtrate was then distilled to partially remove the solvent to obtain fine and white crystals of **I** (7.64 g, yield 93.5%, DSC mp 132–133°C, lit.³³ mp 126°C).

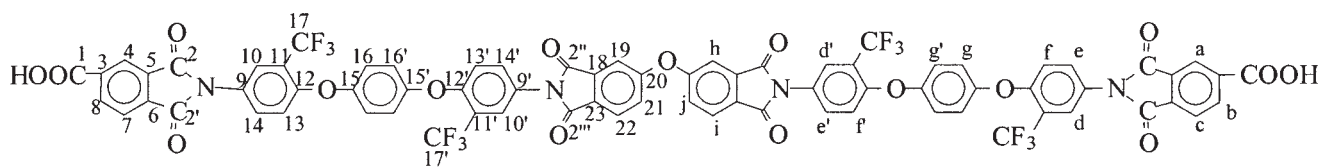
ANAL. Calcd for (**I**) C₂₀H₁₄N₂O₂F₆ (428): C, 56.06%; H, 3.3%; N, 6.54%. Found: C, 56.39%; H, 3.75%; N, 6.58%.

Synthesis of TIDA (IV)

A mixture of 0.384 g (2 mmol) of TMA and 0.856 g (2 mmol) of BAFPB was first dissolved in 5 mL of NMP. After the mixture had completely dissolved, 0.31 g (1 mmol) of ODPA was added in one portion and the mixture was stirred at room temperature for 2 h. About 8 mL of toluene was then added, and the mixture was heated at reflux for about 3 h until about 0.1 mL of water was distilled off azeotropically via a Dean–Stark trap. The water was completely removed, and then the residual toluene was distilled off under reduced pressure. After cooling, the obtained solution (TIDA-NMP) was trickled into water and the precipitated product was collected by filtration, washed several times with water, and dried in a vacuum to give diacid **IV** as a gray powder (yield 98%, DSC mp 197°C).

Characterization

ANAL. Calcd for (**IV**) C₇₄H₃₄N₄O₁₇F₁₂ (1478): C, 60.09%; H, 2.32%; N, 3.79%. Found: C, 59.25%; H, 2.08%; N, 3.76%. IR (KBr): 3500–2500 (acid —OH), 1783 (symmetric imide C=O stretching), 1733 (acid C=O stretching and asymmetric imide C=O stretching), 1369 (imide, imide ring vibration, axial), 1101 (imide, imide ring vibration, transverse), 728 cm⁻¹ (imide, imide ring vibration, out of plane). ¹H-NMR (400 MHz, DMSO-*d*₆, δ): 8.43 (H_b, 2H, d), 8.31 (H_a, 2H, s), 8.10 (H_c, H_i, 2H, 2H, dd), 7.95 (H_d, H_{d'}, 2H, 2H, ss), 7.75 (H_e, H_{e'}, 2H, 2H, dd), 7.65 (H_f, 2H, d), 7.63 (H_h, 2H, s), 7.29 (H_g, H_{g'}, 4H, 4H, dd), 7.25 (H_f, H_{f'}, 2H, 2H, dd). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ): 166.13, 166.09 (C², C^{2'}, C^{2''}, C^{2'''}), 165.93 (C¹), 160.08 (C²⁰), 154.62, 154.52 (C¹², C^{12'}), 151.98 (C¹⁵, C^{15'}), 136.57 (C⁶), 135.55 (C⁵), 134.86 (C³), 134.48 (C¹⁸), 133.39 (C⁸), 132.02 (C⁹, C^{9'}), 127.19 (C²²), 126.69 (C⁴), 126.21 (C¹⁴, C^{14'}), 125.04 (C²¹), 123.87 (C²³), 123.44 (C⁷), 121.71 (C¹⁰, C^{10'}, C¹⁶, C^{16'}), 119.28 (C¹³), 119.53, 121.93, 124.10, 126.26 (C¹⁷, C^{17'}, quartet, ¹J_{CF} = 271 Hz), 119.53 (C¹¹, C^{11'}, multiplet, ²J_{CF} = 31 Hz), 113.75 (C¹⁹).



Synthesis of PAIs

Method 1: 1p2s process

A typical example of polycondensation began with dissolving 0.856 g (2 mmol) of BAFPB in 5 mL of NMP, and then 0.384 g (2 mmol) of TMA was added. After the mixture was completely dissolved, 0.31 g (1 mmol) of ODPa was added to it in one portion with stirring at room temperature for 2 h. Then, 8 mL of toluene was added and the mixture was heated under reflux for 3 h until water was azeotropically distilled from the mixture. The residual toluene was then distilled off under reduced pressure. After cooling, 0.394 g (1 mmol) of diamine **VI_g**, 0.12 g of CaCl₂, 1.2 mL of Py, and 0.6 mL of TPP were added to the obtained solution (TIDA-NMP) and the mixture was heated with stirring at 100°C for 3 h. The viscosity of the reaction solutions increased after 30 min, and an additional 2–3 mL of NMP was added to the reaction mixture. At the end of the reaction the obtained polymer solution was trickled into stirred methanol. The yellow, stringy polymer was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100°C under reduced pressure. The inherent viscosity (η_{inh}) of PAII **VII_g** was 0.85 dL/g, which was measured with a polymer concentration of 0.5 g/dL in DMAc at 30°C. All other PAIs were synthesized with similar methods.

Method 2: 2p2s process

A typical example of polycondensation was a mixture of 1.08 g (0.73 mmol) of tetraimide-diacid **IV**, 0.288 g (0.73 mmol) of diamine **VI_g**, 0.1 g of CaCl₂, 1 mL of Py, 0.5 mL of TPP, and 3.8 mL of NMP was heated while being stirred at 100°C for 3 h. The viscosity of the reaction solutions increased after 30 min, and an additional 3.0 mL of NMP was added to the reaction mixture. At the end of the reaction the obtained 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 at 100°C under reduced pressure. The inherent viscosity was 0.86 dL/g for polymer **VII_g** in DMAc with a 0.5 g/dL concentration at 30°C.

Measurements

The IR spectra were recorded on a Nicolet Magna-560 with Fourier transform IR (FTIR) spectroscopy. Ele-

mental analyses were run in a PerkinElmer model 2400 C, H, and N analyzer. The ¹H and ¹³C spectra were recorded by using a JEOL EX-500 FT-NMR spectrometer. The FT-NMR apparatus is capable of being used at frequencies as high as 500 MHz; however, actual characterization was usually performed at lower frequencies. The inherent viscosities of the polymers were determined at a 0.5 g/dL polymer concentration in DMAc with an Ubbelohde viscometer at 30°C. Thermogravimetric analysis (TGA) was conducted with a TA Instruments model TGA 2050. Experiments were carried out on 9–11 mg film samples heated in flowing nitrogen or air (100 cm³/min) at a heating rate of 20°C/min. DSC traces were measured on a TA Instruments DSC 2010 at a rate of 15°C/min in flowing dry nitrogen (40 cm³/min). The glass-transition temperatures (T_g) were read as the midpoint of the heat capacity discontinuity, and the T_g values were taken from the second heating scan after quickly cooling from 400°C.

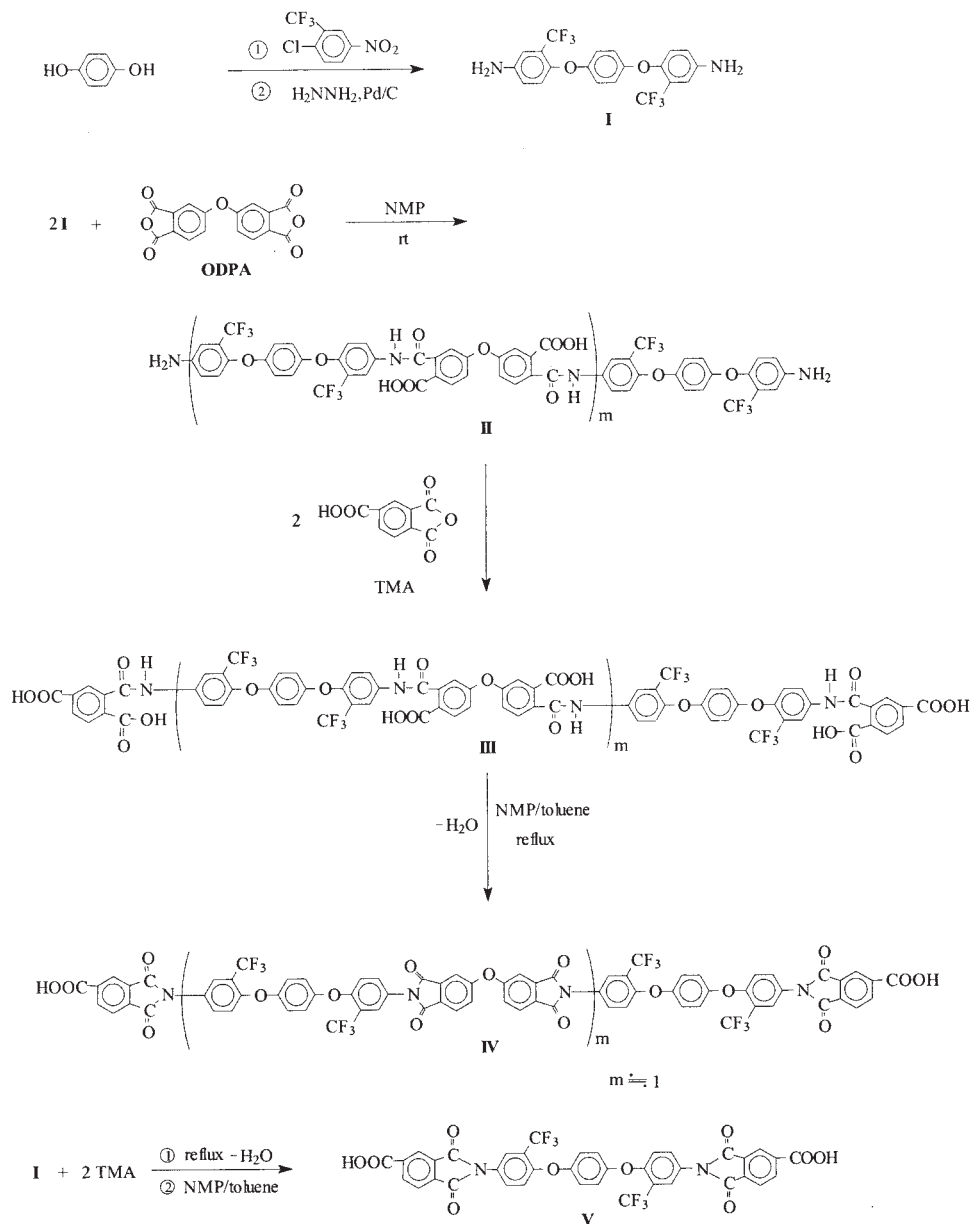
The mechanical properties of the films were measured using a tensile tester (Instron model 1130) with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 50–90 μ m thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. The objective here was to obtain a quick comparison between vast numbers of synthesized polymers; thus, a slightly faster crosshead speed of 5 mm/min was considered to be suitable for quickly evaluating the effect of the structures of different polymers in film forms. In addition, dynamic mechanical analysis (DMA) was performed on a TA Instruments RSA III DMA apparatus in tension mode on thin film (50–90 μ m) samples with a heating rate of 3°C/min.

RESULTS AND DISCUSSION

Synthesis of TIDA monomer

TIDA (**IV**) was synthesized starting from the ring-opening addition of BAFPB, TMA, and ODPa with a 2:2:1 molar ratio at room temperature in an amide-type solvent (such as NMP or DMAc), followed by the intramolecular cyclodehydration of the intermediate tetra-amic hexacarboxylic acid **III** (Scheme 1).

For synthesis of imide-containing dicarboxylic acid, pure **V** was easily obtained because the aromatic amine groups of BAFPB hardly react with the carbox-



Scheme 1 The routes of the synthesis of the TIDA monomer.

ylic acid group of TMA in pure solvent. For synthesis of **IV**, the addition of BAFPB, TMA, and ODPA might not have completely formed the structure of intermediate **III** in the initial period and some other diacids were produced. However, the exchange reaction of amic acid was carried out during a long period of stirring,³⁸ and the product with the lowest free energy was prepared. From the molar ratio of the monomers, **IV** is a more stable structure among the intermediates. Therefore, higher purity **IV** might be obtained after the cyclodehydration of **III**. The structures of diacid **IV** were confirmed by IR, ¹H-NMR, and ¹³C-NMR spectroscopy.

For direct comparisons, the IR spectra for the diacid and the polymers synthesized from it are listed in

Figure 1. The typical IR spectrum for diacid monomer **IV** is shown in Figure 1(A). The absorption bands appear between 3500 and 2500 (carboxyl —OH), 1783 (imide, asymmetric C=O stretching), 1733 (carboxyl C=O and symmetric C=O stretching), and 1101 and 728 cm⁻¹ (imide ring deformation), which all confirm the presence of the carboxylic group and imide ring, as shown in the suggested structure of the monomer thus synthesized.

Figure 2 presents the ¹H-NMR and ¹³C-NMR spectra of **IV**. In the ¹H-NMR the protons of the TMA moieties resonate at 8.43 (H_b), 8.31 (H_a), and 8.10 (H_c) ppm and those of ODPA resonate at 8.10 (H_i), 7.65 (H_j), and 7.63 (H_h) ppm. The protons of BAFPB moieties resonate at 7.95 (H_d, H_{d'}), 7.75 (H_e, H_{e'}), 7.29 (H_g,

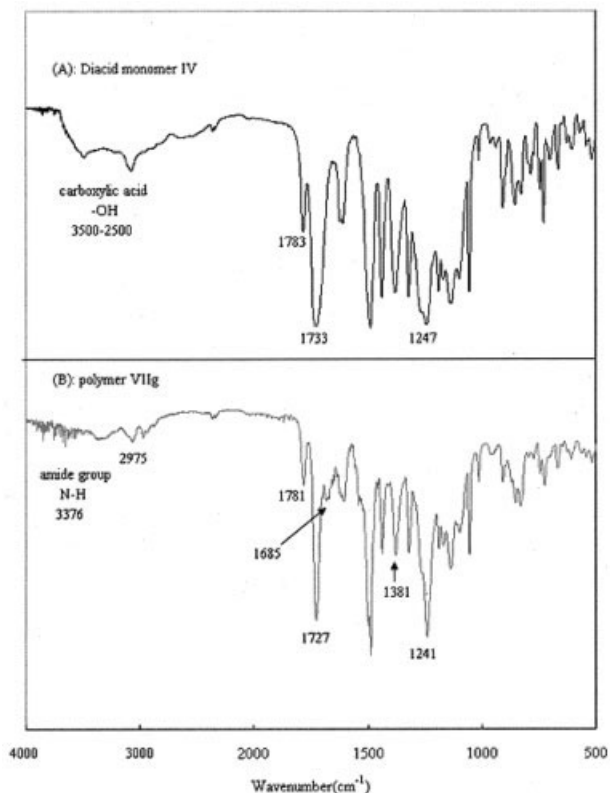


Figure 1 FTIR spectra of (A) tetraimide-diacid (IV) and (B) poly(amide-imide-imide)s (VII_g).

H_g'), and 7.25 (H_f, H_f') ppm; the H_g', H_g' and H_f, H_f' are shifted to higher fields because of the electron donating property of aromatic ether. The ¹³C-NMR spectrum of IV shows 25 signals, including 4 signals of carbonyl, 18 signals of carbon of benzene, and 3 signals of aliphatic. It should exhibit 18 signals for all carbons of benzene if C⁹⁻¹⁶ and C^{9'-16'} have the same chemical environments. However, there will be 26 signals if they have different environments. The results show that the former is closer to the found number. Therefore, the shifts of C⁹⁻¹⁶ and C^{9'-16'} are close to or overlapped in the spectrum. The splitting of the ¹³C signals caused by couplings between the carbon and fluorine are also observed in this spectrum. The large quartet centered at about 123 ppm is due to the CF₃ carbon. The 1-bond C—F coupling constant in this case is about 271 Hz. The CF₃-attached carbon (C¹¹) also shows a clear quartet centering at about 119.53 ppm with a smaller coupling constant of about 31 Hz attributed to 2-bond C—F coupling.

Synthesis of PAIIs

A series of PAIIs (VII_{a-j}) were synthesized in two ways. Scheme 2 illustrates the routes of the syntheses

used in this study, which are based on the Yamazaki method³⁹ for polyamide direct polycondensation in mixtures of TPP and Py (TPP/Py) as a condensing agent in NMP in the presence of calcium chloride. There are two different methods in this scheme. The first is synthesis from TIDA (IV) and various diamines V_{a-j}, whereas the second is via directly using the resultant solution of diacid (IV-NMP) and various diamines V_{a-j}. The former method is termed the 1P2S process, and the latter method is termed the 2P2S process. The suitable solvent for the Yamazaki polyamide direct polycondensation is generally NMP. In this study we also used NMP as the solvent with the addition of BAFPB, TMA, and ODPA to synthesize TIDA. The 1P2S process to synthesize PAII with the addition of the diamine, CaCl₂, Py, and TPP to the resultant solution (TIDA-NMP) is more advantageous, because it uses less NMP and avoids the need for purification of TIDA intermediates. The polymers synthesized by either the 1P2S or 2P2S process all exhibit good chemical and physical properties. However, the former method has been found to be more economical, which can significantly reduce the overall synthesis costs.

Generally speaking, as the reactant concentration increases, the degree of condensation will increase. The most suitable reaction concentration of the PAII is to use initially 4–5 mL of NMP for each mole of IV. With the increase in viscosity, another 2–3 mL of solvent was added to the mixture. At the early stage, the PAII presented as a gel form and became difficult to stir; but it resumed a fluidlike state with the further addition of the solvent.

The inherent viscosities of the VII series polymers were 0.72–0.96 dL/g. All synthesized PAIIs could be solution cast into transparent and tough films, indicating a sufficiently high molecular weight. The composition and structures of these PAIIs were characterized and confirmed by IR spectra and elemental analyses. The typical IR spectrum for the synthesized polymer is provided in Figure 1(B). The FTIR spectrum of polymer VII_g shows characteristic absorption bands for the imide ring at 1781 and 1727 (asymmetrical and symmetrical C=O stretching vibrations), 1381 (C—N stretching vibration), 1101, and 727 cm⁻¹ (imide ring deformation). The absorptions of amide groups appear at 3376 (N—H stretch) and 1685 cm⁻¹ (C=O stretch). In addition, the results of the elemental analyses of all the synthesized PAIIs are listed in Table I. The table also shows that the uptake of water/moisture in the polymers is in the range of 1.28–2.90%, which was calculated from the weight change of the polymer samples that were vacuum dried at 120°C for 5 h after being exposed in air at room temperature for several hours.

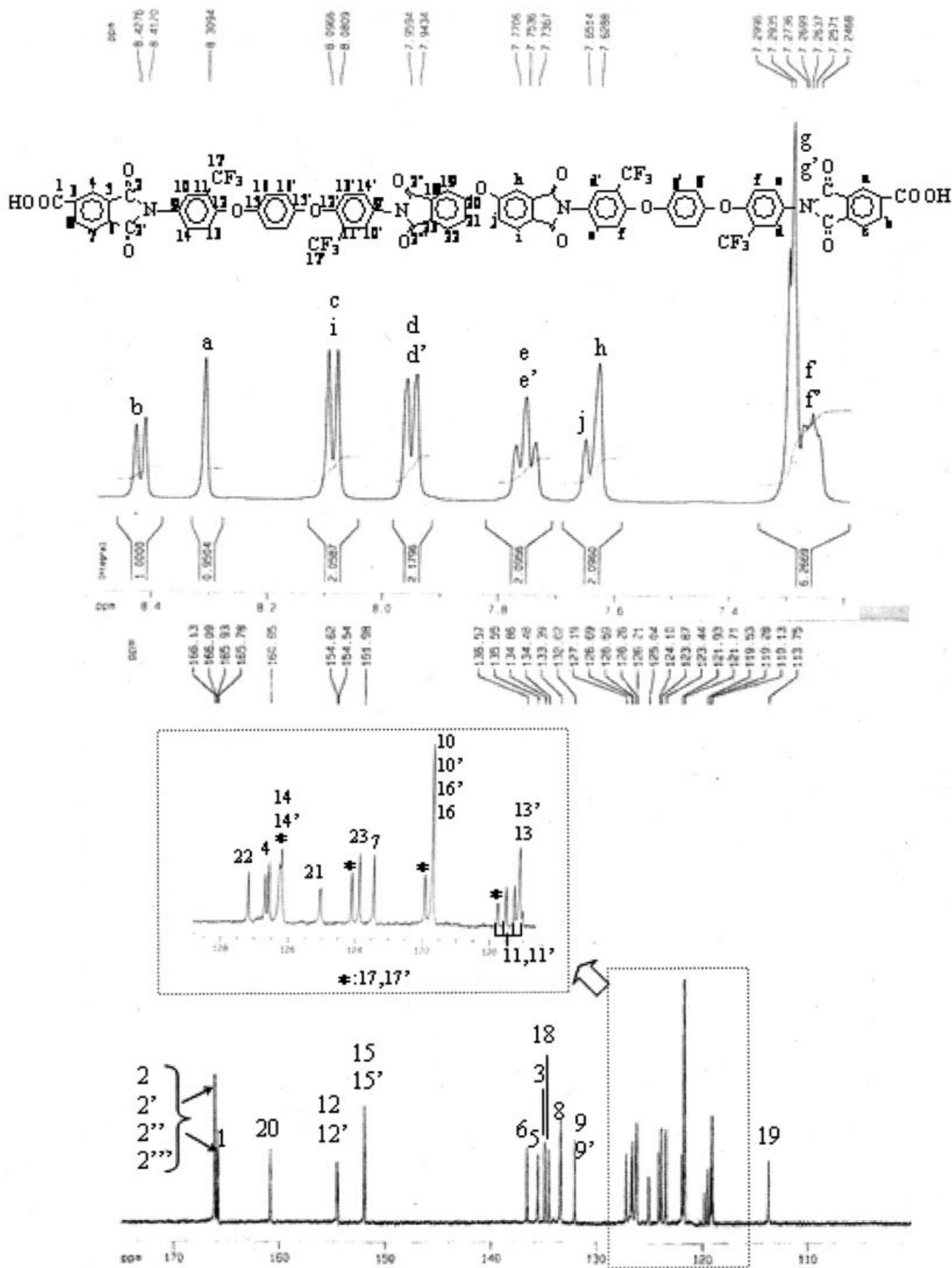
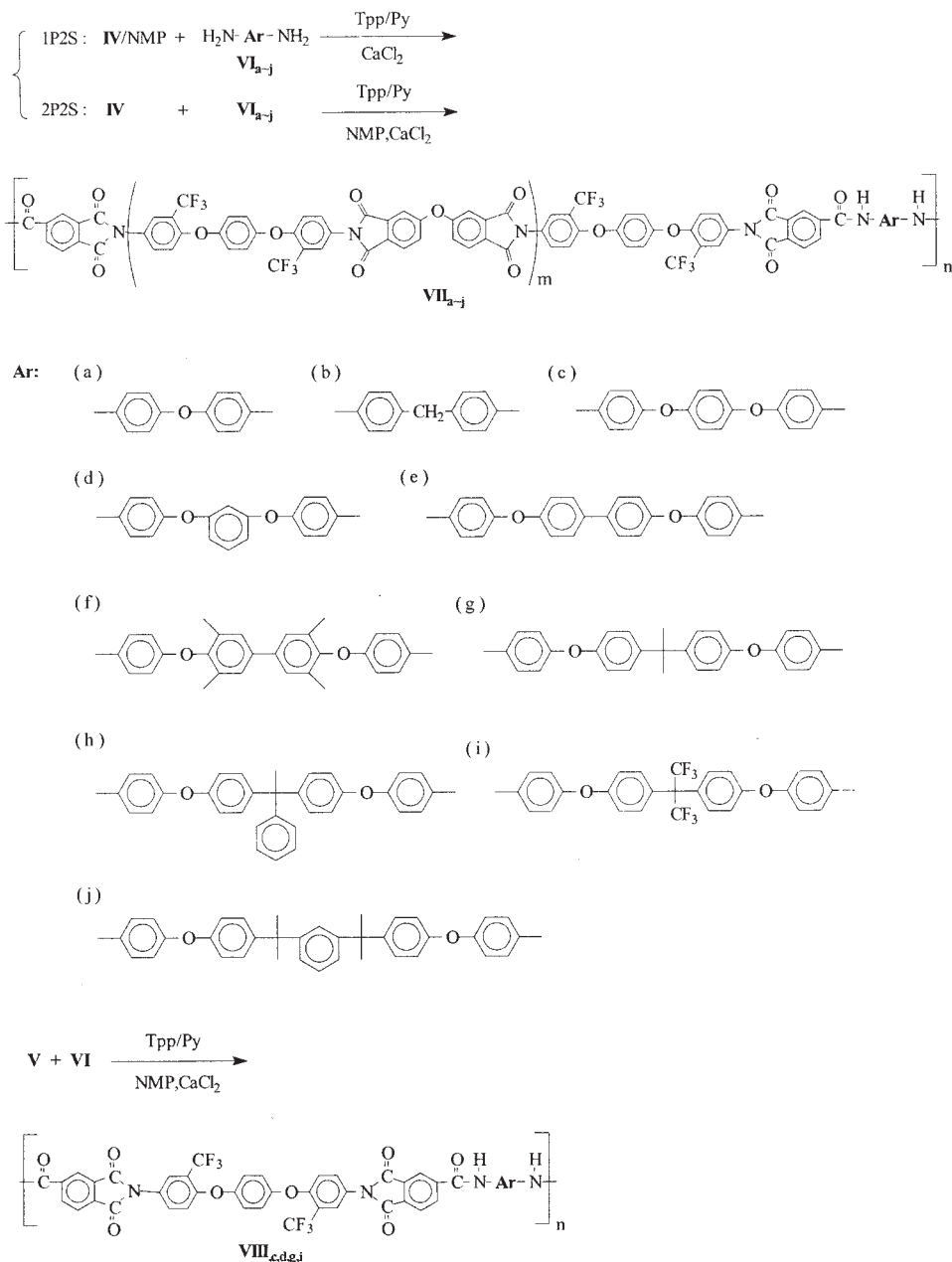


Figure 2 The ¹H and ¹³C spectra of tetramide-diacid (IV) in DMSO-d₆.



Scheme 2 The two routes for the synthesis of a series of poly(amide-imide-imide)s used in this study, which are based on the Yamazaki method.³⁹

Properties of PAIIs

Solubility

The solubilities of PAIIs (**VII**_{a-j}) and PAIs (**VIII**_{c,d,g,i}) in various solvents are listed in Table II. The table shows that the PAIs (**VIII**_c) were soluble in aprotic polar solvents such as NMP, DMAc, and DMF and could be soluble at more than 10% (w/v) at room temperature or slightly above. The PAIIs (**VII**_c) showed better solubility than **VIII**_c and were also soluble in less polar solvents like *m*-cresol or Py. Ex-

cept for **VII**_e, all **VII** series were soluble in most of the solvents tested in this study. The PAIIs (**VII**_e), derived from diamine with a more rigid structure such as **VI**_e, showed lower solubility and were soluble in less polar solvents like *m*-cresol and Py at less than 1% (w/v). Table II shows that PAIIs (**VII**) possess better solubility than PAIs (**VIII**). This may be attributable to the presence of a structurally more flexible ether, bulky trifluoromethyl, and flexible oxydi(phthalimide) substitute groups in **IV**, which disturbs the coplanarity of the aromatic units and thereby reduces the packing order and the crystallinity.

TABLE I
Inherent Viscosity and Elemental Analysis of Poly(amide-imide-imide)s

Polymer	η_{inh}^a (dL/g)	Formula (molecular weight)		Elemental analysis (%) ^b			Moisture uptake (%) ^c
				C	H	N	
VII _a	0.94	(C ₈₆ H ₄₂ O ₁₆ N ₆ F ₁₂) _n (1643.29) _n	Calcd	62.86	2.58	5.11	2.90
			Found	61.04	2.35	5.11	
			Corrected	62.81	2.42	5.26	
VII _b	0.96	(C ₈₇ H ₄₄ O ₁₆ N ₆ F ₁₂) _n (1641.32) _n	Calcd	63.67	2.70	5.12	2.26
			Found	62.23	2.48	4.98	
			Corrected	62.45	2.49	5.00	
VII _c	0.83	(C ₉₂ H ₄₆ O ₁₇ N ₆ F ₁₂) _n (1735.39) _n	Calcd	63.68	2.67	4.84	2.50
			Found	62.09	2.47	4.93	
			Corrected	63.64	2.53	5.05	
VII _d	0.77	(C ₉₂ H ₄₆ O ₁₇ N ₆ F ₁₂) _n (1735.39) _n	Calcd	63.68	2.67	4.84	2.56
			Found	62.05	2.54	4.70	
			Corrected	63.64	2.61	4.82	
VII _e	0.72	(C ₉₈ H ₅₀ O ₁₇ N ₆ F ₁₂) _n (1811.49) _n	Calcd	64.98	2.78	4.64	2.62
			Found	63.28	2.53	4.49	
			Corrected	64.94	2.60	4.61	
VII _f	0.83	(C ₁₀₂ H ₅₈ O ₁₇ N ₆ F ₁₂) _n (1867.59) _n	Calcd	65.60	3.13	4.50	2.67
			Found	63.85	2.88	4.33	
			Corrected	65.55	2.96	4.45	
VII _g	0.85	(C ₁₀₁ H ₅₆ O ₁₇ N ₆ F ₁₂) _n (1853.57) _n	Calcd	65.45	3.05	4.53	1.93
			Found	64.19	2.82	4.56	
			Corrected	65.43	2.87	4.65	
VII _h	0.78	(C ₁₀₆ H ₄₈ O ₁₇ N ₆ F ₁₂) _n (1905.56) _n	Calcd	66.81	2.54	4.41	2.74
			Found	64.98	2.80	4.27	
			Corrected	66.76	2.88	4.39	
VII _i	0.83	(C ₁₀₁ H ₅₀ O ₁₇ N ₆ F ₁₈) _n (1961.51) _n	Calcd	61.85	2.57	4.28	1.28
			Found	61.06	2.41	4.14	
			Corrected	61.84	2.44	4.19	
VII _i	0.86	(C ₁₁₀ H ₆₆ O ₁₇ N ₆ F ₁₂) _n (1971.74) _n	Calcd	67.01	3.37	4.26	2.84
			Found	65.11	3.11	4.10	
			Corrected	66.96	3.20	4.22	

^a Polymerization was carried out with 1.0 mmol of each monomer, 0.12 g CaCl₂, 0.6 mL of triphenyl phosphite, and 1.2 mL of pyridine in NMP (initial 4 mL slowly added 2–4 mL) at 100°C for 3 h; measured at 30°C with a concentration of 0.5 g/dL in DMAc.

^b For C and N: corrected value = found value × (100% + moisture uptake %). For H: corrected value = found value × (100% - moisture uptake %).

^c Moisture uptake (%) = (W - W₀)/W₀ × 100%; W, weight of polymer sample after standing at room temperature; W₀, weight of polymer sample after dried in a vacuum at 100°C for 10 h.

Tensile properties

All synthesized PAIIs (VII_{a-j}) were readily cast into transparent and flexible films from polymer solutions of DMAc. The polymers all possessed good tensile properties with hard, strong, and tough characters. The results are summarized in Table III. The table shows that these films have yield strengths of 106–124 MPa, tensile strengths of 99–125 MPa, elongations at break of 12–19%, and tensile moduli of 1.6–2.4 GPa. The tensile strengths are ranked in the order of VII_c > VII_d, and the polymers with parasubstituted phenylene are better than those with the metasubstituted one. Two useful pieces of information can be obtained from the DMA: the storage modulus (*E'*) and tan δ . The dynamic mechanical behaviors of the polymer films are shown in Table IV and Figure 3. Similar experimental results were found for PAII (VII) and PAI (VIII), which might be due the simultaneous pres-

ence of the flexible ether and rigid imide groups in VII. The effects on the structures by both the flexible ether and rigid imide groups in the main chains are thus nullified for the tensile properties.

Thermal properties

The thermal properties of the polymer were evaluated by TGA and DSC. The thermal behavior data of all polymers are listed in Table V. Rapid cooling from 400°C to room temperature produced predominantly amorphous samples, so the *T_g* values of all the polymers could be easily identified in the DSC traces. The values for the VII polymers were in the range of 236–276°C, depending on the structure of the diamine component and chain flexibility and steric hindrance of the polymer backbones. For example, CF₃ has greater polarity than CH₃, and the CF₃-containing VII_i

TABLE II
Solubility Behavior of Poly(amide-imide-imide)s and Poly(amide-imide)s

Polymers	Solvents									
	NMP	DMAC	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH ₂ Cl ₂	Acetone
VII _a	+++	+++	+++	+++	++	+++	++	+++	-	-
VII _b	+++	+++	+++	+++	+++	+++	+++	+++	-	-
VII _c	+++	+++	+++	+++	+++	+++	+++	+++	-	-
VII _d	+++	+++	+++	+++	+++	+++	+++	+++	-	-
VII _e	+++	+++	+++	+++	+	++	+	+	-	-
VII _f	+++	+++	+++	+++	++	+++	++	+++	-	-
VII _g	+++	+++	+++	+++	+++	+++	+++	+++	-	-
VII _h	+++	+++	+++	+++	+++	+++	+++	+++	-	-
VII _i	+++	+++	+++	+++	+++	+++	+++	+++	-	-
VII _j	+++	+++	+++	+++	++	+++	++	+++	-	-
VIII _c	+++	+++	+++	+	+	+	-	-	-	-
VIII _d	++	+++	+++	+	+	+	+	-	-	-
VIII _g	+++	+++	+++	+++	+	+	+	-	-	-
VIII _i	+++	+++	+++	+++	+	++	+	++	-	-

Solubility: +++, soluble at 10% (w/v); ++, soluble at 5% (w/v); +, soluble at 1% (w/v); +-, partial soluble on heating; S, swelling (1%) on heating; -, insoluble on heating; NMP, *N*-methyl-2-pyrrolidone; DMAC, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; Py, pyridine; THF, tetrahydrofuran.

revealed a higher T_g than the CH₃-containing VII_g. In general, incorporation of less symmetric *m*-phenylene units leads to a decrease in the T_g . Compounds VII_c and VII_d contain triphenylene and diether groups, and VII_c has a higher T_g value because the structure of its parasubstituted phenylene ring is more rigid. In comparison, the T_g values taken from the DSC data were higher than those from tan δ by DMA.

Figure 4 illustrates typical TGA curves of PAII (VII) and PAI (VIII). The thermal stability of VII is obviously better than that of VIII in both nitrogen and air as a result of the higher proportion of the thermostable imide group in the main chain. The TGA results show that the temperatures at 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from the original thermo-

grams, and these are tabulated in Table V. The T_{10} of the PAIIs (VII) stays in the range of 504–559°C in nitrogen and 499–544°C in air, and the char yield of all PAIIs at 800°C are in the range of 54–58%. A comparison of diamines shows that the T_{10} of the *p*-phenylene-containing VII_c is higher than that of *m*-phenylene-containing VII_d. This might be attributable to the stiffer structure leading to a higher packing order for the polymer chains. In addition, the fluorine-containing VII_i PAIIs possess better thermal stability than their nonfluoro analogous VII_g because the C—F bond in the CF₃ group is stronger than that in the CH₃ group.

CONCLUSIONS

The new monomer TIDA (IV) was first synthesized by starting from ring-opening addition of ODP, TMA,

TABLE III
Tensile Properties of Poly(amide-imide-imide)s (VII) and Poly(amide-imide)s films (VIII)

Polymer	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
VII _a	124	118	16	2.4
VII _b	—	107	15	1.6
VII _c	—	125	12	2.1
VII _d	108	104	12	1.6
VII _e	—	119	12	2.2
VII _f	106	104	14	2.0
VII _g	116	103	19	2.3
VII _h	—	109	12	1.7
VII _i	—	116	12	2.3
VII _j	121	99	13	1.9
VIII _c	116	110	15	2.6
VIII _d	108	105	11	2.6
VIII _g	108	107	13	2.3
VIII _i	—	110	17	2.4

TABLE IV
Dynamic Storage and Loss Moduli of Poly(amide-imide-imide)s (VII) and poly(amide-imide)s (V)

Polymer	Storage modulus (GPa)					
	40°C	100°C	150°C	200°C	250°C	300°C
VII _a	1.83	1.15	0.99	0.91	0.04	—
VII _b	1.81	1.29	1.08	0.91	0.03	—
VII _c	1.79	1.48	1.26	1.12	0.01	—
VII _d	2.49	2.29	2.29	1.79	0.01	—
VII _e	1.02	0.79	0.69	0.66	0.66	0.02
VII _f	1.02	0.83	0.75	0.72	0.95	0.01
VII _g	1.87	1.32	1.13	0.96	0.01	—
VII _h	2.66	2.34	1.96	1.47	0.01	—
VII _i	1.16	0.93	0.82	0.70	0.01	—
VII _j	2.60	2.12	1.44	1.12	0.01	—
VIII _c	2.66	2.25	1.97	1.23	0.01	—
VIII _d	1.65	1.13	0.94	0.87	0.01	—
VIII _g	2.07	1.62	1.09	0.82	0.01	—
VIII _i	2.14	1.71	1.22	0.91	0.01	—

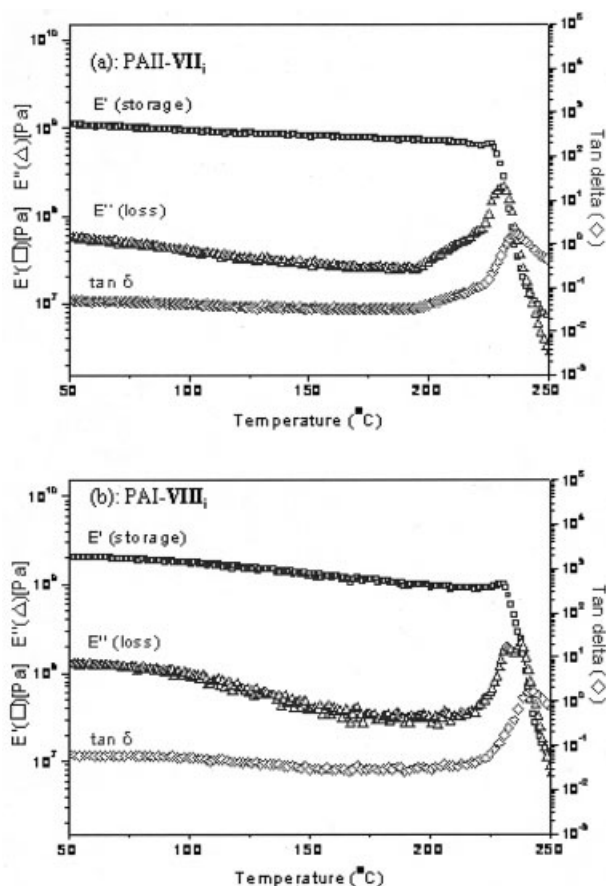


Figure 3 DMA curves for VII_i and VIII_i at a heating rate of 3°C/min.

TABLE V
Thermal Behavior Data of Poly(amide-imide)s (VII) and Polyamide (VIII)

Polymer	T_g (°C)		T_{10}^c (°C)		Char yield ^d (%)
	DSC ^a	DMA ^b (tan δ)	In N ₂	In air	
VII _a	253	250	559	540	56
VII _b	261	247	542	529	57
VII _c	246	242	554	544	55
VII _d	243	233	537	531	56
VII _e	255	244	549	533	58
VII _f	276	267	504	499	55
VII _g	241	238	535	527	57
VII _h	236	233	535	526	58
VII _i	245	237	546	535	54
VII _j	254	217	547	527	55
VIII _c	278	232	530	526	61
VIII _d	256	239	533	525	59
VIII _g	257	241	526	496	55
VIII _i	255	242	527	527	45

^a Baseline shift in the second heating DSC traces, with a heating rate of 15°C/min.

^b The glass-transition temperatures were measured at the peak tops of tan δ .

^c Temperatures at which 10% weight loss was recorded by TG at a heating rate of 20°C/min.

^d Residual weight (%) when heated to 800°C in nitrogen.

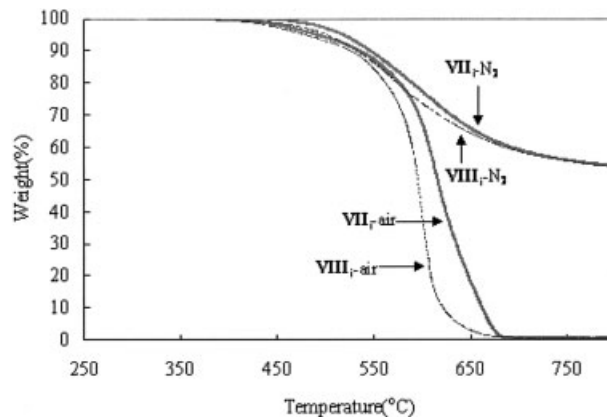


Figure 4 TGA curves for VII_i and VIII_i at a heating rate of 20°C/min.

and BAFFB with a 1:2:2 molar ratio in NMP. From TIDA and various conventional aromatic diamines, a series of novel PAIIs with alternating sets of four imide and two amide groups were synthesized, which are unlike the traditional diimide-diamide or imide-amide PAIs. Detailed tests of the solubility in various solvents and characterization of the physical/mechanical properties and thermal stability were performed. These newly synthesized PAII polymers showed better solubility in a variety of amide-type solvents and even in less polar solvents. In addition, these polymers also maintained and exhibited good film-forming ability, a wide temperature gap between T_g and the decomposition temperature, excellent thermal stability, and good mechanical properties. In summary, these new polymers demonstrated a good combination of mechanical properties and solution-aided processability for applications that demand easy film forming with excellent thermal and mechanical performance.

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