

Synthesis and Characterization of Two Polytrimellitimide Series With Different Segment Order by Direct Polycondensation

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ABSTRACT: Poly(amide-imide) (PAI) could be synthesized in regular segment order from trimellitic anhydride (TMA) and various aromatic diamines. By different processes, PAI_{h-h-t-t} containing alternating (amide-amide)-(imide-imide) sequences and PAI_{h-t} containing amide-imide sequences could be obtained through direct polycondensation. Comparison of PAI_{h-h-t-t} and PAI_{h-t}, which had different sequence orders and were prepared from TMA and 12 diamines, showed that the latter had better solubility and needed less quantity of solvent and salt (CaCl₂) during polymerization, but both two series PAI using *p*-substituted diamines (e.g., *p*-phenylenediamine) showed poor solubility. Series PAI_{h-h-t-t} possessed larger initial modulus but smaller elongation at break than series PAI_{h-t}. For the thermal properties, most of series PAI_{h-t} had glass transition temperatures higher than corresponding series PAI_{h-h-t-t}, but these two series were similar in the 10% weight loss temperatures and the char yields at 800°C in nitrogen. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1556–1567, 2001

Key words: polytrimellitimide; regular segment order; polycondensation

INTRODUCTION

Aromatic polyamides (PA), a kind of polymer material with superior mechanical strength, are synthesized from aromatic diamines and aromatic dicarboxylic acids. For example, both Kevlar and Nomex have excellent high-temperature resistance and mechanical properties. Because of their intermolecular hydrogen bonds, most PA have good solubility in polar amide solvents and are widely used for a variety of applications.^{1–5} Aromatic polyimides (PI) are polymers resistant to high temperature that are noted for their excel-

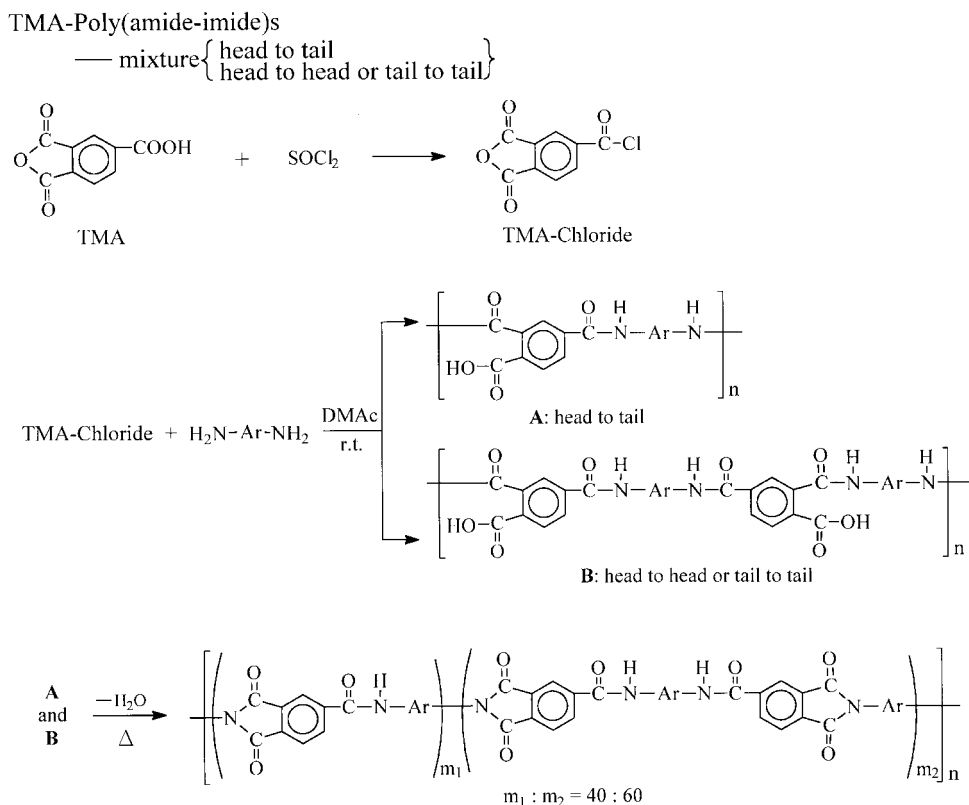
lent physical and electrical/insulating properties.^{1,2} PI are difficult to process because of their high softening or melting temperatures and their insoluble nature. To overcome this drawback, several copolymers have been developed,^{6–12} among them poly(amide-imide) (PAI), whose amide groups can improve the solubility.

PAI can be synthesized by polycondensation from various monomers containing anhydride, carboxylic acid, or aromatic amino groups. To synthesize PAI, one can usually use dicarboxylic acid, dianhydride, diamine, amino acid, or anhydride acid, among which trimellitic anhydride (TMA) is a commercially available aromatic anhydride. TMA and diisocyanate or diamine can produce PAI. Because of the low reactivity of aromatic amine to an aromatic carboxylic acid at room temperature, TMA has to be reacted to form 4-chloroformyl phthalic anhydride (TMA chloride),^{13,14}

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Scheme 1 Preparation of poly(amide-imide) (PAI_{mix} type).

although this approach is costly. Industries generally produce resins from diisocyanate and TMA¹⁵⁻¹⁷ at lower cost, but are both limited in the varieties of polymers from synthesizing and low in inherent viscosities.¹⁸

Trimellitimides (TMA-type PAI) are high-performance polymers with excellent thermal stability and processability.¹⁹ Two cases may arise simultaneously when the polymerization is carried out by the addition of TMA chloride to diamine, as shown in scheme 1. One is that the acid chloride groups of TMA chloride react with the two ends of diamines; the remaining diamines then react with anhydride groups. The resulting polymers have head-to-head and tail-to-tail structures (PAI_{h-h-t-t}), that is, amide-amide and imide-imide sequences (A-A-I-I). The other is that the polycondensation from both acid chloride and anhydride groups of TMA chloride occurs simultaneously with diamines. The resulting polymers have head-to-tail structures (PAI_{h-t}), that is, amide-imide sequences (A-I). PAI formed by the latter process are random copolymers incorporating A-A-I-I and A-I sequences and have A-I/A-A-I-I units at a ratio of 40/60 in the main-chain.^{18,20}

A successful method starting from TMA to synthesize PAI is initiated at our laboratory. The method involves using 2 mole TMA and 1 mole aromatic diamine, to prepare an imide ring-preformed dicarboxylic acid, which is then reacted with aromatic diamine to synthesize PAI containing A-A-I-I sequences by direct polycondensation with triphenyl phosphite and pyridine as condensing agents.²¹⁻⁴¹ Recently, we attempted to synthesize PAI containing A-I sequences from aromatic diamines and equivalent TMA by direct polycondensation. In this study, we prepared two series of PAI possessing regular A-A-I-I or A-I sequences using the above-described method, with each polymer containing one kind of aromatic diamine. The differences in solubility, crystallinity, mechanical properties, and thermal behaviors of these two series PAI were investigated.

EXPERIMENTAL

Materials

p-Phenylenediamine (I_a, from TCI) and *m*-phenylenediamine (I_b, from TCI) were distilled under

vacuum before use. The other diamines, such as 2,4-diaminotoluene (I_c , from TCI), 4,4'-diaminodiphenyl methane (I_d , from TCI), 4,4'-oxydianiline (I_e , from TCI), 3,4'-oxydianiline (I_f , from TCI), 1,4-bis(4-aminophenoxy)benzene (I_g , from TCI), 1,3-bis(4-aminophenoxy)benzene (I_h , from Chriskev), 1,2-bis(4-aminophenoxy)benzene (I_i , from Chriskev), bis[4-(4-aminophenoxy)phenyl]ether (I_j , from Chriskev), 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (I_k , from Chriskev), and 2,2'-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (I_l , from Chriskev), were used as received. Commercially available anhydrous calcium chloride ($CaCl_2$) was dried under reduced pressure at 150°C for 6 h before use. Trimellitic anhydride (TMA; from Wako) and triphenyl phosphite (TPP; from TCI) were used without purification. *N*-Methyl-2-pyrrolidone (NMP; from Fluka), *N,N*-dimethylacetamide (DMAc; from Fluka), *N,N*-dimethylformamide (DMF; from Fluka), and pyridine (Py; from Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Synthesis of Diimide–Dicarboxylic Acids (II_a – II_l)

In previous reports from our laboratory,^{42–44} diimide–dicarboxylic acids were synthesized as follows. A mixture of 1 mole diamine and 2 mole TMA was dissolved in DMAc or NMP before toluene was added; diimide–dicarboxylic acid could then be obtained after water was distilled off azeotropically.

As an example of II_d , a mixture of 5.95 g (0.03 mol) of diamine I_d and 11.5 g (0.06 mol) of TMA was dissolved in 50 mL of dry DMF at 40°C. About 20 mL of toluene was then added, and the mixture was heated with reflux for 4 h until about 1.1 mL of water was distilled off azeotropically. The residual toluene was then distilled off under reduced pressure. After cooling, the yellow precipitate was collected by filtration and recrystallized from DMF and was then dried in vacuum to product 15.02 g of diimide–dicarboxylic acid II_d (yield, 91.6%; melting point, 372°C).

IR (KBr): 3500–2500 (carboxyl—OH), 1778, 1722 (imide C=O), 1099 and 729 cm^{-1} (imide ring C—N).

¹H-NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 8.41 (*d*, $H_b + H_{b'}$, 2H), 8.30 (*s*, $H_c + H_{c'}$, 2H), 8.08 (*d*, $H_a + H_{a'}$, 2H), 7.45 (two overlapped AB doublets, $H_d + H_{d'}$, 4H), 7.40 (two overlapped AB doublets, $H_e + H_{e'}$, 4H), 4.10 (*s*, H_f , 2H).

Other dicarboxylic acids II_{a-1} were prepared according to the methods reported,^{42–44} and the results of the preparation were as shown in Table I.

Polycondensation of Polymer

Poly(Amide–Imide) III

Taking III_d as an example, a mixture of 0.198 g (1.00 mmol) of diamine I_d , 0.546 g (1.00 mmol) of diimide–diacid II_d , 0.30 g of $CaCl_2$, 0.6 mL of TPP, 0.8 mL of Py and 3.0 mL of NMP was heated while being stirred at 100°C under nitrogen for 3 h. The viscosity of reaction solution increased after 1 h, and an additional volume of 1 mL of NMP was added to the reaction mixture. At the end of the reaction, the viscous solution was trickled into stirring methanol to obtain a stringy precipitate, which was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100°C. The quantitative product was 0.73 g. The inherent viscosity of the polymer was 0.77 dL g^{-1} , measured at a concentration of 0.5 g dL^{-1} in DMAc at 30°C. Other polymers III_{a-1} were prepared in an analogous manner.

IR (film): 3359 (amide group N—H), 1778, 1720 (imide C=O), 1672 (amide C=O), 1601 (amide N—H), 1092, and 727 cm^{-1} (imide ring C—N).

¹H-NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 10.57 (*s*, amide group N—H, 2H), 8.52 (*s*, $H_c + H_{c'}$, 2H), 8.43 (*d*, $H_b + H_{b'}$, 2H), 8.09 (*d*, $H_a + H_{a'}$, 2H), 7.74 (two overlapped AB doublets, $H_g + H_{g'}$, 4H), 7.43 (*s*, $H_d + H_{d'}$ + $H_e + H_{e'}$, 8H), 7.24 (two overlapped AB doublets, $H_h + H_{h'}$, 4H), 4.10 (*s*, H_f , 2H), 3.92 (*s*, H_i , 2H).

Poly(Amide–Imide) V

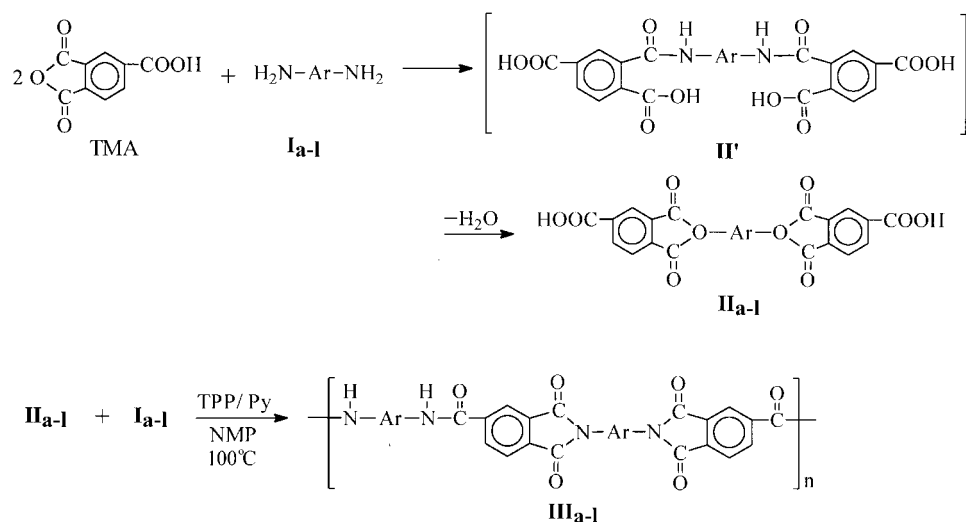
As an example of V_d , 1.983 g (10 mmol) of diamine I_d was dissolved in 18 mL of NMP; 1.920 g (10 mmol) of TMA was then added with stirring at room temperature. After 30 min, 10 mL of toluene

Table I Dicarboxylic Acids

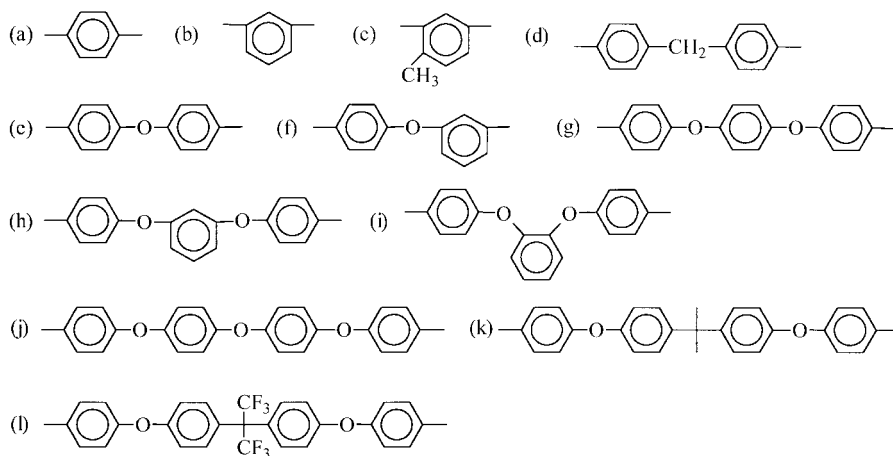
Diimide-Dicarboxylic Acid	Yield (%)	Melting Point (°C)
II_a	98.0	473.5
II_b	97.0	412.2
II_c	100.0	371.0
II_d	91.6	372.0
II_e	95.0	392.9
II_f	94.0	357.2
II_g	90.0	399.0
II_h	99.0	350.0
II_i	100.0	344.7
II_j	95.5	351.0
II_k	95.4	329.0
II_l	90.0	338.0

TMA-Poly(amide-imide)s

— {head to head or tail to tail}



Ar :

**Scheme 2** Preparation of poly(amide-imide) (PAI_{h-h-t-t} type).

was added, and the mixture was heated at 130–140°C under nitrogen for 3 h, until the toluene was distilled off. A part of the resulting solution was poured into methanol. The precipitated compound IV_d was filtered, washed with hot methanol, and dried under vacuum. The structure of IV_d was confirmed by IR and ¹H-NMR spectroscopy. The rest of the resulting solution was cooled to 100°C; 4.0 mL of Py, 1.60 g of CaCl₂, and 3.2 mL of TPP was then added to the mixture with stirring at this temperature. An additional 6 mL of NMP was added as the solution became too viscous such that the magnetic stirrer could no longer work. After 3 h of stirring, the obtained solution was poured into methanol to produce the stringy polymer. After immersing in methanol

overnight, the stringy polymer was washed thoroughly with hot water and immersed in hot water for 2 h; it was then collected by filtration and dried. The quantitative product was 3.54 g. The inherent viscosity of the polymer was 0.94 dL g⁻¹, measured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C. Other polymers V_{a-1} were prepared in an analogous manner.

IR (film): 3363 (amide group N—H), 1778, 1722 (imide C=O), 1672 (amide C=O), 1601 (amide N—H), 1093, and 725 cm⁻¹ (imide ring C—N).

¹H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 10.59 (*d*, amide group N—H, 3H), 8.51 (*s*, H_c + H_{c'} + H_{c''}, 3H), 8.42 (*s*, H_b + H_{b'} + H_{b''}, 3H), 8.08 (*s*, H_a + H_{a'} + H_{a''}, 3H), 7.78 (*d*, H_n, 2H), 7.74 (*s*, H_g + H_{g'}, 4H), 7.43 (*s*, H_d + H_{d'} + H_e

+ H_{e'}, 8H), 7.39 (s, H_j + H_k, 4H), 7.29 (s, H_m, 2H), 7.24 (d, H_h + H_{h'}, 4H), 4.10 (s, H_f, 2H), 4.01 (s, H_i, 2H), 3.92 (s, H_i, 2H).

Characterization

¹H-NMR spectrum was recorded on a JEOL EX-400 nuclear magnetic resonance (NMR) spectrometer operated at 30°C with DMSO-*d*₆ as the solvent. The inherent viscosities were measured with a Cannon–Fenske viscometer at 30°C. IR spectra were recorded on a Horiba Fourier transform infrared spectrometer FTIR-720. Differential scanning calorimeter (DSC) traces were measured on TA Instrument DSC 2010 at a rate of 15°C min⁻¹ in flowing nitrogen (40 cm³ min⁻¹). Thermogravimetry analysis (TGA) was conducted with a TA Instrument TGA 2050. 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. Wide-angle X-ray measurements were performed on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer by means of Ni-filtered Cu-*K*_α radiation (40 kV, 15 mA) at a scanning rate of 4° min⁻¹. Mechanical properties were measured by Instron Universal Tester model 1130 with a load cell of 5 kg, and a strain rate of 5 cm min⁻¹ was 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 used.

RESULTS AND DISCUSSION

Polymer Synthesis

The synthesis of PAI with regular head-to-head and tail-to-tail sequences (series III) was first processed by the ring-opening addition of 1 mole aromatic diamines I_{a-1} and 2 mole TMA to form diamide–tetracid II' in DMF solvent at room temperature, followed by cyclodehydration to the diimide–dicarboxylic acids II_{a-1} by means of toluene–water azeotropic distillation. Then 1 mole the same diamines was added to prepare PAI_{h-h-t-t} III_{a-1} by the polycondensation method using TPP as condensing agent,⁴⁵ as shown in scheme 2. As the results showed in the Experimental section, these diimide–diacids and polymers could be synthesized with high yield. The chemical structures of the diimide–dicarboxylic acids II_{a-1} and PAI_{h-h-t-t} III_{a-1} were confirmed by ¹H-NMR spectroscopy; the results were in good agreement with the designed compounds.

Taking diacid II_d and PAI_{h-h-t-t} III_d as examples, the diimide–dicarboxylic acid II_d was confirmed by ¹H-NMR spectrum (Fig. 1), and the absorptions of H_{a-e} and H_{a'-e'} appeared almost at the same shift positions because of the symmetric structure. The 10 peaks of protons in the ¹H-NMR spectrum of II_d were in agreement with the predictive values. The PAI_{h-h-t-t} III_d was also confirmed by ¹H-NMR spectrum (Fig. 2). Comparing the ¹H-NMR spectrum of III_d with that of II_d, the

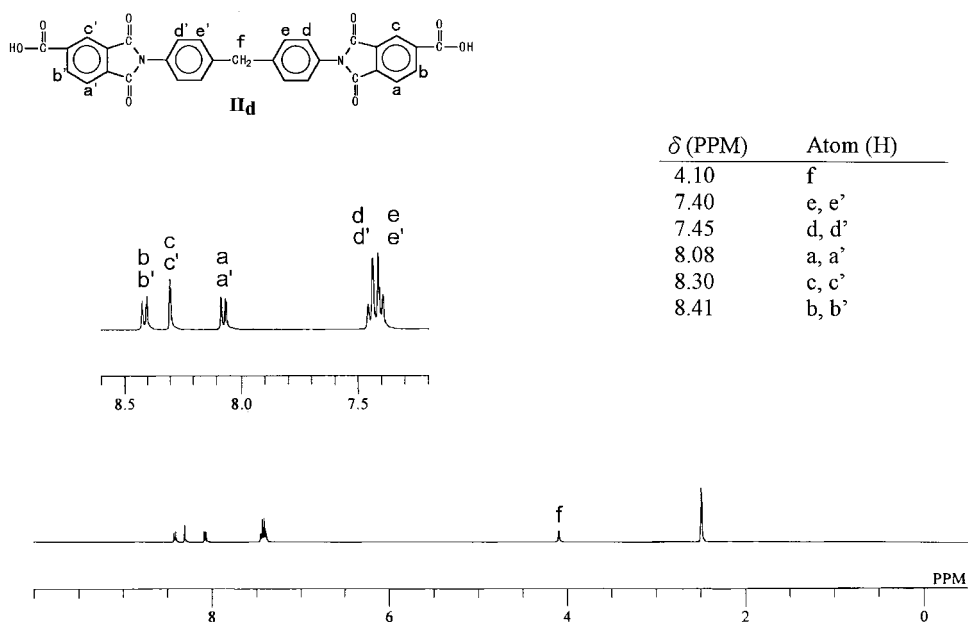


Figure 1 ¹H-NMR spectrum of diimide–diacid II_d in DMSO-*d*₆.

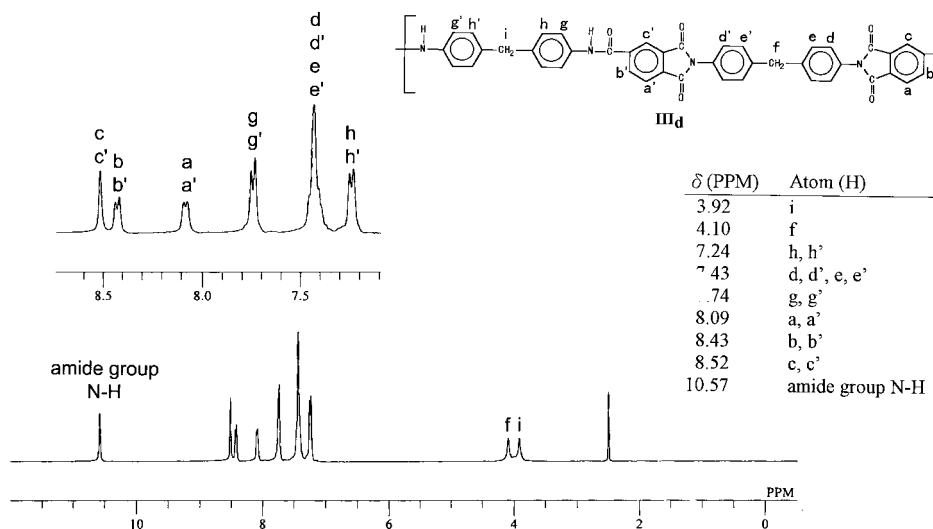
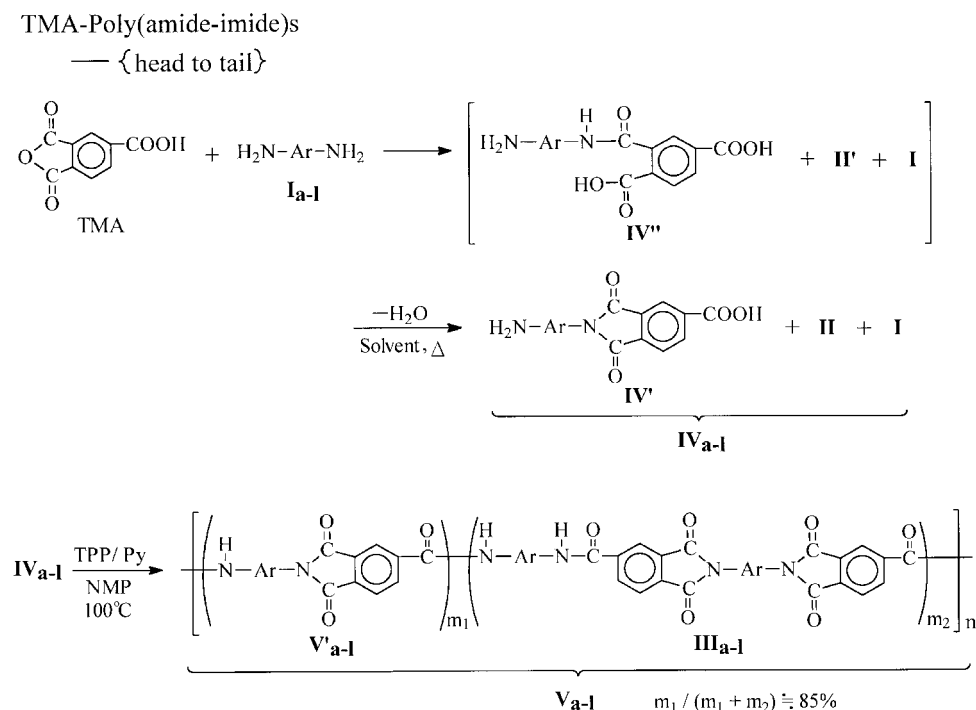


Figure 2 $^1\text{H-NMR}$ spectrum of $\text{PAI}_{\text{h-h-t-t}}$ III_d in $\text{DMSO-}d_6$.

appearance of the proton-shift position of amide group at 10.57 ppm showed that the amide group has been formed successfully from the carboxylic acid group of II_d with the amine group of I_d . The absorptions of $\text{H}_{\text{a-e}}$ and $\text{H}_{\text{a'-e'}}$ or that of $\text{H}_{\text{g,h}}$ and $\text{H}_{\text{g',h'}}$ appeared almost at the same shift positions in Figure 2, as described in the II_d $^1\text{H-NMR}$ spectrum. Both proton ratios of $-\text{CH}_2-$ group (H_f to H_i) and of phenylene group ($\text{H}_{\text{d+d'+e+e'}}$ to

$\text{H}_{\text{g+g'+h+h'}}$) are about 1 : 1, showing that III_d was an alternating PAI [$\text{PAI}_{\text{h-h-t-t}}$] having head-to-head and tail-to-tail structure, that is, amide-amide and imide-imide sequence with an equal ratio.

Similar to series III, synthesis of PAI with regular head-to-tail sequences (series V) was first processed by the ring-opening addition of 1 mole aromatic diamines ($\text{I}_{\text{a-1}}$) and 1 mole TMA to form



Scheme 3 Preparation of poly(amide-imide) ($\text{PAI}_{\text{h-t}}$ type).

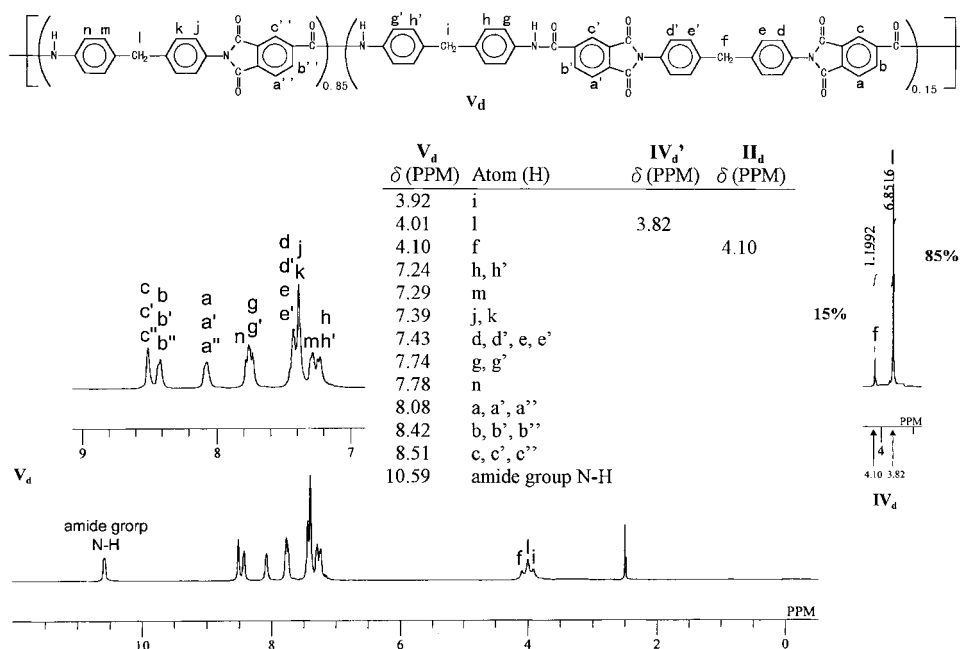


Figure 3 $^1\text{H-NMR}$ spectrum of IV_d and $PAI_{h-t} V_d$ in $\text{DMSO-}d_6$.

amine–amide–dicarboxylic acids in NMP, followed by cyclodehydration to the imide–amino carboxylic acids (IV_{a-1}). TPP was then added as a condensing agent to prepare $PAI_{h-t} V_{a-1}$ by direct polycondensation, as shown in scheme 3. The chemical structures of IV_{a-1} and series V were confirmed by the $^1\text{H-NMR}$ spectrum. Taking IV_d and $PAI_{h-t} V_d$ as examples (Fig. 3), the appearance of the proton-shift positions for methylene group of IV_d at 4.10 (H_f in imide–imide moiety, II_d) and 3.82 ppm (H_l in imide–amine moiety, IV'_d) showed that the imide–amino carboxylic acid IV_d was a mixed monomer containing II_d and IV'_d . From the integration ratio of protons (H_f , H_l), about 85% [$6.8516/(1.1992 + 6.8516) \approx 85\%$] of IV_d was the structure of IV'_d . $PAI_{h-t} V_d$ was also confirmed by the NMR spectrum, and the appearance for methylene group (H_f , H_l , H_i) at 4.10, 4.01, and 3.92 ppm demonstrated that the $PAI V_d$ contained some moieties of $PAI_{h-h-t-t} III_d$ which had two proton-shift positions for the methylene group (H_f , H_l) at 4.10 and 3.92 ppm, separately. From the integration ratio of IV_d (H_f : H_l = 85% : 15%), $PAI V_d$ should contain about 85% moieties with a V'_d sequence.

Although the $PAI_{h-t} V$ synthesized in this study is unable to reach complete head-to-tail sequences, 85% is better than the passed result^{18,20} that PAI prepared from TMA chloride. When TMA chloride, which contains acid chloride and anhydride groups, reacts with diamine by low-

temperature polycondensation (scheme 1), head-to-tail structure and (head-to-head)–(tail-to-tail) structure are formed simultaneously in the poly-

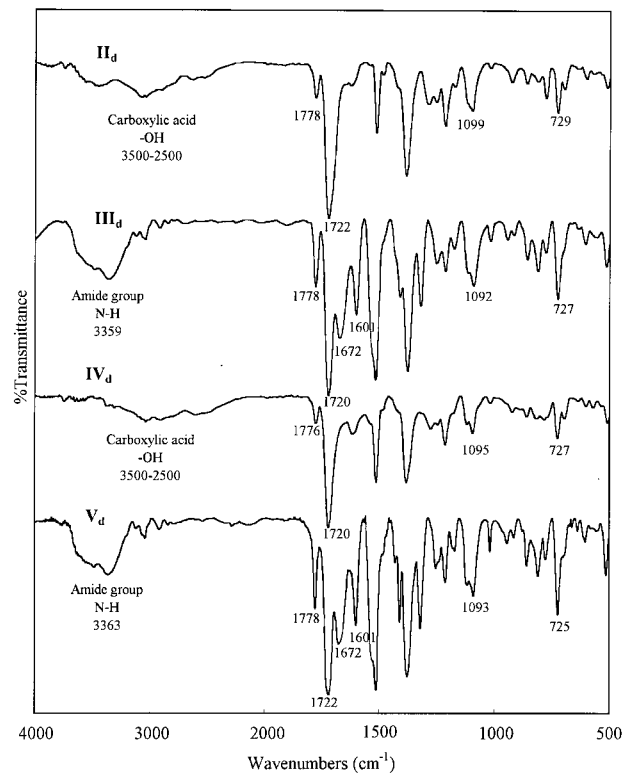


Figure 4 FTIR spectra of II_d , IV_d , $PAI_{h-h-t-t} III_d$, and $PAI_{h-t} V_d$.

Table II Preparation of Poly(Amide-Imide)

Polymer	Each Monomer (mmol)	Reaction Condition					Polymer	
		Initial NMP (mL)	CaCl ₂ (g)	Py (mL)	TPP (mL)	Additional NMP (mL)	η_{inh}^a (dL g ⁻¹)	Appearance
Head-to-head and tail-to-tail type								
III _a	0.5	4.0	0.45	1.0	0.4	—	0.38 ^b	Powder
III _b	0.9	4.4	0.32	1.0	0.6	—	1.00	Stringy
III _c	1.0	3.0	0.24	0.7	0.6	—	0.65	Stringy
III _d	1.0	3.0	0.30	0.8	0.6	1.0	0.77	Stringy
III _e	0.6	3.5	0.30	0.8	0.4	—	0.72 ^c	Stringy
III _f	1.0	4.0	0.34	1.0	0.8	—	0.81	Stringy
III _g	0.5	4.0	0.45	0.8	0.4	—	0.57 ^b	Powder
III _h	1.0	4.5	0.42	1.0	0.8	—	1.08 ^c	Powder
III _i	1.0	3.5	0.32	0.8	0.6	—	0.67	Powder
III _j	0.5	4.0	0.45	0.8	0.4	—	0.53 ^c	Powder
III _k	1.0	4.5	0.37	1.0	0.6	—	1.28	Stringy
III _l	1.0	4.5	0.32	1.0	0.6	2.0	0.93	Stringy
Head-to-tail type								
V _a	2.4	14.0	0.80	3.0	1.0	—	0.29 ^b	Powder
V _b	10.0	13.0	1.30	3.0	3.2	4.0	0.76	Stringy
V _c	10.0	14.0	1.20	3.0	2.4	—	0.88	Stringy
V _d	10.0	18.0	1.60	4.0	3.2	6.0	0.94	Stringy
V _e	10.0	15.0	1.60	3.0	3.2	5.0	1.17	Stringy
V _f	5.0	8.0	0.80	2.0	1.6	4.0	0.75	Stringy
V _g	3.0	10.0	0.62	2.0	0.9	—	0.82 ^c	Stringy
V _h	5.0	9.0	0.90	2.0	1.6	5.0	0.84	Stringy
V _i	5.0	8.0	0.70	2.0	1.6	3.0	0.76	Stringy
V _j	2.5	5.0	0.42	1.0	0.8	2.0	0.70	Stringy
V _k	5.0	8.0	0.80	2.0	1.6	4.0	0.80	Stringy
V _l	5.0	8.0	0.80	2.0	1.6	4.0	0.84	Stringy

^aMeasured at a polymer concentration of 0.5 g dL⁻¹ in DMAc at 30°C.

^bMeasured at a polymer concentration of 0.5 g dL⁻¹ in H₂SO₄ at 30°C.

^cMeasured at a polymer concentration of 0.5 g dL⁻¹ in DMAc + 5 wt % LiCl at 30°C.

mer chain and the former has a mere mole ratio of 40%. Thus, the method used in this study is a good approach to the preparation of PAI_{h-t}. IR spectroscopy permits monitoring of the monomer or polymer formations of each synthesis. Typical IR spectra are shown in Figure 4, confirming the chemical structures of monomers and polymers.

The polycondensation conditions and results of series III and V are listed in Table II. The reaction condition for the choice of the quantities of solvents and salts (CaCl₂) was to keep the polymers soluble with high concentration during polymerization. Besides III_{a,g,j} and V_{a,g,j}, all the polymers used a considerable quantity of solvents, and series III needed 3–5 mL of NMP and 0.3–0.5 g of CaCl₂ per mmole of each monomer. The monomer of series V needed 1.3–1.8 mL of NMP and 0.12–0.18 g of CaCl₂ per mmole, but additional solvents should be added, as the viscosity of the polymer

solution increased in the later stages of polymerization. The reaction conditions for the two series of PAI were similar as far as weight unit was concerned, but smaller quantities of solvents and salts could be used for series V, so that precipitation would not occur. Because of the insoluble nature of III_{a,g,j} and V_a, powder precipitates of these polymers with low viscosities would be obtained despite the increase of considerable quantities of solvents and salts. The inherent viscosity of III_h could reach 1.08 dL g⁻¹ because it precipitated in the later stages of polymerization. In general, series V had better solubility than series III in the reaction solution, producing stringy precipitates.

Properties of Polymers

The solubilities of two series PAI with regular sequences in organic solvents are shown in Table

Table III Solubility of Poly(Amide-Imide)

Polymer	Solvent							
	DMAc	DMAc + 5% LiCl	NMP	DMF	DMSO	<i>m</i> -Cresol	Py	Conc. H ₂ SO ₄
Head-to-head and tail-to-tail type								
III _a	—	—	—	—	—	—	—	+
III _b	+	+	+	—	—	+h	—	+
III _c	+	+	+	+	+	+	+	+
III _d	+	+	+	+	+	+	—	+
III _e	+	+	+	+	±	—	—	+
III _f	+	+	+	+	+	+	+	+
III _g	—	—	—	—	—	—	—	+
III _h	—	+	+	—	—	—	—	+
III _i	+	+	+	+	+	+	+	+
III _j	±	+	+	—	—	—	—	+
III _k	+	+	+	—	—	—	+	+
III _l	+	+	+	+	+	+	+	+
Head-to-tail type								
V _a	—	±	—	—	—	—	—	+
V _b	+	+	+	—	—	+	—	+
V _c	+	+	+	+	+	+	+	+
V _d	+	+	+	+	+	+	±	+
V _e	+	+	+	+	+	—	—	+
V _f	+	+	+	+	+	+	+	+
V _g	—	+	+	—	—	—	—	+
V _h	+	+	+	+h	+	—	—	+
V _i	+	+	+	+	+	+	+	+
V _j	+	+	+	—	+h	—	—	+
V _k	+	+	+	+	+h	+	+	+
V _l	+	+	+	+	+	+	+	+

DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; Py, pyridine. Measured at a polymer concentration of 0.2 mg mL⁻¹ in 24 h; +, soluble at room temperature; ±, partially soluble; —, insoluble; +h, soluble on heating.

III. Their solubilities varied with different structures of linkage Ar. To compare PAI with the same regular sequence order, PAI with *m*-oriented phenylene ring (e.g., III_{b,f,h} and V_{b,f,h}) had better solubility than that of their isomers with *p*-oriented phenylene ring (e.g., III_{a,e,g} and V_{a,e,g}). Comparing polymers III_d, V_d with polymers III_e, V_e, the latter containing ether structure had poorer solubility. For the polymers with an Ar of triphenylenediether, the solubility of polymers with *o*-substituted phenylene (e.g., III_i and V_i) was superior to those of polymers with *m*-substituted phenylene (e.g., III_h and V_h) or with *p*-substituted phenylene (e.g., III_g and V_g). As described above, PAI synthesized from I_g had the worst solubility among the three isomers, and the results were all the more obvious in series III. Furthermore, for the polymers with Ar of four phenylenes containing the ether linkages (e.g., III_{j-1} and V_{j-1}), the solubility of III_l, V_l with

hexafluoroisopropylidene group was superior to that of III_{j,k} and V_{j,k}. III_k and V_k with the isopropylidene group had better solubility than III_j and V_j with no pendant group.

Comparison of the two series PAI with different regular sequences showed that the PAI containing amide-imide sequences (series V) had slightly higher solubility than that of the PAI containing amide-amide-imide-imide sequences (series III). In fact, PAI V could be dissolved within a short time while testing in various solvents, but PAI III required a longer time to be dissolved. Therefore, although the two series showed the same solubility within 24 h in Table III, series V was more soluble than series III. In the two series, polymers III_{a,g} were insoluble in all testing solvents except conc. H₂SO₄, which may be attributable to their higher crystallinity. The crystallinity of all polymers was measured with the X-ray diffractometer over a range of 2θ

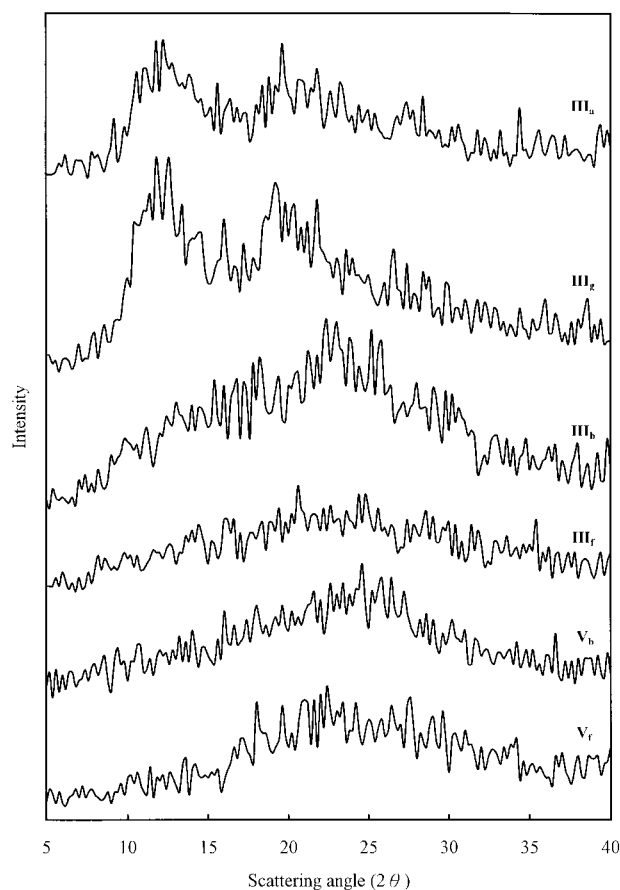


Figure 5 Wide-angle X-ray diffractograms of poly-(amide-imide).

= 5–40°. As shown in Figure 5, III_{a,g} were measured in powder form, and the others were measured in film form cast from DMAc solution. Figure 5 shows that the peak of diffractograms for the two series (as examples of III_{b,f} and V_{b,f}) was weak, indicating that there was no crystallinity in those PAI. By contrast, III_{a,g} in Figure 5 demonstrated semicrystallinity in III_{a,g}, giving them the worst solubility.

Besides the PAI containing diamines I_{a,g-j}, the remaining PAI could be cast into films with transparent and tough properties (~ 0.05 mm thick) in pure DMAc solutions. Mechanical properties of films are listed in Table IV. For series III polymers, the films had yield strength of 63–82 MPa, break strength of 62–106 MPa, elongation at break of 7–17%, and initial modulus of 2.3–3.1 GPa. For series V polymers, the films had strength at a yield of 82–96 MPa, strength at break of 77–109 MPa, elongation at break of 11–65%, and initial modulus of 1.4–2.6 GPa. These results showed that the two series of PAI exhibited good tensile strength. The results showed that the polymers whose diamine monomers lacking the flexible groups, such as III_{b-e} and V_{b-e}, either did not have yield strength or had strength at yield close to strength at break. In general, comparison of series III with series V showed that the former had larger initial modulus and the latter has larger elongation to break; however, the two series PAI had similar strength at yield and break.

Table IV Mechanical Properties of Poly(Amide-Imide) Films*

Polymer	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
Head-to-head and tail-to-tail type				
III _b	—	97	7	2.7
III _c	—	106	11	2.3
III _d	82	81	12	3.1
III _e	—	94	7	2.3
III _f	82	71	17	2.8
III _k	63	62	13	2.3
III _l	82	77	14	2.3
Head-to-tail type				
V _b	85	82	14	2.2
V _c	—	109	11	2.6
V _d	83	82	45	1.4
V _e	—	97	49	1.7
V _f	96	80	19	2.1
V _k	82	77	65	1.5
V _l	86	77	13	2.0

*Films were cast from slow evaporation of polymer solutions in DMAc.

Table V Thermal Behavior Data of Poly(Amide-Imide)

Polymer	DSC ^a		TGA	
	T_g (°C)	T_{10} (°C) ^b in N ₂	Char Yield ^c (wt %)	
Head-to-head and tail-to-tail type				
III _a	—	527	66	
III _b	306	546	64	
III _c	340	515	63	
III _d	317	543	66	
III _e	268	559	59	
III _f	251	554	58	
III _g	—	532	61	
III _h	227	575	59	
III _i	248	537	64	
III _j	229	533	54	
III _k	204	518	63	
III _l	224	548	58	
Head-to-tail type				
V _a	—	556	54	
V _b	327	531	59	
V _c	340	514	64	
V _d	307	538	57	
V _e	288	552	45	
V _f	272	557	53	
V _g	—	525	48	
V _h	227	562	64	
V _i	237	529	59	
V _j	240	507	62	
V _k	233	508	60	
V _l	251	543	55	

DSC, differential scanning calorimetry; TGA, thermogravimetry analysis.

^aMidpoint of baseline shift in the second heating DSC trace with a heating rate of 15°C min⁻¹ under a nitrogen atmosphere.

^bTemperatures at which 10% weight loss were recorded by T_g at a heating rate of 20°C min⁻¹.

^cResidual weight percent (wt %) at 800°C under a nitrogen atmosphere.

The thermal properties of series III and V are determined by DSC at a rate of 15°C min⁻¹ and by TGA at a rate of 20°C min⁻¹. The thermal behavior data are listed in Table V. The more amorphous samples could be obtained after quenching the samples from an elevated temperature (~ 400°C) to room temperature in air by DSC; as a consequence, the glass transition temperatures (T_g) could be easily observed in the second heating traces of DSC. Although III_{a,g} exhibited semicrystallinity in their X-ray measurements, no step transition corresponding to T_g and no endothermic peak corresponding to the melting transition temperature (T_m) was detected

within the test range. T_g values of series III ranged within 204–340°C and those of series V ranged within 227–340°C. Series III and V had the highest T_g values for polymers III_c and V_c, which contained tolyl group. In view of the fact that polymers III_d and V_d had higher T_g values than those of polymers III_{e,f} and V_{e,f}, it became obvious that the incorporation of phenoxy group into the backbone of polymer could reduce the T_g . Polymers III_e and V_e had higher T_g values than those of polymers III_f and V_f, possibly because the former had symmetric Ar linkages. Furthermore, for PAI III_{e-j} and V_{e-j}, which contained the aryl ether, their structures would be more flexible when the number of aryl ether increased. Thus, T_g values of polymers III_{g-j} and V_{g-j} would be lower than those of polymers III_{e,f} and V_{e,f}. Moreover, III_l and V_l had higher T_g than those of III_k and V_k. This may be because the hexafluoroisopropylidene group is larger than the isopropylidene group; thus, macromolecular backbones of III_l and V_l rotated in higher temperature. Comparison of series III with series V showed that most series III polymers had lower T_g values.

TGA showed that series III polymers had 10% weight loss temperatures (T_{10}) of 515–575°C under nitrogen, and their char yields at 800°C in nitrogen were within a range of 54–66 wt %. The T_{10} of series V polymers stayed within the range of 507–562°C in nitrogen, and the char yields of them at 800°C in nitrogen were higher than 45 wt % and up to 64 wt %. To sum up, both series polymers had excellent heat resistance. Comparing the PAI of the same series, the incorporation of phenoxy group into the polymer chain exerted little influence on heat resistance based on the comparison of polymers III_{e-1} or V_{e-1}, and polymers III_h and V_h had the highest T_{10} in two series. For the substituted position of phenylene, *p*-phenylene-containing polymer V_a had higher T_{10} value than that of its *m*-phenylene-containing isomer V_b, but the temperature for III_a was unexpectedly lower than that for III_b. Although the char yields of PAI III_c and V_c were close to those of PAI III_b and V_b, which had structures similar to those of III_c and V_c, the latter had obviously higher T_{10} than the former. Moreover, both the T_{10} and the char yields for the isomers of the diphenylether-containing III_{e,f} or V_{e,f} were close in spite of the differences in the benzene ring linkage positions. For polymers III_{k,1} or V_{k,1}, the fluorine-containing III_l and V_l had higher T_{10} than its nonfluoro analogous III_k and V_k because the C—F bond of the CF₃ group was stronger than the C—H bond of the CH₃ group. Comparison of

T_{10} and the char yields of series III with series V showed that they did not display any clear deference dependent on different sequence orders.

CONCLUSIONS

Two kinds of regular sequential-order PAI could be prepared from TMA and aromatic diamines by different processes. In general, both two-series PAI were soluble in nonprotic solvents and had good thermal and mechanical properties. To compare polymers with the same monomers, the PAI with regular amide-imide sequences possessed slightly better solubility and higher T_g values than those with alternating (amide-amide)-(imide-imide) sequences. The thermal stabilities of these two series polymers were similar in spite of differences in their sequential order. When rigid diamines were used to synthesize PAI, the preparation of PAI with regular structures in amide-imide sequential order could form the polymer materials with better mechanical properties.

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