

Preparation and Properties of Poly(amide-ether-imide)s Derived from 1,4-Bis(4-aminophenoxy)benzene, Trimellitic Anhydride, and Various Aromatic Diamines

Chin-Ping Yang*, Sheng-Huei Hsiao and Wen-Long Chou

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., Sec. 3, Taipei, Taiwan, Republic of China

Abstract: An imide ring containing dicarboxylic acid, 1,4-bis(4-trimellitimidophenoxy)benzene (III), was prepared by the condensation of 1,4-bis(4-aminophenoxy)benzene and trimellitic anhydride. A series of new poly(amide-ether-imide)s were prepared by the direct polycondensation of diimide-diacid III with various aromatic diamines using triphenyl phosphite and pyridine as condensing agents in *N*-methyl-2-pyrrolidone (NMP) in the presence of calcium chloride. The highest inherent viscosity value of a poly(amide-ether-imide) obtained was 1.78 dL/g (in *N,N*-dimethylacetamide, DMAc, at 30 °C). Flexible films with excellent tensile properties were cast from DMAc solutions. Glass transition temperatures of these poly(amide-ether-imide)s were recorded in the range of 248-297 °C. These polymers do not show obvious weight loss before 400 °C; the decomposition temperatures at which 10% weight loss in nitrogen and in air were observed for these poly(amide-ether-imide)s in the range of 521-564 °C and 501-539 °C, respectively. The polymers derived from *p*-phenylenediamine or the diamines containing 1,4-bisphenoxy units exhibited a higher degree of crystallinity and higher initial decomposition temperatures but poor solubility in organic solvents.

Keywords: 1,4-Bis(4-trimellitimidophenoxy)benzene, Direct polycondensation, Poly(amide-ether-imide)s.

Introduction

Aromatic polyimides have earned a reputation as high-performance materials based on their excellent thermal stability, chemical resistance, and outstanding mechanical properties [1, 2]. However, poor handling and intractable characteristics have been major problems due to high melting point and insolubility. To extend the utility of such high performance materials, it has been a long-desired goal to synthesize soluble polymers without much sacrifice in their thermomechanical properties. It is well known that the synthesis of poly(amide-imide)s can offer a compromise between excellent thermal stability and processability.

Various approaches have been carried out successfully in the synthesis of poly(amide-imide)s [3]. A recently developed direct polycondensation method reported by Yamazaki et al. [4] using triphenyl phosphite and pyridine as condensing agents has been used

to prepare high molecular weight poly(amide-imide)s from imide ring-preformed dicarboxylic acids and aromatic diamines [5]. This route provides significant advantages in manufacturing operations compared with conventional methods. Thus, many new series of poly(amide-imide)s were readily prepared by this convenient technique in our laboratory [6]. As a continuation of our efforts on screening new poly(amide-imide)s, we describe here the preparation and characterization of a novel series of poly(amide-ether-imide)s based on the ether-imide-diacid prepared from the condensation of 1,4-bis(4-aminophenoxy)benzene and trimellitic anhydride.

Experimental

1. Materials

1,4-Bis(4-aminophenoxy)benzene (II; IV_b) was synthesized from the chlorodisplacement of *p*-

* To whom all correspondence should be addressed

chloronitrobenzene (TCI) with hydroquinone in the presence of potassium carbonate, followed by catalytic reduction of the dinitro compound using hydrazine (Wako) and palladium on activated carbon (Pd-C; from Fluka) [7]. *p*-Phenylenediamine (IV_a) and *m*-phenylenediamine (IV_b) were distilled under vacuum before use. Other diamines were of high purity when received from the manufacturers and used without any further purification; they including: 2,4-diaminotoluene (IV_c, TCI); 4,4'-oxydianiline (IV_d, TCI); 3,4'-oxydianiline (IV_e, from Teijin Ltd., Tokyo); 4,4'-thiodianiline (IV_f, TCI); 4,4'-methylenedianiline (IV_g, TCI); 1,3-bis(4-amino-phenoxy)benzene (IV_i, Chriskev); 2,2-bis[4-(4-aminophenoxy)phenyl]propane (IV_j, Chriskev); bis[4-(4-aminophenoxy)phenyl]sulfone (IV_k, Chriskev); 9,9-bis(4-amino-phenyl)fluorene (IV_l, Chriskev). Trimellitic anhydride (from Wako) was used without additional purification. Commercially obtained anhydrous lithium chloride and calcium chloride were dried under vacuum at 150 °C for 6 hrs and 180 °C for 10 hrs, respectively. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethyl-formamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (from TCI) was purified by distillation under reduced pressure.

2. Synthesis of monomers

2.1 Synthesis of 1,4-bis(4-nitrophenoxy)benzene (I)

A mixture of 25 g (0.227 mol) of hydroquinone, 75 g (0.476 mol) of *p*-chloronitrobenzene, 72 g (0.521 mol) of anhydrous K₂CO₃, and 230 mL of dry DMF was refluxed at 160 °C in an oil bath for 8 hrs and cooled. The mixture was then poured into 500 mL of 1:1 methanol-water. The precipitate was collected by filtration and recrystallized from glacial acetic acid to obtain yellow crystals of dinitro compound I; mp. 236-237 °C. The yield was 51.3 g (67%).

Anal. calcd. for C₁₈H₁₂N₂O₆ (352.30): C, 61.36; H, 3.43; N, 7.95 %. Found: C, 61.23; H, 3.51; N, 7.88%.

2.2 Synthesis of 1,4-bis(4-aminophenoxy)benzene (II)

The dinitro compound I 28.4 g (0.08 mol), 0.3 g of 10% Pd-C, and 210 mL of ethanol were introduced into a three-necked flask to which 80 mL of hydrazine monohydrate was added in drops over a period of 1 hr at 85 °C. After completion of addition, the reaction was continued to keep refluxing for another 4 hrs. The mixture was then filtered to remove the Pd-C. After cooling, the precipitated white powders were isolated by filtration and washed thoroughly with methanol; mp 173-174 °C (lit. [7] 173 °C). The yield was 23.4 g

(65%).

Anal. calcd. for C₁₈H₁₆N₂O₂ (292.34): C, 73.95; H, 5.51; N, 9.58%. Found: C, 73.84; H, 5.64; N, 9.51%.

3. Synthesis of 1,4-bis(4-trimellitimidophenoxy)benzene (III)

A mixture of 8.76 g (0.03 mol) of 1,4-bis(4-aminophenoxy)benzene (II) and 11.4 g (0.06 mol) of trimellitic anhydride were dissolved in 50 mL of dry DMF. Stirring and heating at 40 °C were continued for 1 hr. Then, about 20 mL of toluene was added, and the mixture was heated with reflux about 4 hrs until about 1.1 mL of water was distilled off azeotropically under a Dean-Stark trap, and the heating was continued to distill the residual toluene. After cooling, the precipitated diimide-diacid III was isolated by filtration and recrystallized from DMAc. After isolation by filtration, the purified product was dried in vacuum, and the yellow powder obtained was 17.29 g (Yield: 90%, mp. 399 °C by DSC). The infrared (IR) spectrum (KBr) exhibited characteristic absorptions at 2500-3000 cm⁻¹ (carboxylic -OH), 1705 cm⁻¹ (carboxylic C=O), 1790 and 1720 cm⁻¹ (imide C=O), 730 cm⁻¹ (imide ring). Anal. calcd. for C₃₆H₂₀N₂O₁₀ (640.56): C, 67.5; H, 3.15; N, 4.37%. Found: C, 67.4, H, 3.19; N, 4.32%.

4. Polymerization

A typical example of polymerization was as follows. A mixture of 0.8 g (1.25 mmol) of diimide-diacid III, 0.135 g (1.25 mmol) of *m*-phenylenediamine (IV_b), 0.8 g of calcium chloride, 0.8 mL of triphenyl phosphite, 1.5 mL of pyridine, and 8 mL of NMP was heated with stirring at 100 °C for 3 hrs under nitrogen. As the polycondensation proceeded, the suspended CaCl₂ dissolved and the solution gradually became viscous. The obtained polymer solution was trickled over 500 mL methanol giving rise to a stringy yellow precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was 0.88 g (99%). Inherent viscosity of the poly(amide-ether-imide) V₆ in DMAc was 1.78 dL/g. Anal. calcd. for (C₄₂H₂₄N₄O₈)_n: C, 70.78; H, 3.39; N, 7.86%. Found: C, 68.57; H, 4.01; N, 7.12%.

All other poly(amide-ether-imide)s were prepared by a similar procedure.

5. Measurements

Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform Infrared Spectrometer. The inherent viscosities were measured with a Cannon-Fenske viscosimeter thermostated at 30 °C.

The DSC traces were measured on a Sinku-Riko

7000 differential scanning calorimeter coupled to a Basic Component TA 7000 Thermal Analyzer at the rate of 20 °C/min in flowing nitrogen (30 cm³/min). Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (50 cm³/min) at a heating rate of 20 °C/min.

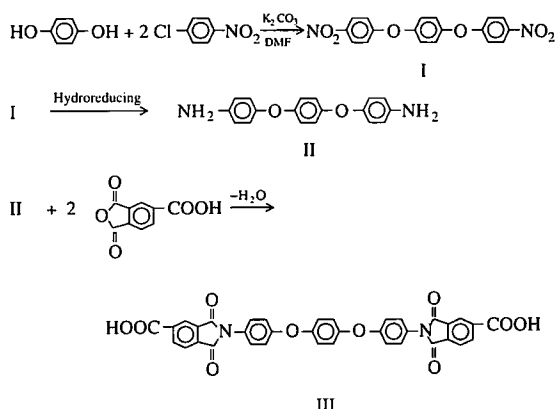
Wide-angle X-ray diffraction measurements were performed at room temperature (about 25 °C) with film specimens of about 0.1 mm thick (or powder) on a Rigaku Geiger Flex D-Max III_a X-ray diffractometer, using Ni-filtered CuK_α radiation (40 kV, 15 mA). The scanning rate was 2°/min.

An Instron Universal Tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick) and an average of at least five individual determinations was used.

Results and Discussion

1. Synthesis of diimide-diacid III

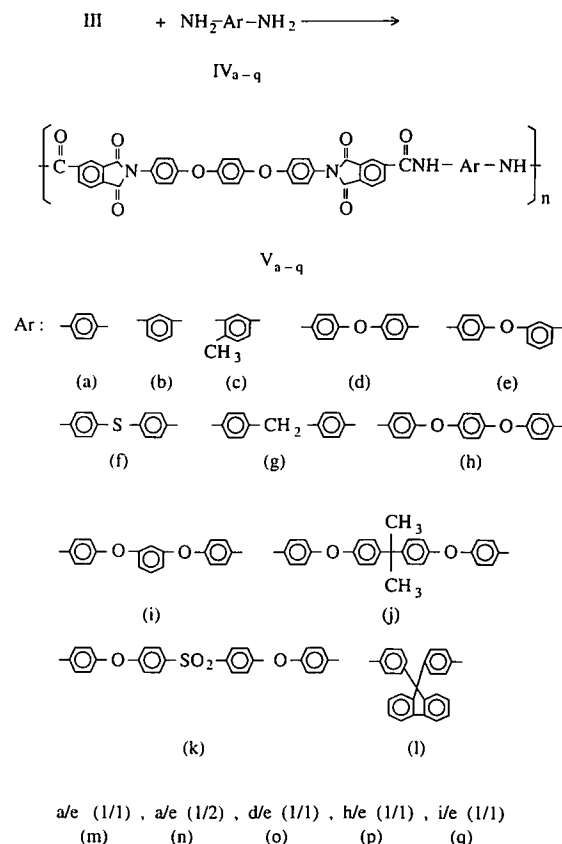
The reaction scheme to produce the imide-containing dicarboxylic acid III is outlined in Scheme 1. The dinitro compound I was synthesized from the nucleophilic chlorodisplacement of hydroquinone and *p*-chloronitrobenzene, and then catalytically reduced to yield 1,4-bis(4-aminophenoxy)benzene (II). Thereafter, diamine II was condensed with trimellitic anhydride (TMA) in 1:2 molar ratio to form the diimide-



diacid III.

2. Synthesis of polymers

The purified diacid III was condensed directly with various aromatic diamines in the mixture of NMP and pyridine in the presence of triphenyl phos-



phite (TPP) and calcium chloride at 100 °C for 3 hrs (Scheme 2).

It is well-known that homogeneity of the reaction medium favors the polycondensation of dicarboxylic acids and aromatic diamines in the phosphorylation reaction. A sufficient amount of metal salts such as CaCl₂ dissolved in the reaction solvent is necessary to prevent an early precipitation which probably hinders the polycondensation reaction. Numerous experiments in which solvent, added amount of calcium chloride, reactant concentration, temperature, etc., were varied convinced us that the conditions listed in Table I are optimal. When the polycondensation reaction was carried out under such conditions, clear and highly viscous polymer solutions could be obtained from non-*para* substituted diamines such as

IV_b, IV_c, IV_e, from diamines with sulfide or methylene group, such as IV_f and IV_g, and from isopropylidene-containing diamine IV_j, sulfone-containing diamine IV_k, or fluorene-containing diamine IV_l, which were trickled and stirred into methanol to obtain stringy polymers. However, while diamines were *p*-phenylenediamine (IV_a) or *p*-phenoxy groups-containing diamines (such as IV_d, IV_h, and IV_i), an early precipitation occurred during polymerization, and increasing the amount of CaCl₂ or solvent in order to carry out the reaction in a homogeneous phase has met with failure in obtaining clear, viscous polymer solutions. The unsatisfactory results may be attributed to their poor solubility, possibly due to the presence of the rigid and more symmetric polymer backbones which give a higher crystallinity. While copolymerization was proceeded with equivalent mole ratio of unsymmetrical 3,4'-oxydianiline (IV_e) and each of these four diamines, a clear, viscous polymer solution was obtained, and a stringy precipitate could be obtained when pouring the resulting polymer solution into methanol.

Inherent viscosities of most poly(amide-imide)s were determined at 30 °C using 0.5 g/dL solutions in DMAc. Some polymers which were insoluble in DMAc were measured in DMAc with 5 wt% LiCl dissolved or concentrated sulfuric acid. As shown in Table I, the inherent viscosities of most polymers were near or above 1.00 dL/g, except for polymers V_e, V_j, and V_l. It is worthwhile noting that the inherent viscosities of polymers V_a, V_d, V_h, and V_i were near

Table I. Preparation of poly(amide-imide)s^(a) from diimide-diacid (III) and diamines (IV_{a-l}).

Polymer	Diamine	Initial amount of NMP (mL)	Additional amount of NMP (mL)	Yield (%)	$\eta_{inh}^{(b)}$ (dL/g)
V _a	IV _a	7	1	98	0.89 ^(d)
V _b	IV _b	8	0	99	1.78
V _c	IV _c	8	0	99	1.15
V _d	IV _d	8	0	99	1.04 ^(d)
V _e	IV _e	7	1	99	0.81 ^(c)
V _f	IV _f	8	0	99	1.15 ^(c)
V _g	IV _g	8	0	99	1.02 ^(c)
V _h	IV _h	8	0	97	1.00 ^(c)
V _i	IV _i	7	1	99	0.96 ^(c)
V _j	IV _j	7	1	99	0.86
V _k	IV _k	7	1	99	1.10
V _l	IV _l	7	1	99	0.62

(a) Polymerization was carried out with 1.25 mmol of each monomer, 0.8 mL of TPP, 1.5 mL of pyridine, and 0.8 g of CaCl₂ in NMP at 100 °C for 3 hrs.

(b) Measured in DMAc on a concentration of 0.5 g/dL at 30 °C.

(c) Measured in DMAc containing 5 wt% of LiCl dissolved at 30 °C.

(d) Measured in conc H₂SO₄ on a concentration of 0.5 g/dL at 30 °C.

Table II. Preparation of copoly(amide-imide)s^(a) from diimide-diacid (III) and mixed diamines (IV_{a, d, h, i}/IV_e).

Copolymer	Diamine (mol ratio)	Initial NMP (mL)	Additional NMP (mL)	Yield (%)	$\eta_{inh}^{(b)}$ (dL/g)
V _m	IV _a /IV _e (1/1)	8	9	99	0.95
V _n	IV _a /IV _e (1/2)	8	9	99	1.60
V _o	IV _d /IV _e (1/1)	8	10	99	1.66
V _p	IV _h /IV _e (1/1)	8	8	99	1.65
V _q	IV _i /IV _e (1/1)	8	6	99	1.53 ^(c)

(a) Polymerization was carried out with 1.25 mmol of each monomer, 0.8 mL of TPP, 1.5 mL of pyridine, and 0.8 g of CaCl₂ in NMP at 100 °C for 3 hrs.

(b) Measured in DMAc on a concentration of 0.5 g/dL at 30 °C.

(c) Measured in DMAc containing 5 wt% of LiCl dissolved at 30 °C.

1.00 dL/g, indicating that they still had a moderate degree of polymerization, although an early precipitation occurred during the polycondensation reactions. The solubility of polymers was improved by copolymerizing diacid III with mixed diamines of 3,4'-oxydianiline (IV_e) and the diamines that resulted in less soluble poly(amide-imide)s; hence, homogeneous polymer solutions were obtained and their inherent viscosities could be enhanced, for example that of polymer V_o, to 1.66 dL/g (Table II).

The structures and compositions of these polymers were confirmed by their IR spectra and elemental analyses. Figure 1 shows the IR spectra of diimide-diacid III, diamine IV_e, and their derived poly(amide-imide) V_e. Obviously, after condensation, the characteristic absorption bands for carboxylic acid at 2500-3000 cm⁻¹ of III and amine N-H stretching vibrations at 3300-3500 cm⁻¹ of IV_e disappeared, while the absorption bands of amide groups appear at 3300 cm⁻¹ (N-H) and 1663 cm⁻¹ (C=O). The characteristic absorption peaks of imide rings appear at 1779 and 1721 cm⁻¹ due to the asymmetrical and symmetrical C=O stretching vibrations, and at 1118 and 725 cm⁻¹, due to ring deformation.

The elemental analyses of all poly(amide-imide)s are listed in Table III. The results of analyses indicated these polymers absorb a small amount of water (about 2-3 wt%) at room temperature. Therefore, the results of analyses generally agree with the proposed structure, assuming 1 to 1.5 molecules of water absorbed per repeating unit.

3. Properties of polymers

The qualitative solubility of all the poly(amide-imide)s is shown in Table IV. The solubility is related to the nature of the diamine. The polymers derived from symmetrical diamines, such as IV_a, sulfide-containing diamine IV_f, methylene-containing diamine IV_g, or oxygen-bridged diamines, such as IV_d, IV_e,

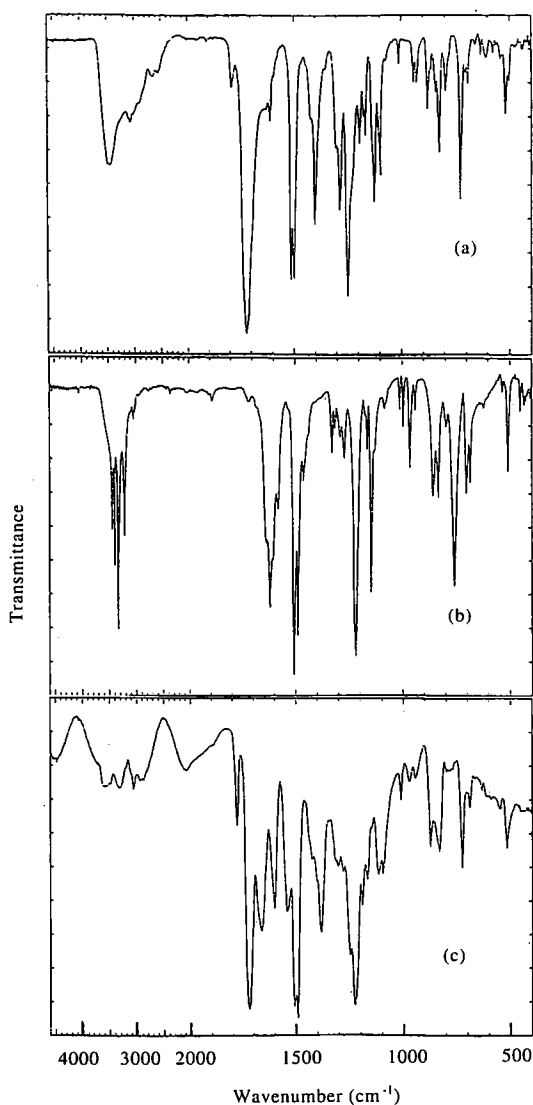


Figure 1. FTIR spectra of (a) diimide-diacid III, (b) diamine IV_c, and (c) poly(amide-imide) V_c.

IV_h and IV_i, show poor solubility in the organic solvents listed in Table IV, whereas polymers V_b, V_c, and V_j show higher solubility. They are soluble in DMAc and NMP. Polymers V_k and V_l show much higher solubility and are readily soluble in polar solvents, such as DMAc, DMF, NMP and DMSO, and are also soluble in *m*-cresol and *o*-chlorophenol.

Copolymers such as V_m, V_n, V_o, V_p and V_q derived from mixed diamines show improved solubility in NMP and DMAc-5 wt% LiCl. All the polymers are soluble in concentrated sulfuric acid, but they are insoluble in common organic solvents like benzene, acetone, tetrahydrofuran, chloroform, etc.

The thermal properties of the polymers were evaluated by means of thermogravimetry (TG) and differential scanning calorimetry (DSC). The TG data, temperatures at various percentages of weight loss and char yield at 800 °C of all poly(amide-imide)s are summarized in Table V. Dynamic TG data indicated that all the polymers showed no obvious weight loss up to temperatures of approximately 400 °C in nitrogen, and their 10% weight loss temperatures were recorded between 521-564 °C in nitrogen. The amount of carbonized residue of the poly(amide-imide)s at 800 °C in nitrogen atmosphere was above 48 wt% and reached up to 60 wt%.

DSC measurements were conducted with a heating rate of 20 °C/min. Quenching from the elevated temperatures to room temperature in air yields more amorphous samples so that in some cases the glass transition temperatures (T_g s) could be measured in the second heating trace of DSC. The T_g s of the poly(amide-imide)s with observable shifts on the DSC curves were in the range of 248-297 °C. Most of the polymers did not show clear glass transition before decomposition, probably due to high degree of crystallinity.

To confirm further the crystalline characteristics of these polymers, which were subjected to wide-angle X-ray diffraction measurements. Polymers V_a, V_d, V_h and V_i were measured in powder form, and some polymers which could be cast into films from DMAc were measured in films, such as polymers V_{b,c,e,j,k,l,q}. Figure 2 presents the X-ray diffractograms of some representative polymers (V_{a-d}, V_h and V_i). Polymers V_a, V_d, V_h, and V_i revealed crystalline patterns due to a better packing of the symmetrical polymer backbones. The poly(amide-imide)s showing crystalline patterns are insoluble in polar solvents (such as DMAc, DMF, and DMSO), which is in agreement with the general rule that the solubility decreases with increasing crystallinity. On the other hand, all the poly(amide-imide) films cast from polymer solutions of DMAc (such as V_b and V_c) exhibit amorphous patterns.

Strong and flexible films could be cast from the DMAc solutions of some polyamides. The tensile properties of seven typical poly(amide-imide) films are summarized in Table VI. The films had strength at break of 54-95 MPa, especially polymer V_j with the highest value. Polymers V_b and V_c containing *meta*-substituted phenylene groups behave as ductile materials with high strength at break, a yield point, and moderate elongation-to-break. Polymers V_j, V_k and V_l, with smaller elongation to break behave as a hard and strong material.

Because those polymers obtained from etherdiamines of more symmetrical structure, such as V_d, V_h and V_i, had poor solubility, they could not be

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

Polymer	Formula (molecular weight)	C (%)		H (%)		N (%)	
		Calcd	Found	Clacd	Found	Calcd	Found
V _a	(C ₄₂ H ₂₄ N ₄ O ₈ •H ₂ O) _n (730.66) _n	69.03	69.20	3.59	3.84	7.67	7.16
V _b	(C ₄₂ H ₂₄ N ₄ O ₈ •3/2H ₂ O) _n (739.67) _n	68.25	68.57	3.68	4.01	7.57	7.12
V _c	(C ₄₃ H ₂₆ N ₄ O ₉ •H ₂ O) _n (744.69) _n	69.34	68.96	3.79	4.10	7.52	7.16
V _d	(C ₄₈ H ₂₈ N ₄ O ₉ •H ₂ O) _n (822.75) _n	70.06	70.66	3.68	3.89	6.81	6.55
V _e	(C ₄₈ H ₂₈ N ₄ O ₉ •H ₂ O) _n (822.75) _n	70.06	70.30	3.68	3.99	6.81	6.49
V _f	(C ₈₄ H ₂₈ N ₄ O ₈ S•H ₂ O) _n (838.81) _n	68.73	68.86	3.61	3.92	6.68	6.24
V _g	(C ₉₄ H ₃₀ N ₄ O ₈ •H ₂ O) _n (820.78) _n	71.70	71.83	3.93	4.24	6.83	6.57
V _h	(C ₅₄ H ₃₂ N ₄ O ₁₀ •H ₂ O) _n (914.85) _n	70.89	71.08	3.75	3.92	6.12	5.82
V _i	(C ₅₄ H ₃₂ N ₄ O ₁₀ •H ₂ O) _n (914.85) _n	70.89	71.07	3.75	3.95	6.12	6.01
V _j	(C ₆₃ H ₄₂ N ₄ O ₁₀ •H ₂ O) _n (1033.02) _n	73.24	73.37	4.29	4.59	5.42	5.16
V _k	(C ₆₀ H ₃₆ N ₄ O ₁₂ S•H ₂ O) _n (1054.99) _n	68.30	68.19	3.63	3.96	5.31	4.98
V _l	(C ₆₁ H ₃₆ N ₄ O ₈ •3/2H ₂ O) _n (979.96) _n	74.76	74.84	4.01	4.33	5.72	5.53
V _m	(C ₉₀ H ₅₂ N ₈ O ₁₇ •2H ₂ O) _n (1553.41) _n	69.58	69.66	3.63	3.96	7.21	6.78
V _n	(C ₉₀ H ₅₂ N ₈ O ₁₇ •2H ₂ O) _n (1553.41) _n	69.58	69.62	3.63	3.94	7.21	6.56
V _o	(C ₉₆ H ₅₆ N ₈ O ₁₈ •2H ₂ O) _n (1644.50) _n	70.06	70.27	3.68	3.93	6.81	6.48
V _p	(C ₁₀₂ H ₆₀ N ₈ O ₁₉ •2H ₂ O) _n (1737.54) _n	70.50	70.38	3.71	4.03	6.44	6.10
V _q	(C ₁₀₂ H ₆₀ N ₈ O ₁₉ •2H ₂ O) _n (1737.54) _n	70.50	70.66	3.71	3.99	6.44	6.13

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

Solvent ^(b)	Polymer																
	V _a	V _b	V _c	V _d	V _e	V _f	V _g	V _h	V _i	V _j	V _k	V _l	V _m	V _n	V _o	V _p	V _q
DMAc	-	+	+	-	-	-	-	-	-	+	+	+	-	-	-	-	+
DMF	-	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	-
NMP	-	+	+	+-	+	+	-	-	+-	+	+	+	+	+	+	+	+
DMSO	-	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	+
<i>m</i> -Cresol	-	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	-
Pyridine	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-
<i>o</i> -Chlorophenol	-	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	+
DMAc + 5% LiCl	+-	+	+	+-	+	+	+	+-	-	+	+	+	+	+	+	+	+
Conc. H ₂ SO ₄	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

(a) Solubility: +, soluble; -, insoluble; +-, partially soluble.

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

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

Polymer	DSC	TG ^(c)				wt% residul at 800 °C in nitrogen (wt%)
	T _g ^(a) (°C)	Temperature (°C) at various weight loss				
		5%	10%	20%	30%	
V _a	— ^(b)	476 (459)	542 (501)	611 (553)	650 (574)	55
V _b	297	465 (460)	539 (529)	595 (577)	638 (594)	55
V _c	292	460 (455)	526 (515)	584 (578)	635 (597)	58
V _d	—	490 (474)	556 (516)	608 (554)	653 (571)	55
V _e	—	495 (474)	538 (521)	586 (562)	631 (578)	58
V _f	—	477 (462)	541 (507)	589 (554)	632 (575)	56
V _g	—	472 (464)	529 (501)	576 (535)	612 (551)	48
V _h	—	486 (457)	563 (507)	616 (550)	676 (568)	60
V _i	—	502 (470)	560 (516)	611 (549)	660 (563)	56
V _j	248	494 (479)	521 (513)	557 (552)	586 (601)	49
V _k	269	487 (487)	525 (525)	573 (573)	578 (578)	57
V _l	—	490 (479)	552 (539)	618 (585)	648 (601)	57
V _m	—	506 (474)	564 (512)	628 (546)	678 (562)	56
V _n	277	478 (468)	555 (515)	609 (556)	658 (573)	55
V _o	—	486 (468)	537 (521)	597 (565)	648 (582)	53
V _p	270	499 (469)	553 (510)	607 (548)	658 (565)	55
V _q	249	485 (470)	529 (514)	583 (558)	627 (557)	53

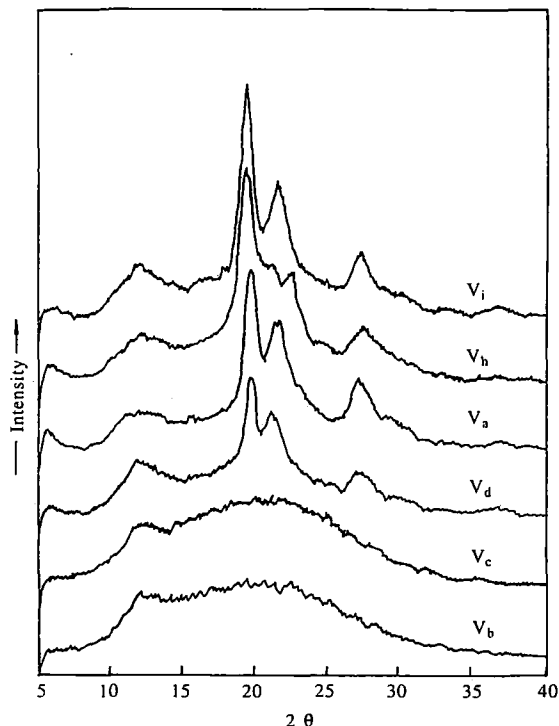
(a) From the second heating traces of DSC measurements conducted at a heating rate 20 °C/min in nitrogen.

(b) No T_g was observed in DSC traces.

(c) Thermogravimetry was conducted at a heating rate of 20 °C/min in nitrogen (or air).

solution-processed. However, the polymer derived from unsymmetrical diamine IV_e revealed high solubility and could be solution-cast into a tough film which exhibited a yield point on its stress-strain curve. Polymer V_d derived from two mixed diamines of IV_i and IV_e had a strength at break higher than V_e, but was without a yield point, and its elongation decreased possibly because of the increased rigidity of the polymer backbone caused by the incorporation of the moiety of diamine IV_i.

References

**Figure 2.** Wide-angle X-ray diffractograms of poly(amide-imide)s.**Table VI.** Tensile properties of poly(amide-imide)s films.

Polymer ^(a)	Strength at yield point (MPa)	Strength at break point (MPa)	Elongation at break point (%)	Initial modulus (GPa)
V _b	86	83	24	2.1
V _c	89	83	45	2.3
V _e	61	56	13	1.8
V _j	—	95	9	2.3
V _k	—	62	9	1.5
V _l	—	54	4	1.9
V _q	—	89	6	2.9

(a) Films were cast from polymer solutions of DMAc.

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