

Preparation of Poly(amide-Imide)s by Direct Polycondensation with Triphenyl Phosphite. IV. Aliphatic-Aromatic Poly(amide-Imide)s Based on *N,N'*-Bis(ω -Carboxyalkyl)pyromellitimides

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Synopsis

Four diimide-diacids **3a-d** were synthesized from pyromellitic dianhydride and amino acids of the formula $\text{HOOC} - (\text{CH}_2)_m - \text{NH}_2$, with $m = 1, 3, 5, 10$. These diacids were condensed directly with various aromatic diamines using triphenyl phosphite in *N*-methyl-2-pyrrolidone (NMP)-pyridine solution in the presence of calcium chloride. The resulting poly(amide-imide)s have an aliphatic-aromatic structure and the relation between the general properties and the amount of the aliphatic part in the repeat unit was studied. IR spectroscopy, elemental analysis, and inherent viscosity measurements were used for the characterization. Studies of solubility, DSC traces, thermal stability, and crystallinity were also made.

INTRODUCTION

In the previous parts of this series¹⁻³ the reaction promoted by triphenyl phosphite and pyridine has been successfully applied to the direct polycondensation of imide-containing dicarboxylic acids and aromatic diamines, where the imide diacids were synthesized from trimellitic anhydride. Continuing this line, the diimide-diacids **3a-d** were previously obtained from pyromellitic dianhydride and aliphatic ω -amino acids and then directly polycondensed with aromatic diamines via the phosphorylation reaction preparing several aliphatic-aromatic poly(amide-imide)s. The resultant polymers have been characterized with special interest in their solubility, thermal properties, and crystallinity.

EXPERIMENTAL

Materials

Glycine (Hanawa), γ -amino-*n*-butyric acid (TCI), ϵ -amino-*n*-caproic acid (TCI), and 11-aminoundecanoic acid (Sigma) were used without purification. Pyromellitic dianhydride (Fluka) was recrystallized from boiling acetic anhydride. *p*-Phenylenediamine (Wako) was vacuum distilled before use. All other diamines were of high purity when received from the manufacturers and used

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TABLE I
Yields and Properties of the Diacids **3a-d** Prepared from
Pyromellitic Dianhydride and Various Amino Acids

Diacids (<i>m</i>)	Yield (%)	mp (°C)	Formula (Molecular weight)	Elemental analysis			
				C	H	N	
3a (1)	78 (95) ^a	> 360	C ₁₄ H ₈ N ₂ O ₈ (332.22)	Calcd	50.61	2.42	8.43
				Found	50.69	2.12	8.18
3b (3)	80 (98)	279–280	C ₁₈ H ₁₆ N ₂ O ₈ (388.33)	Calcd	55.67	4.15	7.21
				Found	55.66	4.04	7.32
3c (5)	84 (98)	235–236	C ₂₂ H ₂₄ N ₂ O ₈ (444.44)	Calcd	59.45	5.44	6.30
				Found	59.55	5.43	6.32
3d (10)	75 (90)	194–195	C ₃₂ H ₄₄ N ₂ O ₈ (584.17)	Calcd	65.73	7.58	4.79
				Found	65.58	7.48	4.70

^a Yield before recrystallization.

without any further purification. Commercially obtained anhydrous CaCl₂ was dried under vacuum at 180°C for 10 h. *N*-Methyl-2-pyrrolidone (NMP) (Merck) and pyridine (Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TCI) was purified by vacuum distillation.

Synthesis of *N,N'*-Bis(ω -Carboxyalkyl)pyromellitimides

Pyromellitic dianhydride (0.2 mol) and an ω -amino acid (0.4 mol) were heated in 250–300 mL of dry dimethylformamide to 60°C for 1 h. About 80 mL of toluene was added, and the mixture was further heated with reflux for about additional 3 h until about 7.2 mL of water was distilled off azeotropically. Afterwards, the reaction mixture was poured into cold water; the precipitated crude diacids were isolated by filtration and recrystallized from hot dimethylformamide by dropwise addition of water. Yields and properties of the diacids **3a-d** are summarized in Table I.

Polymerization

A typical example of polymerization was as follows. A mixture of 0.83 g (2.5 mmol) of diacid **3a**, 0.50 g (2.5 mmol) of 4,4'-oxydianiline (**4a**), 2.0 g of calcium chloride, 1.61 g (5.2 mmol) of triphenyl phosphite, 3.3 mL of pyridine, and 13.3 mL of NMP was heated with stirring at 100°C for 3 h under nitrogen. The obtained polymer solution was trickled on 500 mL of methanol giving rise to a fibrous yellow precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was quantitative. Inherent viscosity of the polymer in dimethylacetamide (DMAc) containing 5 wt % LiCl was 1.60 dL/g, measured on a concentration of 0.5 g/dL at 30°C.

IR(film): 1780 and 1720 (C=O imide), 1100 and 720 (imide ring), 1650 (C=O amide), 3300 (N—H amide) cm⁻¹.

ANAL. Calcd for (C₂₆H₁₆N₂O₇)_{*n*}: C, 66.67; H, 3.44; N, 5.98. Found: C, 66.58; H, 3.50; N, 5.90.

All the other poly(amide-imide)s were synthesized by an analogous procedure.

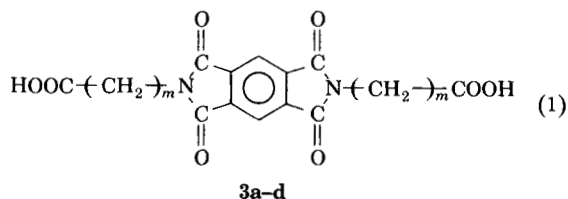
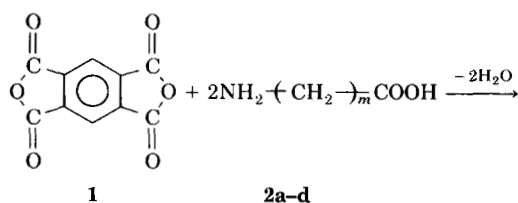
Measurements

The inherent viscosities were measured with a Cannon-Fenske viscosimeter thermostated at 30°C. IR spectra were recorded on a Jasco IRA-2 Grating Infrared Spectrophotometer. The DSC traces were measured on a Dupont 910 differential scanning calorimeter coupled to a Dupont 1090 thermal analyzer at the rate of 10°C/min in flowing nitrogen (30 cm³/min). Thermogravimetry (TG) was performed with a Dupont 951 thermogravimetric analyzer coupled to a Dupont 1090 thermal analyzer. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (50 cm³/min) at a heating rate of 10°C/min. Wide-angle x-ray diffractograms were obtained on a Rigaku Geiger D-max IIIa, using Ni-filtered Cu-K_α radiation (30 kV, 15 mA).

RESULTS AND DISCUSSION

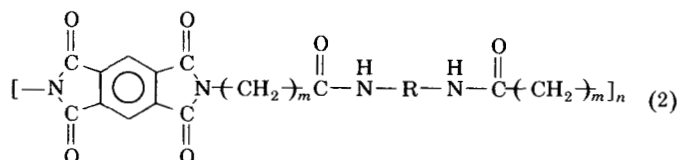
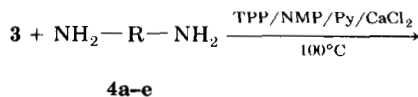
Polymer Synthesis

Two steps were taken to obtain these poly(amide-imide)s: first diacids containing imide rings were obtained [eq. (1)], and second these diacids were condensed directly with aromatic diamines by a method discussed here below.

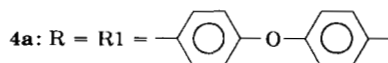


2a-d: $m = 1, 3, 5, 10$

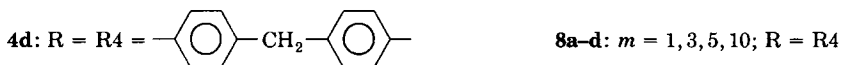
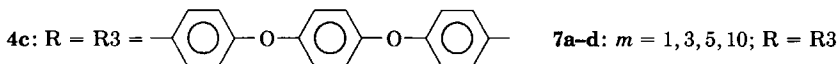
3a-d: $m = 1, 3, 5, 10$



5, 6, 7, 8, 9



5a-d: $m = 1, 3, 5, 10$; R = R1



As explained in the experimental section, diacids containing preformed imide groups were obtained by the condensation of pyromellitic dianhydride (**1**) with ω -amino acids (**2a-d**) in a 1 : 2 molar ratio. The method generally used was a reaction in solution, first obtaining open amic acids; then the chains were closed by heat treatment. In this work, the complete cyclization of the intermediate amic acids was achieved by the toluene-water azeotropic distillation. Yields, melting points, and elemental analyses of all diacids used in this work are summarized in Table I. The yields of diacid diimides were high, and their elemental analyses and characteristic bands on the IR spectra agree with the proposed structures.

The recrystallized diacids **3a-d** were condensed directly with various diamines in the mixture of NMP and pyridine (Py) in the presence of triphenyl phosphite (TPP) and calcium chloride at 100°C [eq. (2)]. All poly(amide-imide)s were isolated as yellowish materials with almost quantitative yields; their inherent viscosities are summarized in Table II. The reaction has been proposed to proceed via an acyloxy *N*-phosponium salt of pyridine followed by aminolysis.⁴ The inherent viscosities of the resulting polymers mainly depend on such factors as the nature of the monomer, solubility of polymers, monomer concentration, reaction temperature, solvent composition, and stoichiometry. Many experiments in which solvent, amount of CaCl₂, monomer concentration, temperature, etc., were varied convinced us that the conditions listed in Table II have been optimized.

In comparison with the analogous poly(amide-imide)s derived from 4,4'-oxydianiline (**4a**), the series of poly(amide-imide)s **6a-d** derived from 3,4'-oxydianiline (**4b**) showed lower inherent viscosities. This may be attributable to the lower basicity of the latter diamine owing to meta-substitution. In the preparation of the series of polymers **9a-d** of *p*-phenylenediamine (**4e**), a lower reactant concentration like 0.1 mol/L should be employed in order to prevent precipitation of the resulting polymers. Higher concentrations produced precipitation and yielded polymers of low molecular weight. It was noted that those polymers whose repeat unit contains a chain of ten aliphatic carbons were insoluble in polar solvents such as DMAc. Therefore, concentrated sulfuric acid was used as the solvent for viscosity measurements. The values in parentheses indicated in the last column of Table II are the inherent viscosities of the polymers which were prepared from the diacid chloride of **3a** and corresponding diamines.⁵ They are much lower than those reported in

TABLE II
Preparation of Poly(amide-Imide)s from Diacids **3a-d** and Diamines **4a-e**

Formula	<i>(m, R)</i> ^a	Monomer concentration ^b		Polymer	
		mol/L	(wt %)	Yield (%)	η_{inh}^c (dL/g)
5a	(1, R1)	0.15	(7.1)	99	1.60 (0.41) ^d
5b	(3, R1)	0.20	(11.7)	97	0.88
5c	(5, R1)	0.20	(12.9)	98	0.84
5d	(10, R1)	0.15	(10.7)	97	1.00 ^e
6a	(1, R2)	0.15	(7.1)	99	1.13
6b	(3, R2)	0.20	(11.7)	99	0.64
6c	(5, R2)	0.20	(12.9)	99	0.66
6d	(10, R2)	0.15	(10.7)	98	0.83 ^e
7a	(1, R3)	0.15	(8.4)	99	1.55
7b	(3, R3)	0.20	(13.6)	99	0.91
7c	(5, R3)	0.20	(14.7)	99	0.90
7d	(10, R3)	0.15	(13.1)	99	1.47 ^e
8a	(1, R4)	0.15	(7.1)	99	1.55 (0.76) ^d
8b	(3, R4)	0.20	(11.7)	99	0.78
8c	(5, R4)	0.20	(12.8)	99	0.74
8d	(10, R4)	0.15	(10.7)	98	0.88 ^e
9a	(1, R5)	0.10	(4.4)	99	1.07 (0.54) ^d
9b	(3, R5)	0.10	(4.9)	99	0.72
9c	(5, R5)	0.10	(5.5)	99	0.76
9d	(10, R5)	0.10	(6.9)	98	0.83 ^e

^a*m*: number of methylene groups in the spacer; R: substituent in diamine.

^bDiacid = diamine = 2.5 mmol; TPP = 5.2 mmol; NMP/Py = 4/1 by volume; CaCl₂ = 12 wt %; temperature = 100°C; time = 3 h.

^cMeasured with *C* = 0.5 g/dL at 30°C in DMAc-5% LiCl.

^dValues in parentheses were reported in the previous work (see Ref. 5), where the polymers were prepared via acid chloride route.

^eMeasured with *C* = 0.5 g/dL in conc. sulfuric acid.

this work. This indicates that the direct synthesis route by means of triphenyl phosphite provides a more convenient and effective procedure for the preparation of this kind of poly(amide-imide)s.

Polymer Characterization

Solubility

The solubilities of poly(amide-imide)s are listed in Table III. A 10% solution was taken as the criterion for the polymer solubility. Among these five series of poly(amide-imide)s, the series of **6a-d** prepared from 3,4'-oxydianiline showed better solubility due to the existence of an unsymmetrical 3,4'-diphenyl ether unit along the polymer main chain. Another factor affecting the solubility is the number of methylene units introduced in each polymer. For the polymers derived from the para-substituted diamines, those with longer aliphatic chain (e.g., *m* > 3) showed less solubility in polar amide-type solvents, such as DMF, DMAc, NMP, and 1,3-dimethyl-2-imidazolidone (DMI), whereas they showed to be more easily dissolved in *m*-cresol when

TABLE III
 Solubility of Poly(amide-Imide)s^a

Polymer	Solvent ^b								
	DMF	DMAc	NMP	DMI	HMPT	DMSO	<i>m</i> -Cresol	Pyridine	Conc. H ₂ SO ₄
5a	+	+	+	+	+h	+h	-	-	+
5b	-	-	-	-	+h	+h	s	-	+
5c	-	-	+h	-	+	+	+	-	+
5d	+h	+h	+h	+h	+h	+h	+h	-	+
6a	+	+	+	+	+h	+	+	+	+
6b	+	+	+	+	+h	+	+	+	+
6c	+h	+	+	+	+	+	+	-	+
6d	+h	+h	+h	+h	+	+h	+	+h	+
7a	-	+h	+h	+h	+h	-	-	-	+
7b	-	-	-	-	+h	-	s	-	+
7c	-	-	-	-	+h	-	+	-	+
7d	-	sh	sh	+h	-	-	sh	-	+
8a	-	+	+	+	sh	+	-	-	+
8b	-	-	-	-	+	-	+	-	+
8c	-	-	+h	-	+	-	+	-	+
8d	-	-	-	-	-	-	+h	-	+
9a	+	+	+	+	+h	+	-	-	+
9b	-	-	-	-	+h	-	s	-	+
9c	-	-	-	-	+h	-	+h	-	+
9d	-	-	-	-	-	-	sh	-	+

^aSolubility: +, soluble at room temperature; s, swelling at room temperature; +h, soluble on heating; sh, swelling on heating; -, insoluble.

^bDMF, dimethylformamide; DMAc, dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMI, 1,3-dimethyl-2-imidazolidone; HMPT, hexamethylphosphoric triamide; DMSO, dimethylsulf-oxide.

compared to those containing only one methylene group. All the poly(amide-imide)s were practically insoluble in common organic solvents like benzene, acetone, methanol, and hexane; however, they were soluble in concentrated sulfuric acid. In general these poly(amide-imide)s based on pyromellitimide showed less solubility than their homologs with trimellitimide units as described in our previous reports.^{1,3}

DSC Measurements

All poly(amide-imide)s of this work were characterized by DSC measurements with a heating rate of 10°C/min. The DSC measurements of the poly(amide-imide)s **7c-d** and **8b-d** display two endotherms in the first and second heating traces (Fig. 1). Upon cooling from the melt the DSC traces exhibit an exotherm below 300°C which represents the crystallization process. This exotherm is detectable regardless of the cooling rate, indicating that the rates of crystallization are high. The poly(amide-imide)s **6b** and **6c** derived from 3,4'-oxydianiline also showed two endotherms in the first heating traces; however, they crystallized so slowly that after quenching in air only glass-transition temperatures (T_g s) were measurable in the second heating traces (Fig. 2). In the case of shorter aliphatic chains (e.g., $m = 1$), rapid thermal degradation prevents observation of endotherms (Table IV). Similar behavior

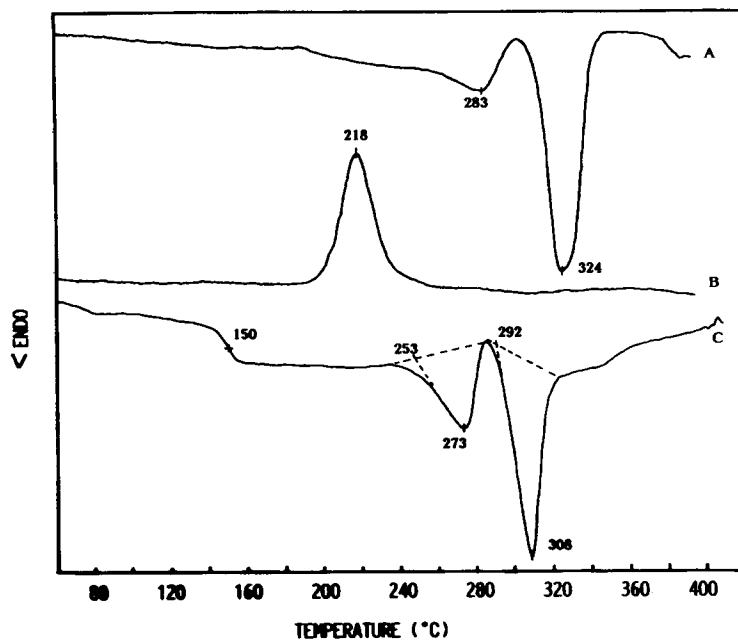


Fig. 1. DSC traces (with heating and cooling rates of $10^{\circ}\text{C}/\text{min}$) of the poly(amide-imide) 7c: (A) first heating; (B) cooling; (C) second heating .

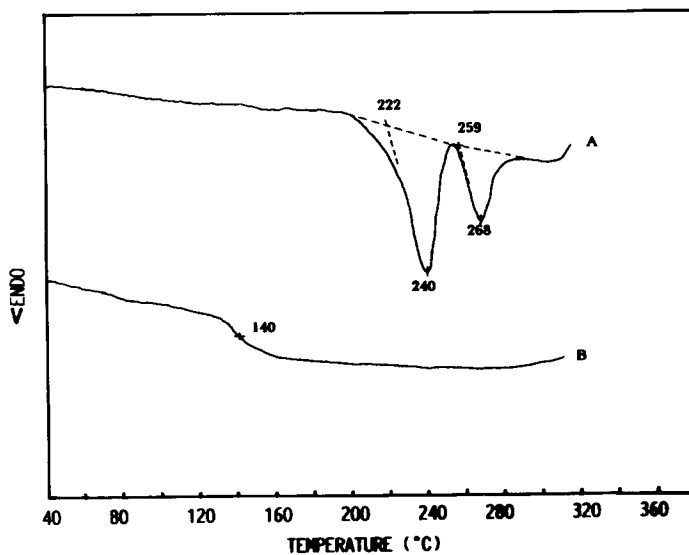
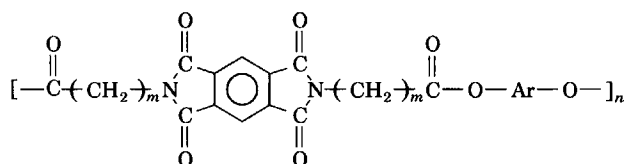


Fig. 2. DSC traces (rate $10^{\circ}\text{C}/\text{min}$) of poly(amide-imide) 6c: (A) first heating; (B) second heating.

was also found in the DSC traces of polymer **9b** and **9c** containing more rigid *p*-phenylene unit even though they have longer aliphatic chains. Anyway the polymer **9d** with 10 methylene units showed a sharp endotherm at 300°C.

Quenching from the melt in air yielded more amorphous samples so that in all cases T_g 's could be easily measured in the second heating traces of DSC. The T_g 's listed in Table IV show an obvious tendency to increase with decreasing length of the aliphatic chains. This tendency is reasonable because the segmental mobility decreases in the same order.

It is of interest to compare the poly(amide-imide)s of this report with structurally similar poly(ester-imide)s (**10**):



10

For the poly(ester-imide)s containing hydroquinone or bis(4-hydroxyphenyl) ether with $m = 4, 5, 10, 11$, Kricheldorf et al.⁶ have reported that they exhibited a mesophase, even though both bisphenols are not mesogenic. Obviously,

TABLE IV
Thermal Behavior Data of Poly(amide-Imide)s^a

N. Polymer	DSC			TGA			Wt % residual at 800°C
	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	Temperature (°C) at following weight loss			
				5%	10%	30%	
5a	273	—	—	415	432	545	52.1
5b	232	353	—	390	405	565	55.0
5c	156	317	—	428	441	471	42.3
5d	114	268	—	441	457	481	29.9
6a	252	—	—	406	428	544	48.5
6b	197	246	298	400	421	468	47.7
6c	140	222	259	422	441	476	42.0
6d	104	215	—	443	459	482	18.0
7a	271	—	—	409	434	566	53.1
7b	212	348	—	400	421	468	54.8
7c	150	253	292	439	452	481	42.0
7d	109	240	277	445	457	486	24.0
8a	244	—	—	403	435	498	43.5
8b	200	344	360	400	413	549	55.7
8c	167	304	317	412	430	495	53.8
8d	116	252	265	445	460	485	27.0
9a	265	—	—	425	435	491	46.0
9b	230	—	—	410	430	462	49.1
9c	180	—	—	430	442	471	46.0
9d	120	300	—	446	460	480	20.2

^aDSC and TGA were determined with a heating rate of 10°C/min under N₂.

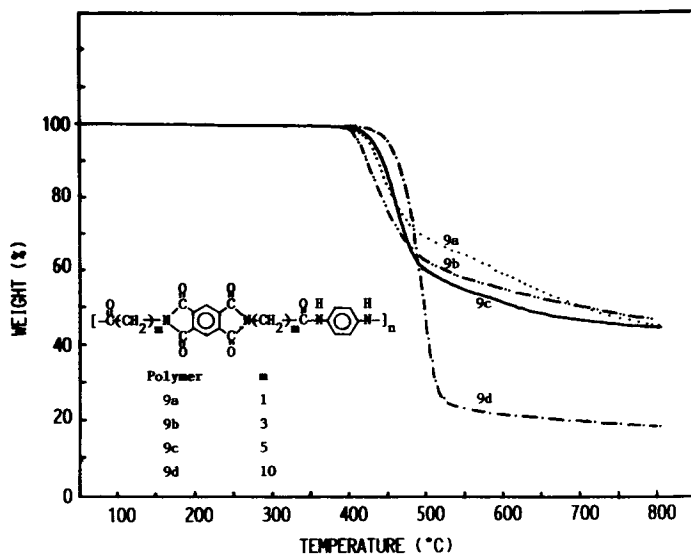


Fig. 3. TG curves of poly(amide-imide)s **9a-d**.

in this case the pyromellitimide unit plays the role of mesogen. Therefore, from the observation of two endotherms in the DSC traces as described above, we expect that some of poly(amide-imide)s of this work are potential for liquid-crystal formation. However, further microscopic characterization is necessary to confirm this assumption. Further study of polarization microscopy is in progress, and the results will be reported in the near future.

Thermal Stability

The thermal stability of the poly(amide-imide)s was characterized by means of thermogravimetical analyses conducted at a heating rate of 10°C/min in nitrogen. Figure 3 shows TG curves of polymer **9a-d**. From the values compiled in Table IV for the degradation temperatures it can be concluded that the thermal stability does not depend directly on the number of aliphatic carbons, contrary to what happened in the case of T_g s and T_m s. There are not great differences for the thermal stability of poly(amide-imide)s with one to ten methylene groups, being more stable in the case of ten or five methylenes than in the case of one or three methylenes. The nature of the diamine does not seem to affect the thermal stability significantly. Table IV also shows the residual weight of poly(amide-imide)s at 800°C under nitrogen. As it could be expected, the lowest values correspond to the polymers containing ten methylene units.

Crystallinity

All the polymers were characterized by wide-angle x-ray diffraction. Almost all poly(amide-imide)s of this kind showed crystalline nature, except some derived from 3,4'-oxydianiline. Figure 4 shows the x-ray diffraction patterns of the **5a-d** series polymers. All of them revealed crystalline nature due to the

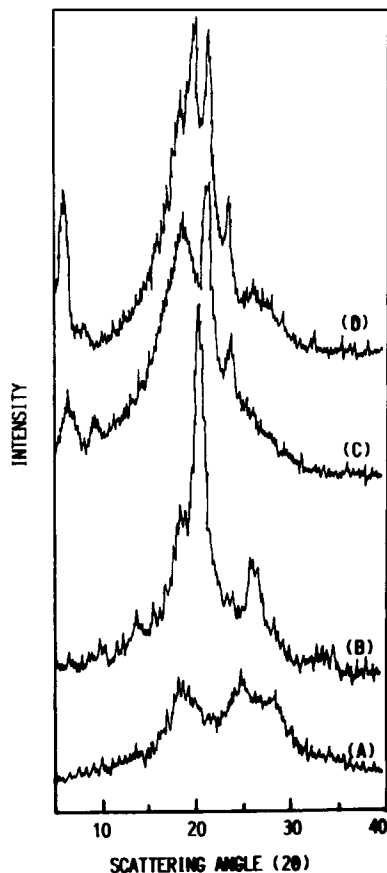


Fig. 4. Wide-angle x-ray diffractograms of poly(amide-imide)s: (A) 5a, (B) 5b, (C) 5c, and (D) 5d.

symmetrical structure of polymer backbone. Longer aliphatic carbons in the repeating units of polymer chain leads to higher crystallinity, and thus, to lower solubility and higher initial decomposition temperatures, as described above.

We wish to thank Dr. T. S. Lin, the President of Tatung Institute of Technology, and the National Science Council of the Republic of China for their generous support (Grant No. NSC-78-0405-E-036-08).

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Received July 24, 1989

Accepted October 31, 1989