

Preparation and Properties of Polyamide-Imides Derived from 1,3-Bis(4-Aminophenoxy)Benzene, Trimellitic Anhydride, and Various Aromatic Diamines

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Abstract: A diamine, 1,3-bis(4-aminophenoxy) benzene (II), was synthesized in two steps; first from the condensation of resorcinol with p-chloronitrobenzene in the presence of potassium carbonate, producing 1,3-bis(4-nitrophenoxy) benzene (I), followed by hydrazine hydrate/Pd-C reduction. A two imide rings-preformed dicarboxylic acid, 1,3-bis(4-trimellitimidophenoxy)benzene (III), was prepared from the condensation of diamine II and trimellitic anhydride in 1:2 molar ratio. A series of structurally new polyamide-imides (V_{a-p}) were directly synthesized from the diacid III and various aromatic diamines (IV_{a-p}). The resultant polyamide-imides had inherent viscosities between 0.56-1.39 dl/g. All polymers, except some derived from diamines with p-phenoxy structure, showed excellent solubility. Some polymer resulted in tough or flexible transparent films. Dynamic TG data indicated that all polymers possess excellent thermal stability with no significant weight loss up to the temperature of approximately 450 °C in nitrogen, and their 10% weight loss temperature was recorded in the range of 489-577 °C. Measurements of wide-angle X-ray diffraction revealed that some polymers derived from p-phenoxy group-containing diamines showed crystalline patterns.

Keywords: Poly(amide-imide)s, Polycondensation, Phosphorylation, Aromatic diamines, 1,3-bis-(4-aminophenoxy)benzene, 1,3-bis(4-trimellitimidophenoxy)benzene.

Introduction

Although aromatic polyimides, conventionally manufactured from precursors, polyamic acids, are well recognized as a class of thermally stable materials, [1-2] their widespread use is limited by their poor handling and processing qualities. To overcome these shortcomings, various copolyimides have been developed. For example, there are many polyamide-imides developed with improved solubility. [3-4] Polyamide-imides, containing the amide groups, are easier to fabricate, they also retain good thermal stability due to the presence of imide rings. So, polyamide-imides exhibit better processability than polyimides.

It is known that the introduction of ether linkage into the polymer backbone imparts processability and solubility to polymers without much loss of thermal stability. [5-7] Therefore, according to the reported methods, [8-9] an ether-containing diamine, 1,3-bis(4-aminophenoxy)benzene (II), was prepared via the

preparation of the dinitro compound from resorcinol and p-chloronitrobenzene and subsequent reduction with hydrazine. Condensation of diamine II with two equivalent amounts of trimellitic anhydride leads to diimide-diacid III, which can be used as a new building block for polyamide-imide synthesis. In continuation of our previous studies, [10-13] we describe a successful synthesis of a novel polyamide-imides by the triphenyl phosphite activated polycondensation of diimide-diacid III, with aromatic diamines. The properties, such as solubility, thermal properties, mechanical properties, and crystallinity of the resultant polyamide-imides are also discussed.

Experimental

1. Materials

1,3-Bis(4-aminophenoxy)benzene was prepared according to the reported method [8] or purchased

from the manufacturer (Chriskev). Trimellitic anhydride (Wako) was used without prior purification. *m*-Phenylenediamine was vacuum distilled before use. All other diamines IV_{b-k} were of high purity when received from the manufacturer and used without further purification. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180 °C for 10 h. 1-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TCI) was purified by distillation under reduced pressure.

2. Synthesis

2.1 Synthesis of 1,3 bis(4aminophenoxy) benzene (II)

A mixture of 30 g (0.2727 mol) of resorcinol, 90.23 g (0.5727 mol) *p*-chloronitrobenzene, 86.91 g (0.6272 mol) of anhydrous K₂CO₃, and 270 ml of dry dimethylformamide was refluxed at 160 °C in an oil bath for 8 h, then left cooled. The mixture was then poured into 270 ml of 1:1 ethanol-water. The obtained crude product was recrystallized from glacial acetic acid to produce crystalline product; mp 110-112 °C. The yield was 85%. The dinitro compound of 1,3-bis(4-nitrophenoxy) benzene (I) 14.23 g, 0.15 g of 10% Pd-C, and 120 ml of ethanol was introduced into a three-necked flask to which 40 ml of hydrazine monohydrate was added in drops at 85 °C. After the addition of hydrazine, the reaction was continued to reflux for another 4 h. The reaction mixture was filtered to remove Pd-C, and the white diamine product precipitated upon cooling was collected by filtration; mp 105-107 °C (yield, 80%).

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

1,3-Bis(4-aminophenoxy)benzene 5.84 g (0.02 mol) and 7.6 g (0.04 mol) of trimellitic anhydride were dissolved in dry DMF and the reaction mixture was heated to 40 °C. Then, 30 ml of toluene was added, and the mixture was heated with reflux for about 4-5 h until about 1 ml of water was distilled off azeotropically under a Dean-Stark trap. After cooling, the precipitated diimide-diacid III was isolated by filtration and washed with methanol. It was purified by recrystallization from DMAc. The purified product was dried in vacuum, and the solid thus obtained was 12.47 g (98%); mp 350-352 °C.

IR(KBr): 2500-3000 cm⁻¹ (carboxylic-OH), 1700 cm⁻¹ (carboxylic C=O), 1712 cm⁻¹ (imide C=O), 727 cm⁻¹ (imide ring). Anal. calcd for (C₃₆H₂₀N₂O₁₀)_n: C, 67.50; H, 3.15; N, 4.37%. Found: C, 67.48; H, 3.18; N, 4.34%.

3. Polymerization

A typical example of polycondensation goes as follows. A mixture of 0.8 g (1.25 mmol) of diimide-diacid III, 0.25 g (1.25 mmol) diamine IV_d, 0.8 g of calcium chloride, 0.8 ml (2.5 mmol) of triphenyl phosphite, 1.6 ml of pyridine, and 8 ml of NMP was heated with stirring at 100 °C for 3 h under nitrogen. The obtained polymer solution, trickled into 500 ml of methanol, gave rise to a stringy precipitate. The precipitate was washed thoroughly with methanol and hot water, then collected by filtration and dried. The yield was quantitative. The inherent viscosity of a 0.5 g/dL polymer solution in DMAc was 1.39 dl/g at 30 °C. IR(film): 1779 and 1725 cm⁻¹ (C=O), 1120 and 725 cm⁻¹ (imide ring), 1676 cm⁻¹ (C=O amide), 3340 cm⁻¹ (N-H amide). Anal. calcd for (C₄₈H₂₈O₉N₄H₂O)_n: C, 70.06; H, 3.68; N, 6.81%. Found: C, 69.77; H, 3.11; N, 6.31%.

All other polyamide-imides were synthesized by an analogous procedure described above.

4. Characterization

Inherent viscosities of the polyamide-imides were determined at 30 °C using 0.5 g/dl solutions in DMAc or DMAc-5% LiCl. A Canon-Fenske capillary viscometer was used without kinetic energy correction, since the solvent flow time exceeds 100s.

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform Infrared Spectrometer. Elemental analyses were carried out with a Perkin-Elmer 240 C microanalyzer.

Thermogravimetry (TG) was done on a Rigaku Thermoflex TG 8110 coupled to a Rigaku Thermal Analysis Station 100. Experiments were performed on 10±2 mg samples heated in flowing nitrogen (50 cm³/min) at a heating rate of 20 °C/min. DSC was performed on a Sinku Riko DSC-7000 coupled to a Sinku Riko TA-7000 thermal analysis controller at the rate of 20 °C/min in flowing nitrogen (30 cm³/min). Wide angle X-ray diffractograms were obtained on a Rigaku Geiger D-Max IIIa, using Ni-filtrated CuK_α radiation (40 kV, 15 mA). 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 (about 20 °C) 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 were used.

Results and Discussion

1. Synthesis of diimide-diacid

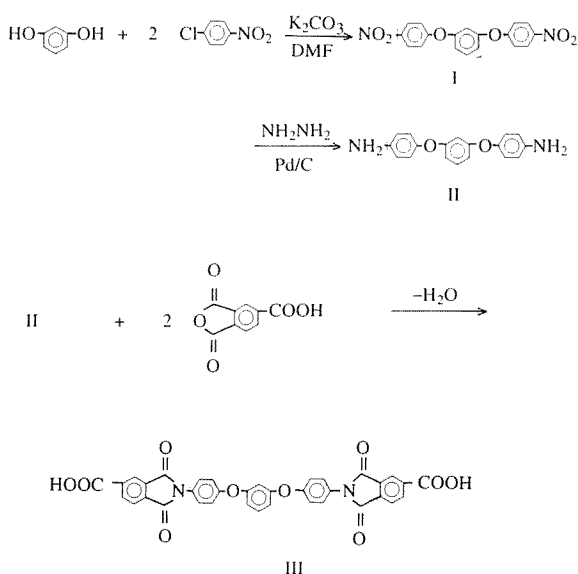
The diamine, 1,3-bis(4-aminophenoxy)benzene

(II), was synthesized in two steps, first from the condensation of resorcinol with *p*-chloronitrobenzene in the presence of potassium carbonate, giving rise to 1,3-bis(4-nitrophenoxy)benzene (I), followed by hydrazine hydrate/Pd-C reduction. 1,3-Bis(4-trimellitimidophenoxy)benzene (III), the polymer forming monomer with two imide rings, was produced by condensation of diamine II with trimellitic anhydride (Scheme 1).

According to the reported method, [8] dinitro compound I was synthesized from condensation of resorcinol with *p*-chloronitrobenzene in the presence of potassium carbonate (K_2CO_3), then was dissolved in dry DMF by refluxing for 8 h to give quantitative yield. Reduction of the nitro group can be carried out in a number of ways. The most frequently used methods employ catalytic hydrogenation, or treatment of the nitro compound with acid and iron, tin, or a metal salt such as $SnCl_2$. Hydrazine/Pd-C can also be used. The latter is a convenient way popularly used in laboratory, and this reduction method is employed in this work. The diimide-diacid III was synthesized via a two-stage procedure that included ring-opening addition of the diamine II with two equivalent amounts of trimellitic anhydride, followed by cyclodehydration to the imidodicarboxylic acid by means of toluene-water azeotropic distillation. The crude diacid was recrystallized from the DMAc/methanol solution before the polymer synthesis.

2. Preparation of polymers

A series of novel polyamide-imides V_a - V_p were prepared by direct polycondensation of diimide-di-

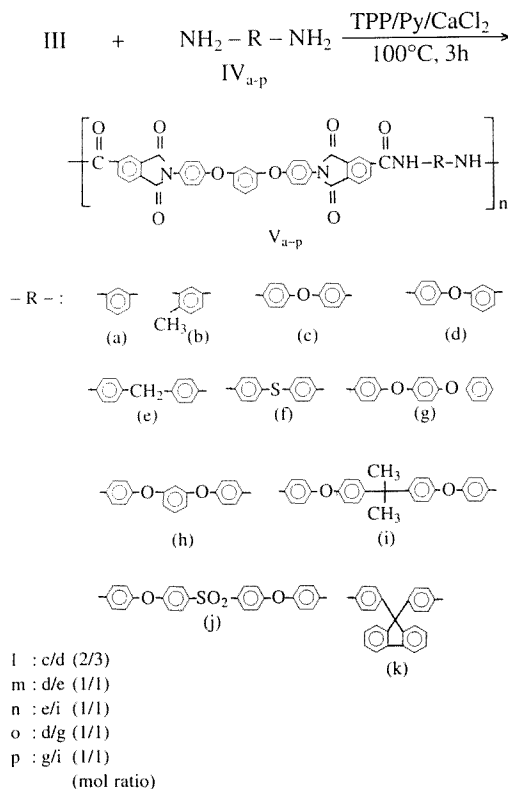


Scheme 1. Synthesis of diimide-diacid III.

acid III and various aromatic diamines IV_{a-k} or their mixtures by using triphenyl phosphite (TPP) and pyridine as condensing agents in NMP in the presence of calcium chloride.

Under the conditions listed in Table I, most of the reaction mixtures showed an appreciable increase in viscosity and were clear (homogeneous) throughout the reaction. All the polyamide-imides were isolated as yellowish materials with yields > 90%, usually quantitative. Also listed in Table I are the inherent viscosities of these polymers. The unsatisfactory results obtained from $V_{c,e,f}$ and V_g may be caused by their poor solubility, which resulted in an early precipitation of reaction medium retarding further polymerization. Increasing the amount of NMP, used as a solvent in order to carry out the reaction in homogeneous phase, has met with failure to obtain viscous polymer solution. The poor solubility may be attributed to the semicrystalline nature of these polymers. Polymers $V_{1,p}$ were derived from mixed diamines. These copolymers, except V_o , would precipitate into a tough string form when trickled in methanol, and they had an increased inherent viscosity.

Table III lists the elemental analyses values of these polymers. In all cases, the found values of carbon were lower than the calculated values for the



Scheme 2. Synthesis of polyamide-imides.

Table I. Preparation of polyamide-imides^(a) from diimide-diacid (III) and diamines (IV_{a-k})

Polymer	Diamine	Initial NMP (ml)	Additional NMP(ml)	Yield (%)	$\eta_{inh}^{(b)}$ (dl/g)
V _a	IV _a	4	0	99	0.98
V _b	IV _b	4	0	99	0.89
V _c	IV _c	8	2	99	0.60 ^(c)
V _d	IV _d	8	0	99	1.39
V _e	IV _e	8	2	99	0.73
V _f	IV _f	8	2	96	0.71
V _g	IV _g	8	2	98	0.62 ^(c)
V _h	IV _h	8	0	94	0.73
V _i	IV _i	8	0	99	0.93
V _j	IV _j	8	0	99	0.86
V _k	IV _k	8	0	99	0.56

(a) Polymerization was carried out with 1.25 mmol of each monomer, 0.8 ml of TPP, 1.6 ml of pyridine, and 0.8 g of CaCl₂ in 7 ml of NMP at 100 °C for 3 h.

(b) Measured in DMAc-5% LiCl at 0.5 g/dl at 30 °C.

(c) Measured in conc. H₂SO₄ at a concentration of 0.5 g/dl at 30 °C.

Table II. Preparation of copolyamide-Imides^(a) from diimide-diacid (III) and diamines (IV_{1-p})

Copolymer	Diamine (mole ratio)	Yield (%)	$\eta_{inh}^{(b)}$ (dl/g)
V _l	IV _d /IV _d (2/3)	92	0.84
V _m	IV _d /IV _e (1/1)	99	0.82
V _n	IV _d /IV _i (1/1)	99	0.91
V _o	IV _d /IV _g (1/1)	91	0.71 ^(c)
V _p	IV _g /IV _i (1/1)	92	0.75

(a) Polymerization was carried out with 1.25 mmol of each monomer, 0.8 ml of TPP, 1.6 ml of pyridine, and 0.8 g of CaCl₂ in 7 ml of NMP at 100 °C for 3 h.

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

(c) Measured in conc. H₂SO₄ at a concentration of 0.5 g/dl at 30 °C.

Table III. Elemental analyses of polyamide-imides

Polymer	Formula (Molecular weight)	C(%)		H(%)		N(%)	
		Calcd	Found	Calcd	Found	Calcd	Found
V _a	(C ₄₂ H ₂₄ N ₄ O ₈ • 1.5H ₂ O) _n (739.66) _n	68.20	67.78	3.27	3.09	7.58	6.85
V _b	(C ₄₃ H ₂₆ N ₄ O ₈ • 1.5H ₂ O) _n (753.69) _n	68.52	68.71	3.48	3.07	7.43	6.96
V _c	(C ₄₈ H ₂₈ N ₄ O ₉ • 0.5H ₂ O) _n (813.74) _n	70.84	70.69	3.47	3.33	6.89	6.64
V _d	(C ₄₈ H ₂₈ N ₄ O ₉ • H ₂ O) _n (822.75) _n	70.06	69.77	3.68	3.11	6.81	6.31
V _e	(C ₄₉ H ₃₀ N ₄ O ₈ • 0.5H ₂ O) _n (811.79) _n	72.49	72.34	3.73	3.52	6.90	6.77
V _f	(C ₄₈ H ₂₈ N ₄ O ₈ • H ₂ O) _n (838.81) _n	68.73	68.85	3.61	3.03	6.68	6.37
V _g	(C ₅₄ H ₃₂ N ₄ O ₁₀ • H ₂ O) _n (914.85) _n	70.89	71.07	3.75	3.10	6.12	5.95
V _h	(C ₅₄ H ₃₂ N ₄ O ₁₀ • H ₂ O) _n (914.85) _n	70.89	71.22	3.75	3.17	6.12	6.02
V _i	(C ₆₃ H ₄₂ N ₄ O ₁₀ • 1.5H ₂ O) _n (1044.04) _n	72.47	72.55	4.06	3.70	5.37	5.17
V _j	(C ₆₀ H ₃₆ N ₄ O ₁₂ S • 1.5H ₂ O) _n (1066.04) _n	67.59	67.49	3.65	3.25	5.26	5.25
V _k	(C ₆₁ H ₃₆ N ₄ O ₈ • 1.5H ₂ O) _n (979.96) _n	74.46	73.84	4.01	3.30	5.72	5.13
V _l	(C ₄₈ H ₂₈ N ₄ O ₉ • H ₂ O) _n (822.74) _n	70.07	69.26	3.65	3.87	6.81	6.65
V _m	(C ₉₇ H ₅₈ N ₈ O ₁₇ • H ₂ O) _n (1642.48) _n	71.66	70.38	3.72	3.94	6.89	6.61
V _n	(C ₈₆ H ₃₆ N ₄ O ₉ • H ₂ O) _n (927.16) _n	72.53	71.90	4.13	3.25	6.04	5.89
V _o	(C ₁₀₂ H ₆₀ N ₈ O ₁₉ • H ₂ O) _n (1719.48) _n	71.24	69.65	3.64	3.91	6.52	6.36
V _p	(C ₁₁₇ H ₇₄ N ₈ O ₂₀ • H ₂ O) _n (1929.85) _n	72.81	70.89	3.96	4.15	5.81	5.89

proposed structures. It is attributed to the hygroscopic nature of these polymers. The elemental analyses of the polymers were in good agreement with the calculated values for the proposed structure carrying 0.5 to 1.5 water molecules per repeating unit.

3. Characterization of polymers

The solubility behavior of all the polyamide-imides is listed in Table IV. It's found that the nature of the corresponding diamines used influence the solubility. The polymers derived from diamines containing *m*-phenylene (IV_a), 2,4-tolylene (IV_b), fluorene (IV_k), isopropylidene (IV_i), or sulfonyl (IV_j) group reveal excellent solubility in most solvents. For example, they dissolve in amide-type solvents and DMSO solvent. Polymers derived from symmetrical diamines such as IV_c, e and f, and double aryl ether groups-containing IV_g and IV_h, reveal very poor solubility in the polar solvents. Some of them were only soluble in the solution of DMAc containing 5 wt% LiCl.

The polymers obtained from the diamines IV_c, e, and IV_g, resulted in an early precipitation of reaction medium retarding further polymerization. Therefore, we used mixed diamines from them with diamines IV_d and IV_i during polymerization to get high molecular weight polymers. These polymers showed improved solubility in NMP and DMAc/5 wt% LiCl.

The thermal stability and glass transition temperatures of polymers were evaluated by thermogravimetric (TG) analysis and DSC, respectively. The thermal behavior data of all polyamide-imides are summarized in Table V. The 10% weight loss temperatures were recorded in the range of 489-567 °C. The thermooxidative stability of these polymers is affected significantly by their components. Some polymers containing phenoxy groups, such as V_c, d, g, h, and fluorene-containing group (V_k) show excellent thermal stability. Their 10 % weight loss temperatures in nitrogen atmosphere and the amount of carbonized residue at 800 °C in nitrogen were above

Table V. Thermal behavior of polyamide-imides

Polymer	DSC		TG ^(b)				wt% residue at 800 °C in nitrogen
	T _g ^(a) (°C)	Temperature (°C) at Various wt. loss					
		5%	10%	20%	30%		
V _a	262	463 (458)	557 (527)	611 (578)	660 (597)	61	
V _b	268	453 (437)	557 (489)	589 (548)	633 (568)	56	
V _c	289	477 (451)	562 (496)	611 (533)	660 (547)	60	
V _d	235	489 (468)	566 (518)	612 (561)	665 (580)	61	
V _e	— ^(c)	454 (446)	489 (475)	576 (522)	644 (541)	63	
V _f	268	476 (464)	557 (531)	610 (552)	667 (567)	61	
V _g	—	506 (472)	564 (517)	607 (556)	666 (574)	63	
V _h	—	496 (457)	567 (508)	612 (561)	671 (581)	62	
V _i	213	477 (469)	530 (514)	581 (571)	628 (597)	61	
V _j	278	469 (464)	494 (500)	575 (551)	611 (575)	55	
V _k	263	464 (447)	558 (518)	619 (560)	693 (576)	65	
V _l	237	495 (480)	576 (523)	624 (555)	691 (570)	61	
V _m	—	507 (473)	560 (513)	614 (545)	677 (561)	61	
V _n	—	497 (462)	537 (493)	588 (533)	647 (552)	59	
V _o	—	512 (476)	577 (525)	637 (554)	724 (568)	64	
V _p	230	466 (464)	541 (506)	602 (552)	662 (572)	59	

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

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

(c) No T_g was observed in DSC traces.

Table IV. Solubility of polyamide-imides^(a)

Solvents ^(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
DMAc	+	+	-	+	-	-	-	-	+	+	+	+-	-	+-	-	+
DMF	+	+	+-	-	-	-	-	-	+	+	+	+-	+	+-	-	-
NMP	+	+	-	+	-	-	-	-	+	+	+	+	+	+	+	+
DMSO	+	+	-	+	-	-	-	-	+	+	+	-	-	-	-	-
<i>m</i> -Cresol	+	+	-	+	-	-	-	-	+	+	+	-	-	-	-	-
Py	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-
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: dimethylsulfoxide; Py: pyridine.

Table VI. Tensile properties of polyamide-imide films

Polymer ^(a)	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
V _a	—	72.7	5	2.74
V _b	64.3	75.6	8	2.10
V _d	—	119.2	10	2.97
V _i	83.2	81.4	8	2.94
V _j	—	84.8	9	2.37

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

558 °C and 60%, respectively. The 10% weight loss temperature in air shows lower thermal stability, in the range of 475-531 °C. However, the sulfone-containing polymer shows higher 10% weight loss temperature in air than in nitrogen, probably because of the sulfone-containing group showing better anti-oxidation. With respect to the copolymers (V_i-V_p), the 10% weight loss temperature in nitrogen was in the range of 537-577 °C, approaching that of polymers such as V_c, V_d, and V_g.

DSC measurements were conducted with a heating rate of 20 °C/min. Quenching from the elevated temperatures to room temperature in air yield more amorphous samples so that in most cases the glass transition temperatures (T_gs) could be easily measured in the second heating rate trace of DSC. The T_gs of the polymers with observable shifts on DSC curves were in the range of 213-289 °C.

The crystallinity of polyamide-imides was determined by X-ray diffraction, as shown in Figure 1. Polymers V_c, e, f, g, and V_h were determined in a powder form, and some polymers, such as V_a, b, d, i, and V_j, which could be cast into films from DMAc solution were measured with films. Among these polymers, the powders show a crystalline pattern, and the films, except V_a, exhibit amorphous patterns. The crystalline nature of those polymers with powder form accounts for their poor solubility in organic solvents as shown in Table IV.

Tough films of polymers derived from diamines, such as m-phenylenediamine (IV_d), 2,4-toluene-diamine (IV_b), 3,4'-oxydianiline (IV_d), and those containing two ether linkages together with one isopropylidene group (IV_i) or one sulfonyl group (IV_j) between three benzene rings, can be cast from the DMAc solution of polyamide-imides. Their mechanical properties are summarized in Table VI. The tensile strength of these films reached as high as 119 MPa (for polymer V_d). Some polymers, like V_b and V_i, behave like a ductile material with a yield point (the yield strength are 63 and 83 MPa, respectively). The initial modulus were in the range of 2.10-2.97 GPa.

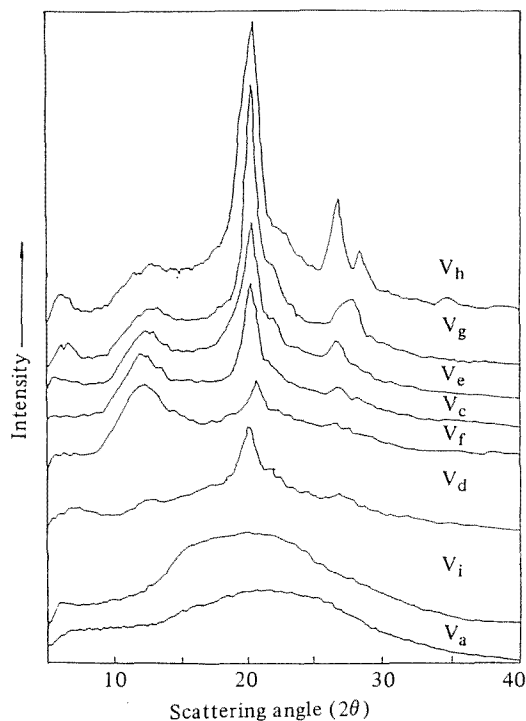


Figure 1. Wide-angle X-ray diffractograms of polyamide-imides.

Conclusion

The diimide-aiacid 1,3-bis(4-trimellitimidophenoxy) benzene was prepared from the condensation of 1,3-bis(4-aminophenoxy)benzene and trimellitic anhydride, and was used as a new polyamide-imide building block. A series of new polyamide-imides having high molecular weights were synthesized from the diimide-diacid with various aromatic diamines through direct polycondensation by using triphenyl phosphite and pyridine as condensing agents in NMP containing CaCl₂ or LiCl. Depending on the diamine used, most of the polymers were characterized with good solubility and high glass transition temperatures of 213-289°C with high thermal stability. Thus, these polyamide-imides may be candidates for high performance polymer materials.

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