Synthesis and Properties of Aliphatic-Aromatic Poly(amide-Imide)s from Sulfonyldianilines and N,N'-Bis(ω-Carboxyalkyl)pyromellitimides

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SYNOPSIS

Seven imide-containing dicarboxylic acids **IIa–g** were synthesized from pyromellitic dianhydride and amino acids of the formula $HOOC-(CH_2)_m-NH_2$, with m = 1, 2, 3, 4, 5, 10, 11. These diacids were condensed directly with 3,3'- or 4,4'-sulfonyldianiline using triphenyl phosphite in N-methyl-2-pyrrolidone (NMP)–pyridine solution containing calcium chloride and lithium chloride. The resulting poly(amide-imide)s have moderate to high inherent viscosities ranging from 0.47 to 2.02 dL/g in dimethylacetamide. These polymers showed excellent solubility in polar solvents such as NMP, and most of them could be cast into transparent and tough films. Glass transition temperatures (T_gs) of these poly(amide-imide)s were recorded in the range 116–258°C and increased with decreasing number of methylene groups in the repeated unit. The polymers with longer aliphatic chains (e.g., m = 10 and 11) exhibited higher crystallinity, higher initial decomposition temperature, and lower solubility in polar solvents.

INTRODUCTION

Direct polycondensation promoted by triphenyl phosphite (TPP) and pyridine is known to be a facile method for polyamide synthesis;[1,2] aromatic-aliphatic and wholly aromatic polyamides were readily obtained from combinations of aromatic diamines with aliphatic and aromatic dicarboxylic acids, respectively. We have successfully applied the direct polycondensation procedure to the poly(amide-imide) formation from imide-containing dicarboxylic acids and aromatic diamines.[3–5] This synthetic approach has been proved to be more efficient and convenient when compared to the imide-containing diacyl chloride + diamine route reported by other researchers.[6,7]

In an earlier article[8] we have described the direct synthesis of a variety of poly(amide-imide)s from various combinations of four N,N'-bis(ω-carboxyalkyl)pyromellitimides (i.e., **IIa, c, e,** and **f**) and

five aromatic diamines. However, most of the polymers described in that article were highly crystalline with poor solubility in most organic solvents. This made them intractable useless materials. In this work, an improvement of the solubility is attempted by introducing sulfonyl groups into the backbone of the polymers by using sulfonyldianilines as the diamine monomers. In general, sulfonyldianilines yielded lower molecular weight polyamides by the reaction with aromatic dicarboxylic acids by means of TPP–pyridine, probably because of the lower basicity of their amino groups. However, aliphatic diacids generally react with aromatic diamines in the polycondensation reaction promoted by TPP to give polyamides of higher inherent viscosity than those obtained using aromatic diacids.[9] We therefore assumed that the direct polycondensation reactions of 3,3'- or 4,4'-sulfonyldianiline and aliphatic carboxylic acid-terminated diimide-diacids may be effected by using TPP as the condensing agent. In addition to the four diimide-diacids employed in the previous article,[8] another three diimide-diacids, i.e., **IIb, d,** and **g,** will be prepared and used in the preparation of poly(amide-imide)s. Solubility, thermal behavior,

crystallinity, and mechanical properties of the obtained polymers will also be investigated.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (Fluka) was recrystallized from boiling acetic anhydride. Seven ω-amino acids, namely glycine (Hanawa), β-alanine (Hanawa), γ-amino-n-butyric acid (TCI), δ-amino-n-pentanoic acid (TCI), ϵ-amino-n-caproic acid (TCI), 11-aminoundecanoic acid (Sigma), and 12-aminolauric acid (TCI), were all used as received. Commercially obtained anhydrous LiCl and $CaCl_2$ were dried under vacuum at 150°C for 6 h and 180°C for 10 h, respectively. N-Methyl-2-pyrrolidone (NMP), N,N'-dimethylacetamide (DMAc), N,N'-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular seives. Triphenyl phosphite (TCI) was purified by distillation under reduced pressure. 3,3'-Sulfonyldianiline and 4,4'-sulfonyldianiline (TCI) were of high purity when received from the manufacturers and used without any further purification. Imide-dicarboxylic acids were obtained as previously reported, from pyromellitic dianhydride and ω-amino acids.[8]

Polymerization

Polymer M-IIIg from I-M and IIg

A mixture of 0.766 g (1.25 mmol) of diacid **IIg**, 0.31 g (1.25 mmol) of 3,3'-sulfonyldianiline (**I-M**), 0.3 g of calcium chloride, 0.6 g of lithium chloride, 0.8 mL of triphenyl phosphite, 1.6 mL of pyridine, and 7 mL of NMP was heated with stirring at 100°C for 3 h under nitrogen. As the polycondensation proceeded, the solution became viscous and the LiCl and $CaCl_2$ suspension dissolved. The poly(amide-imide) was isolated as a stringy mass by precipitation from methanol. It was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was 0.98 g (98%). The product exhibited an inherent viscosity of 1.23 dL/g in conc. H_2SO_4 on 0.5 g/dL.

IR (film): 1771 and 1707 (C=O imide), 1108 and 729 (imide ring), 1667 (C=O amide), 3300 (N—H amide) cm^{-1}.

ANAL. Calcd for $(C_{46}H_{56}O_8N_4S)_n$: C, 66.97; H, 6.84; N, 6.79. Found: C, 66.63; H, 6.90; N, 6.77.

Other poly(amide-imide)s were prepared by a similar procedure.

Measurements

Elemental analyses were run in a Perkin-Elmer Model 240 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 Dupont 910 differential scanning calorimeter coupled to a Dupont 1090 thermal analyzer at the rate of 20°C/min in flowing nitrogen (30 cm^3/min). Thermogravimetry (TG) was conducted 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 cm^3/min) at a heating rate of 20°C/min.

The wide-angle x-ray measurements were performed at room temperature (ca. 25°C) with film specimens of about 0.1 mm thick on a Rigaku Geiger Flex D-Max IIIa x-ray diffractometer, using Ni-filtered $CuK\alpha$ radiation (30 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 gage 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

Synthesis and Characterization of Polymers

The N,N'-bis(ω-carboxyalkyl)pyromellitimides **IIa–g** were synthesized from the corresponding ω-amino acids and pyromellitic dianhydride. The diacids **IIa, c, e,** and **f** have been demonstrated in the previous article.[8] The other diacids were prepared by an analogous procedure previously reported.[8] The yields of these diacids were high, and their elemental analyses and characteristic absorptions on the IR spectra agree well with the proposed structures.
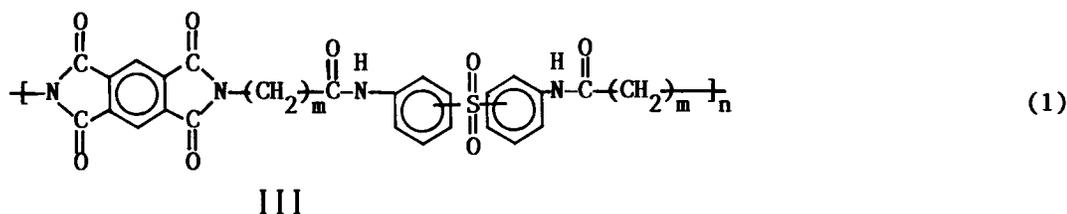
The recrystallized diacids **IIa–g** were condensed directly with 3,3'- (**I-M**) and 4,4'-sulfonyldianiline (**I-P**) in the mixture of NMP and pyridine (about 4 : 1 by volume) in the presence of triphenyl phosphite (TPP), lithium chloride, and calcium chloride at 100°C [eq. (1)].
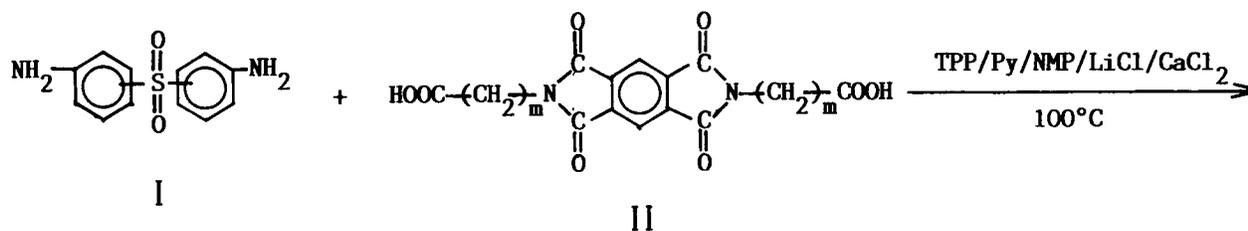
I-M: 3,3'-Sulfonyldianiline

I-P: 4,4'-Sulfonyldianiline

IIa-g: m = 1, 2, 3, 4, 5, 10, 11

(1)

III

IIIa-g: m = 1, 2, 3, 4, 5, 10, 11

Solutions of polymers were precipitated into methanol. Depending on the inherent viscosity, powdered or stringy polymers were obtained. It was also observed that the inherent viscosity is in relation to the ability to form flexible films. The yields and inherent viscosities of all poly(amide-imide)s are summarized in Table I. The yields of all polymers fall into the range of 94–99% and mainly depend on losses during the mechanical workup. For convenience sake, the polymers are described as **P**- and **M-IIIa-g** with **P** and **M** being the positions of the two amine groups in the starting diaminodiphenyl sulfones (sulfonyldianilines). For example, **M-IIIg** is the polymer prepared from 3,3'-sulfonyldianiline and diimide-diacid **IIg**.

These polycondensation reactions have been proposed to proceed via an acyloxy N-phosphonium salt of pyridine in the work reported by Yamazaki et al.[1] However, Aharoni and co-workers[10] suggested another mechanism for this phosphorylation reaction according to the results of ^{13}C- and ^{31}P-NMR measurements. They demonstrated that the amidation reaction has two steps: in the first an initial reaction intermediate of diphenoxyaminophosphine is formed, which is then attacked by the carboxylic acid group through an intramolecular substitution to give the amide linkage. This polycondensation reaction was proved to be affected significantly by reaction temperature, monomer concentration, solvents, metal salts, and tertiary amine such as pyridine.[1] Many experiments in which solvent, amount

of LiCl and $CaCl_2$, reactant concentration, temperature, etc., were varied convinced us that the conditions listed in Table I have been optimized.

Table I. Preparation of Poly(amide-Imide)s from Diimide-Diacids **IIa–g** and Sulfonyldianiline[a]

Polymer Code	Yield (%)	η_{inh}[b] (dL/g) DMAc	Conc. H_2SO_4
M-IIIa	99	0.47	0.19
M-IIIb	99	2.02	0.84
M-IIIc	94	0.68	0.68
M-IIId	96	1.20	0.85
M-IIIe	97	1.48	1.03
M-IIIf	97	1.56[c]	1.06
M-IIIg	98	Insol.	1.23
P-IIIa	99	0.58	0.23
P-IIIb	99	0.84	0.29
P-IIIc	99	0.75	0.61
P-IIId	98	1.03	0.69
P-IIIe	99	1.00	0.79
P-IIIf	99	1.22[c]	0.86
P-IIIg	99	Insol.	0.79

[a] Polymerization was carried out with 1.25 mmol of each monomer, each monomer, 0.8 mL of TPP, 1.6 mL of pyridine, 0.3 g of $CaCl_2$, and 0.6 g of LiCl in 7 mL of NMP at 100°C for 3 h under nitrogen.

[b] Measured at 30°C on a concentration of 0.5 g/dL.

[c] Measured in DMAc containing 5 wt% of LiCl dissolved.

Table II. Elemental Analysis of Poly(amide-Imide)s

Polymer	Formula (molecular weight)	C (%) Calcd	C (%) Found	H (%) Calcd	H (%) Found	N (%) Calcd	N (%) Found
M-IIIa	$(C_{26}H_{16}O_8N_4S\,2H_2O)_n$ $(580.53)_n$	53.79	54.22	3.13	3.55	9.65	8.97
P-IIIa	$(C_{26}H_{16}O_8N_4S\,2H_2O)_n$ $(580.53)_n$	53.79	53.56	3.13	3.22	9.65	9.26
M-IIIb	$(C_{28}H_{20}O_8N_4S\,H_2O)_n$ $(590.57)_n$	56.95	57.17	3.75	3.71	9.49	9.21
P-IIIb	$(C_{28}H_{20}O_8N_4S\,H_2O)_n$ $(590.57)_n$	56.95	55.98	3.75	3.66	9.49	8.85
M-IIIc	$(C_{30}H_{24}O_8N_4S)_n$ $(600.61)_n$	59.99	58.87	4.03	3.97	9.33	8.89
P-IIIc	$(C_{30}H_{24}O_8N_4S)_n$ $(600.61)_n$	59.99	57.89	4.03	4.01	9.33	8.63
M-IIId	$(C_{32}H_{28}O_8N_4S)_n$ $(628.66)_n$	61.14	60.00	4.49	4.48	8.91	8.57
P-IIId	$(C_{32}H_{28}O_8N_4S)_n$ $(628.66)_n$	61.14	59.47	4.49	4.53	8.91	8.35
M-IIIe	$(C_{34}H_{32}O_8N_4S)_n$ $(656.72)_n$	62.18	61.47	4.91	4.89	8.53	8.29
P-IIIe	$(C_{34}H_{32}O_8N_4S)_n$ $(656.72)_n$	62.18	61.65	4.91	4.89	8.53	8.08
M-IIIf	$(C_{44}H_{52}O_8N_4S)_n$ $(796.99)_n$	66.31	65.99	6.58	6.62	7.03	7.04
P-IIIf	$(C_{44}H_{52}O_8N_4S)_n$ $(796.99)_n$	66.31	65.66	6.58	6.57	7.03	7.07
M-IIIg	$(C_{46}H_{56}O_8N_4S)_n$ $(825.04)_n$	66.97	66.63	6.84	6.90	6.79	6.77
P-IIIg	$(C_{46}H_{56}O_8N_4S)_n$ $(825.04)_n$	66.97	66.19	6.84	6.80	6.79	6.65

Because the inherent viscosity is affected by the chemical structure of polymer, a lower inherent viscosity does not necessarily reflect a lower degree of polymerization. However, from the η_{inh} data summarized in Table I, some conclusions may be drawn. As a rule, most of the poly(amide-imide)s derived from 3,3'-sulfonyldianiline showed higher inherent viscosity than those obtained using 4,4'-sulfonyldianiline. These results are reasonable because the electron-withdrawing sulfonyl group makes the amine group of para-substitution less electron rich and leads to a lower reactivity of polymerization. In addition, the length of aliphatic chain of the aliphatic imide diacids also influences the inherent viscosity of the resulting poly(amide-imide)s. With the exceptions of M-IIIb and P-IIIb, the longer the aliphatic sequence in the repeated unit the higher the inherent viscosity of the polymer. The relatively high inherent viscosity in DMAc obtained for M-IIIb is somewhat surprising. However, the η_{inh} value of M-IIIb decreased dramatically when measured in concentrated sulfuric acid. The other poly(amide-imide)s also showed lower η_{inh} in sulfuric acid than in DMAc. These may indicate molecular aggregate in the latter solvent.

These polymers were initially characterized by elemental analyses and infrared spectroscopy. Elemental analysis values are listed in Table II. It is seen that the longer the aliphatic chain in the repeated unit the closer the theoretical and the found values of analyses. These results are in agreement with the chemical structure as the water absorption ability diminishes when the fatty character of the polymer increases. Figure 1 shows the representative FTIR spectra of polymers M-IIIg and P-IIIg. The IR spectra exhibited characteristic absorptions for the imide ring at 1771 and 1707 cm^{-1}, indicative of the asymmetrical and symmetrical C=O stretching vibration, and at 1108 and 729 cm^{-1}, due to ring deformation. Bands of amide groups appear at 3326, 1667, and 1593 cm^{-1}. Absorptions at 1404 and 1154 cm^{-1} are peculiar to the sulfonyl group.
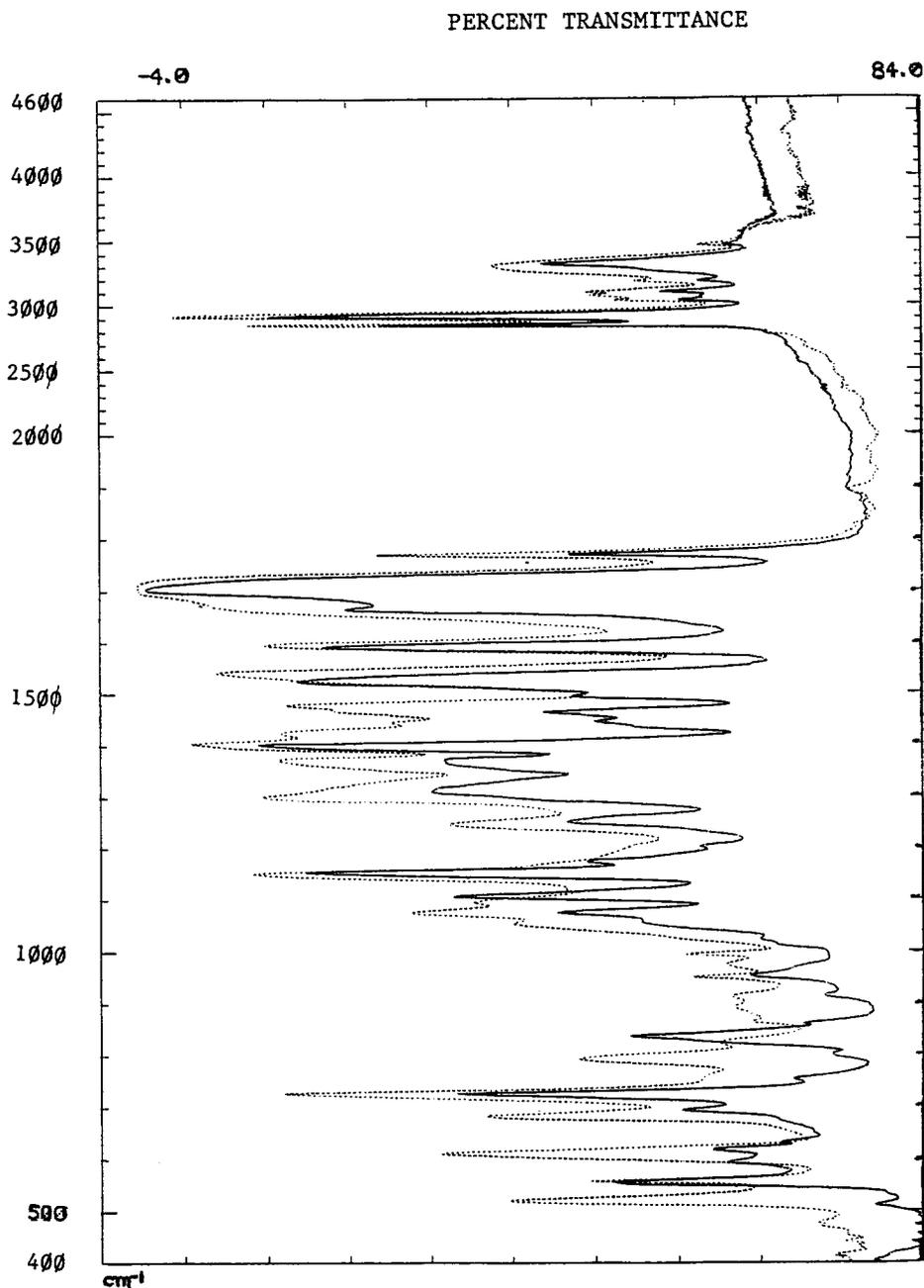
PERCENT TRANSMITTANCE

Figure 1. FTIR spectra of poly(amide-imide)s **M-IIIg** ($\cdots$) and **P-IIIg** (—).

Properties of Polymers

The qualitative solubilities of poly(amide-imide)s are listed in Table III. Almost all polymers are readily soluble in polar solvents such as NMP and 1,3-dimethyl-2-imidazolidone (DMI). This is probably due to the H-bonding and in part to the strong dipole–dipole interaction possible between the sulfonyl group and these amide-type solvents. However, solvents such as DMAc, DMF, and DMSO are not able to dissolve the poly(amide-imide)s with longer aliphatic chain, those containing 10 and 11 aliphatic carbons in the repeated unit, possibly attributable to the lower polarity and higher crystallinity of their polymer chains. All the polymers are practically insoluble in common organic solvents, such as benzene, acetone, tetrahydrofuran, chloroform, etc.; however, they are all soluble in conc. sulfuric acid. In general these poly(amide-imide)s based on sulfonyldianilines show better solubility than their ho-

Table III. Solubility of Poly(amide-Imide)s[a]

Polymer	DMAc	DMF	NMP	DMSO	Py	DMI
			Solvent[b]			
M-IIIa	+	+	+	+	−	+
P-IIIa	+	+	+	+	−	+
M-IIIb	+	+	+	+	−	+
P-IIIb	+	+	+	+	s	+
M-IIIc	+	+	+	+	+	+
P-IIIc	+	−	+	−	−	+
M-IIId	+	+	+	+	+	+
P-IIId	+	+	+	+	+	+
M-IIIe	+	+	+	+	+	+
P-IIIe	+	+	+	−	−	+
M-IIIf	−	−	+	−	s	+
P-IIIf	−	−	s	−	s	+
M-IIIg	−	−	+	−	−	+
P-IIIg	−	s	+	−	s	s

[a] Solubility: +, soluble; s, swelling; −, insoluble.
[b] DMF, dimethylformamide; DMAc, dimethylacetamide; NMP, N-methyl-2-pyrrolidone; DMI, 1,3-dimethyl-2-imidazolidone; DMSO, dimethylsulfoxide; Py, pyridine.

mologs with other diamine moieties as described in our previous report.[8] It may be concluded that the incorporation of sulfonyl groups into the polymer backbones is effective in increasing the solubility of these poly(amide-imide)s.

Thermal characterization was carried out by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). 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 traces of DSC. As expected, the T_gs listed in Table IV show an obvious tendency to decrease with increasing length of the aliphatic chains. This tendency is reasonable because the segmental mobility increases in the same order. Moreover, for the poly(amide-imide)s with the same aliphatic length, m-isomers showed lower T_gs when compared to p-isomers owing to the same reason.

Well-defined melting points of the polymers with shorter aliphatic chain (e.g., $m \leq 5$) could not be detectable by DSC, probably due to the low degree of crystallinity developed. Anyway, the poly(amide-imide)s with longer aliphatic chain (e.g., $m = 10$ and 11) show clearer melting endotherm by DSC measurements. As shown in Figures 2(A) and (B),

Table IV. Thermal Behavior of Poly(amide-Imide)s

Polymer	DSC			TG[c]			
	T_g^a (°C)	T_{m1}^b (°C)	T_{m2}^b (°C)	Temperature (°C) at Various Wt. Loss			Wt % Residual At 800°C
				5%	10%	30%	
P-IIIa	—[d]	—	—	429	455	503	41
P-IIIb	258	—	—	384	394	486	50
P-IIIc	246	—	—	417	426	483	48
P-IIId	226	—	—	394	406	449	47
P-IIIe	198	—	—	438	449	467	34
P-IIIf	141	160	188	448	460	475	14
P-IIIg	129	170	190	447	457	477	18
M-IIIa	—	—	—	426	453	501	34
M-IIIb	221	—	—	377	385	489	49
M-IIIc	214	—	—	413	426	496	50
M-IIId	197	—	—	493	409	459	46
M-IIIe	173	—	—	431	443	466	42
M-IIIf	120	184	224	447	461	480	16
M-IIIg	116	188 (182)[a]	—	441	460	480	17

[a] From the second heating traces of DSC measurements conducted with a heating rate of 20°C/min in nitrogen.
[b] Temperatures of the endotherm peaks in the first heating trace of DSC measurements.
[c] Thermogravimetry was conducted at a heating rate of 20°C/min in nitrogen.
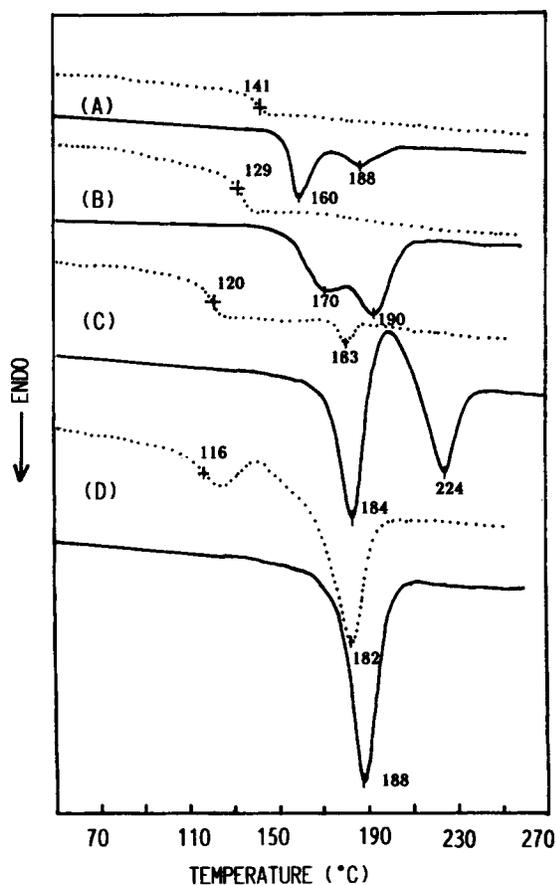[d] Not observed before decomposition.

Figure 2. DSC traces (with heating rate of 20°C/min) of the poly(amide-imide)s: (A) **P-IIIf**, (B) **P-IIIg**, (C) **M-IIIf**, and (D) **M-IIIg**. (—) first heating; (· · ·) second heating.
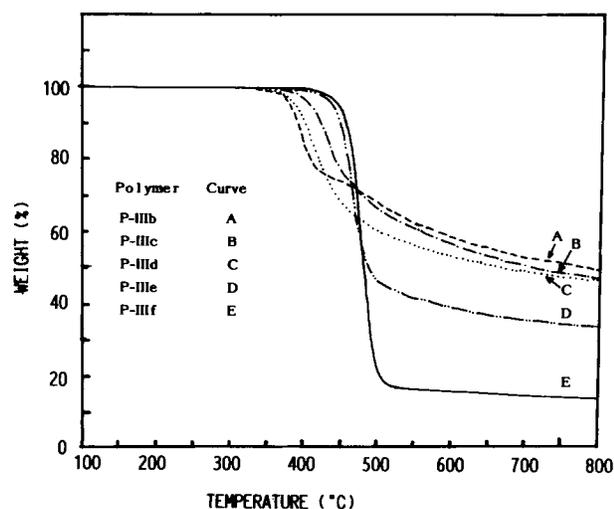

Figure 3. TG curves of poly(amide-imide)s **P-IIIb–f**, with a heating rate of 20°C/min in nitrogen.
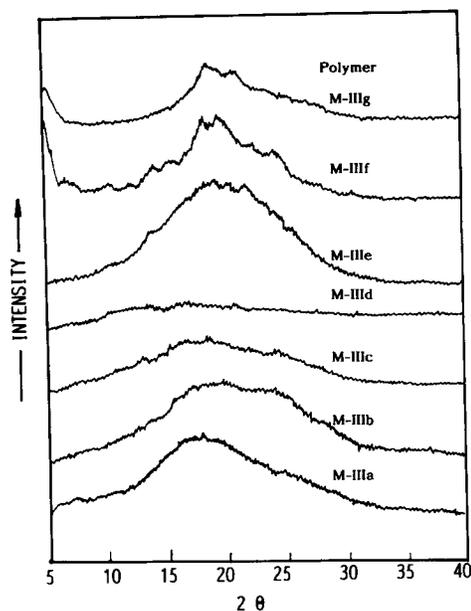

Figure 4. Wide-angle x-ray diffractograms of poly-(amide-imide)s **M-IIIa–g**.

polymers **P-IIIf** and **P-IIIg** displayed two broad closely neighboring peaks in the first heating DSC traces; however, they crystallized so slowly that after quenching in air only T_gs were measurable in the second heating trace. Polymer **M-IIIf** displayed two sharp neighboring peaks in the first heating DSC trace. These peaks coalesce into only one very small
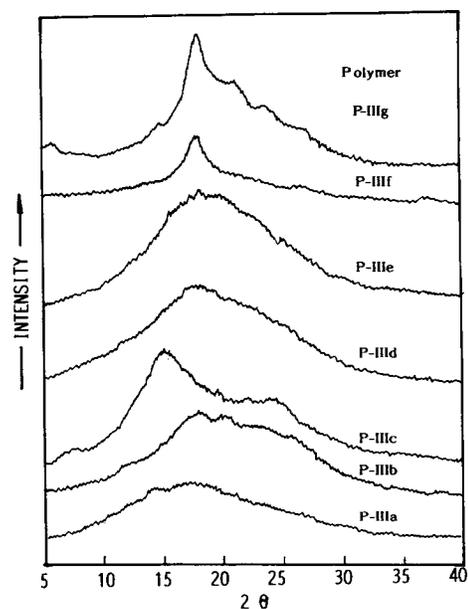

Figure 5. Wide-angle x-ray diffractograms of poly-(amide-imide)s **P-IIIa–g**.

Table V.   Tensile Properties of
Poly(amide-Imide) Films

Poly-mer[a]	Strength At Yield (MPa)	Strength At Break (MPa)	Elongation To Break (%)	Initial Modulus (GPa)
P-IIIc	—	59	6	1.67
M-IIId	—	49	5	1.62
P-IIId	39	51	44	1.43
M-IIIe	—	48	6	1.48
P-IIIe	34	42	161	1.00
M-IIIf[b]	59	43	99	1.46
M-IIIg[b]	34	33	193	0.97
P-IIIg[b]	50	46	50	1.19

[a] Films were cast from polymer solution of DMAc.
[b] Cast from polymer solution of NMP.

endotherm on repeated heating [Fig. 2(C)], and thus, may represent crystallites of different size and low crystallization rate. Only polymer **M-IIIg** showed one sharp endotherm, in addition to the strong glass transition signal, on the second heating DSC trace, indicating that it showed a higher rate of crystallization than the other poly(amide-imide)s. This interpretation is obvious because longer aliphatic chains reduce T_g and enhance the segmental mobility. Annealing did not alter the intensity and position of the endotherm peak to any significant extent, implying that these polymers are inherently slow in crystallization. This may be explained by the fact that the two oxygen atoms in the sulfones lie out of the conjugated plane, thereby inhibiting a closer packing.

Figure 3 shows typical TG curves of poly(amide-imide)s **P-IIIb–f** with a heating rate of 20°C/min under flowing nitrogen. The thermal resistance showed by the poly(amide-imide)s was moderately high. These polymers do not show obvious weight loss until the temperature reached 400°C, being more stable in the case of longer spacers. The TG data, temperatures at various percents of weight loss and char yield at 800°C, of all polymers are summarized in Table IV. In general, these polymers show rapid weight loss in the region 400–500°C in nitrogen. The decomposition temperatures at which 10% weight loss was observed for these poly(amide-imide)s ranged from 385 to 461°C. The polymers containing 3,3'-sulfonyldianiline moieties behaved in TG almost as thermally resistant as those with 4,4'-sulfonyldianiline moieties. The poly(amide-imide)s with larger number of methylene group, e.g., $m = 10$ or 11, started losing weight at higher temperature than those with smaller m. This could be attributed to the better packing of their polymer chains.

To confirm further the crystalline characteristics of these polymers they were subjected to wide-angle x-ray diffraction measurements. Figures 4 and 5 present x-ray diffractograms of the **M-IIIa–g** and **P-IIIa–g** polymers, respectively. Except for **P-IIIc**, all the poly(amide-imide)s with the number of methylene units lower than 5 showed an amorphous pattern. The polymers with ten or eleven methylenes in the repeating unit, such as **P-IIIf, P-IIIg, M-IIIf**, and **M-IIIg**, exhibit weak crystal patterns. The poly(amide-imide)s showing weak crystal patterns were insoluble in polar solvents, such as DMF and DMSO, as shown in Table III, which is in agreement with the general rule that the solubility decreases with increasing crystallinity. Furthermore, the semicrystalline nature of these polymers also accounts for the higher initial decomposition temperature observed in Figure 3.

Strong and flexible films could be cast from the DMAc or NMP solutions of most of the obtained poly(amide-imide)s, except for those with low inherent viscosity like **P-IIIa** and **M-IIIa**. The tensile properties of some typical poly(amide-imide)s are summarized in Table V. In tension, some polymer films like **P-IIId,e,g** and **M-IIIf,g** behave as a ductile material with a yield point and moderate to high elongation to break. Thus, these polymers are available for practical use.

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