

Synthesis and Properties of Poly(amide-Imide)s Derived from Trimellitic Anhydride, ω -Amino Acids, and Aromatic Diamines

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SYNOPSIS

Seven imidodicarboxylic acids **II-1** to **5**, **II-10**, and **II-11** were prepared from trimellitic anhydride and ω -amino acids, such as glycine, β -alanine, 4-aminobutyric acid, 5-aminopentanoic acid, 6-aminohexanoic acid, 11-aminoundecanoic acid, and 12-aminododecanoic acid. Several aliphatic-aromatic poly(amide-imide)s were prepared by triphenyl phosphite promoted polycondensation reaction from the combination of 3-(4-carboxyphthalimido)propionic acid (**II-2**) or 6-(4-carboxyphthalimido)hexanoic acid (**II-5**) with various aromatic diamines and of all the imidodiacids with *p*-phenylenediamine or 4,4'-oxydianiline. All poly(amide-imide)s were characterized by inherent viscosity, gel permeation chromatography (GPC) measurements, solubility, tensile test, wide-angle X-ray scattering patterns, differential scanning calorimetry (DSC) measurements, and thermogravimetric (TGA) analyses. Effects of structural changes such as polymethylene length and diamine moieties on the properties of poly(amide-imide)s were studied. © 1994 John Wiley & Sons, Inc.

Keywords: aliphatic-aromatic poly(amide-imide) • trimellitic anhydride • ω -amino acids • triphenyl phosphite • direct polycondensation

INTRODUCTION

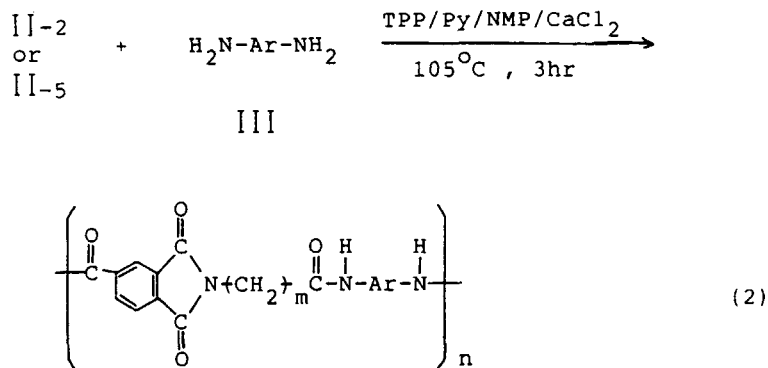
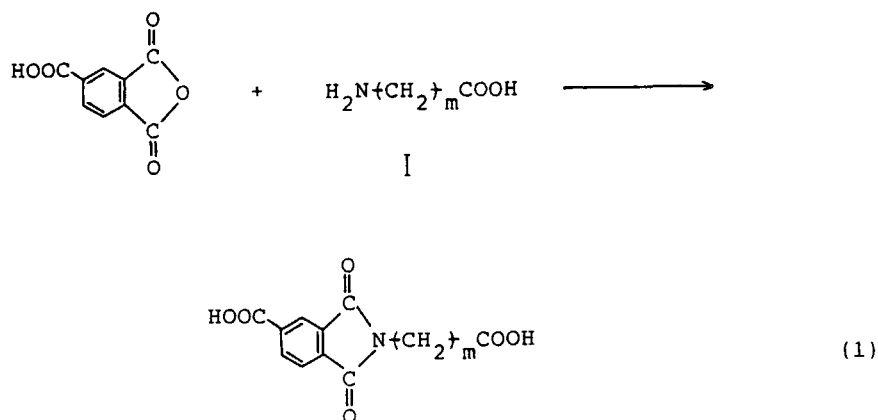
Since 1975 Yamazaki et al.¹ have reported the phosphorylation polyamidation reaction; this reaction has been extensively applied to the polyamides syntheses because of its convenience. This technique employed triphenyl phosphite (TPP) and pyridine as condensing agents to synthesize polyamides directly from aminobenzoic acids and from aromatic diamines with aromatic or aliphatic dicarboxylic acids. In our laboratory, we have successfully extended the phosphorylation reaction to the syntheses of high-molecular-weight poly(amide-imide)s from imide-preformed dicarboxylic acids and aromatic diamines.²⁻⁸ This synthetic approach has proven to be more efficient and convenient when compared to the acid chloride route reported by other researchers.⁹⁻¹⁰

In one of our previous articles,² three imide ring-containing dicarboxylic acids (i.e., **II-1**, **II-3**, and **II-5**) were prepared by the condensation of trimellitic anhydride with three corresponding ω -amino acids [$\text{H}_2\text{N}-(\text{CH}_2)_m-\text{COOH}$], i.e., glycine ($m = 1$), 4-aminobutyric acid ($m = 3$), and 6-aminohexanoic acid ($m = 5$), and several aliphatic-aromatic poly(amide-imide)s derived from these diacids and aromatic diamines were described. In that article, our interest focused on finding the best reaction conditions and also on the characterization of the resultant polymers. However, the effects of structural changes, such as polymethylene length and diamine moiety, in the poly(amide-imide) backbone upon the properties of these polymers have not been discussed in detail. Therefore, four additional dicarboxylic acids with preformed imide ring (i.e., **II-2**, **II-4**, **II-10**, and **II-11**) were prepared from TMA and the corresponding ω -amino acids, i.e., 3-aminopropionic acid ($m = 2$), 5-aminopentanoic acid ($m = 4$), 11-aminoundecanoic acid ($m = 10$), and

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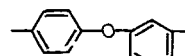
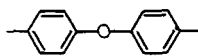
12-aminododecanoic acid ($m = 11$). Together with the three imide ring-containing diacids (i.e., **II-1**, **II-3**, and **II-5**) employed in the previous article, seven imide-diacids containing a different number of methylene groups were used as the diacid monomers in the present article [eq. (1)]. In order to study the effects of structural changes on the properties of polymers, serial poly(amide-imide)s were prepared in the following two cases: in case 1, poly(amide-imide)s of **IV-2** and **IV-5** series were polycondensed from imide-diacids **II-2** and **II-5** with structurally different diamines [eq. (2)]; in case 2,

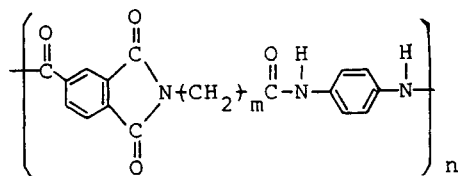
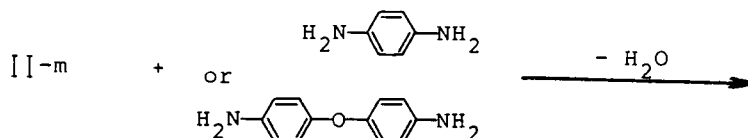
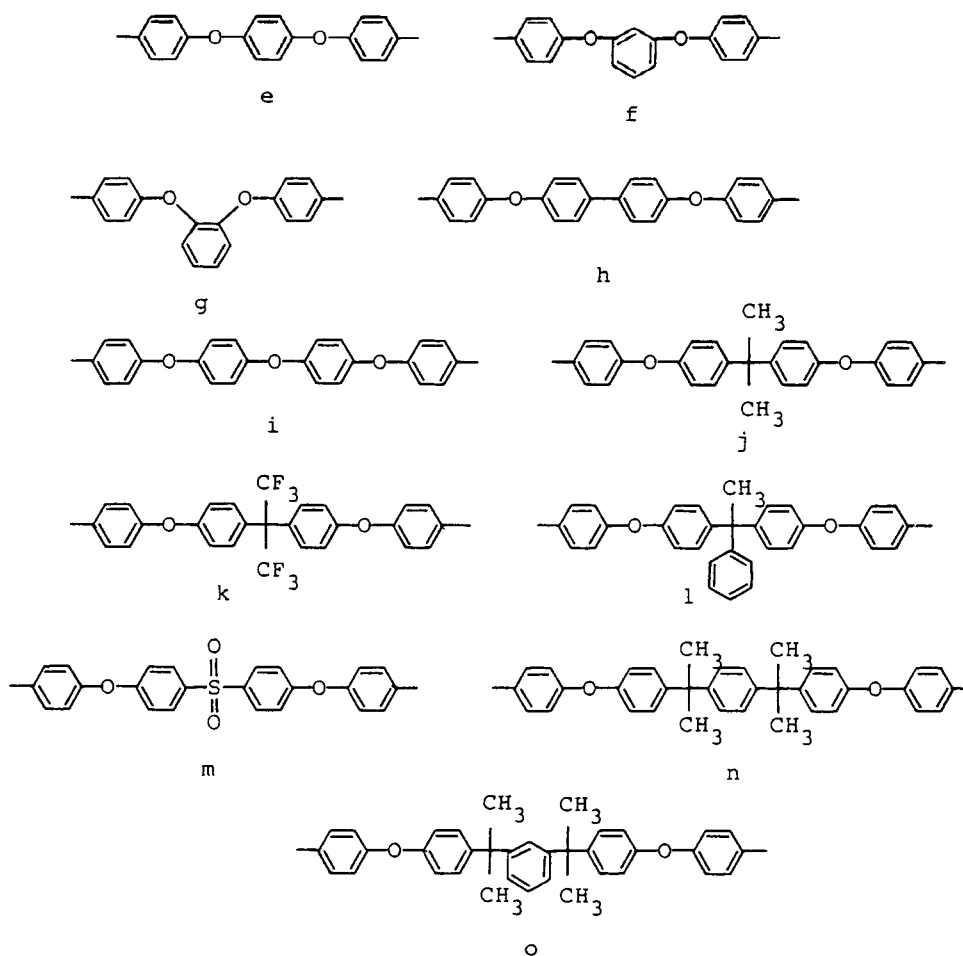
poly(amide-imide)s **IV_a** and **IV_c** series were polycondensed from *p*-phenylenediamine (**III_a**) and 4,4'-oxydianiline (**III_c**) with different polymethylene length-containing imidodicarboxylic acids **II-1-5**, **II-10**, and **II-11**, [eq. (3)]. Except for polymers **IV_a-1**, **IV_a-3**, **IV_a-5**, **IV_c-1**, **IV_c-3**, **IV_c-5**, **IV_d-5**, and **IV_e-5**, the others are of new structure. The purpose of this article is to report the preparation and characterization of the above-mentioned poly(amide-imide)s, and to investigate the effect of the length of the aliphatic chain and also the effect of the structures from the diamines on the characteristics of poly(amide-imide)s.



IV-2 ($m = 2$)
or
IV-5 ($m = 5$)

Ar:

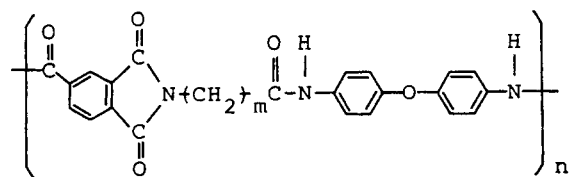




IVa-m (m = 1, 2, 3, 4, 5, 10, 11)

or

(3)



IVc-m (m = 1, 2, 3, 4, 5, 10, 11)

EXPERIMENTAL

Materials

Trimellitic anhydride (TMA) (from Wako) was used without previous purification. Seven ω -amino acids, that is, glycine (TCI), β -alanine (3-amino-propionic acid) (Hanawa), γ -amino-*n*-butyric acid (4-aminobutanoic acid) (TCI), δ -amino-*n*-pentanoic acid (5-aminopentanoic acid) (TCI), ϵ -amino-*n*-caproic acid (6-aminocaproic acid) (TCI), 11-aminoundecanoic acid (σ), and 12-aminododecanoic acid (TCI), were all used as received. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180°C for 10 h. *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 sieves. Triphenyl phosphite (from TCI) was purified by distillation under reduced pressure. *p*-Phenylenediamine was vacuum distilled prior to use. With a conventional synthetic method,¹¹ diamines **III**_{g-o} were prepared in high purity and high yield by condensing catechol (for **III**_g) or their bisphenol precursors (for **III**_{h-o}) with *p*-nitrochlorobenzene in the presence of potassium carbonate in dry DMF, followed by reduction by means of hydrazine and palladium (Pd) on activated carbon. The other aromatic diamines were of high purity when received from the manufacturers and used without any further purification.

Synthesis of Imide-Diacid

Imide-dicarboxylic acids **II**-1 to 5, **II**-10, and **II**-11 were synthesized by condensation of trimellitic anhydride with ω -amino acids, $\text{NH}_2\text{---}(\text{CH}_2)_m\text{---COOH}$, containing different number of methylene group, $m = 1, 2, 3, 4, 5, 10,$ and 11 . As an example, we describe the preparation **II**-2, corresponding to $m = 2$ for β -alanine.

19.2 g (0.1 mol) of trimellitic anhydride and 8.9 g (0.1 mol) of β -alanine were dissolved in 100 mL of dried DMF. The stirred reaction mixture was first heated at 60°C for 1 h. Then, 50 mL of toluene was added, and the mixture was heated at reflux until about 1.8 mL of water was distilled azeotropically. On cooling, a white precipitated product was separated from the final reaction solution, which was recrystallized from DMF/water. 19.7 g (74.7% yield) of pure imide-diacid **II**-2 of mp 247°C was obtained.

IR (KBr): 2500–3100 cm^{-1} (carboxylic, —OH), 1715 cm^{-1} (carboxylic, C=O), 1773 and 1700 cm^{-1} (imide, C=O), 727 cm^{-1} (imide ring).

ANAL. Calcd for $\text{C}_{12}\text{H}_9\text{NO}_6$ (263.20): C, 54.76%; H, 3.45%; N, 5.32%. Found: C, 54.71%; H, 3.55%; N, 5.13%.

The other imide-diacids were obtained by a similar procedure.

Polymerization

A typical polymerization was as follows. A mixture of 0.66 g (2.5 mmol) of diacid **II**-2, 0.50 g (2.5 mmol) of 4,4'-diaminodiphenyl ether (**III**_c), 0.8 g of calcium chloride, 1.6 mL of TPP, 1.5 mL of pyridine, and 5 mL of NMP was heated with stirring at 105°C for 3 h. As the polycondensation proceeded, the solution became viscous. The obtained polymer solution was trickled into 500 mL of methanol giving rise to a stringy precipitate, which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was quantitative and the inherent viscosity of the polymer (**IV**_c-2) in DMAc containing 5 wt % LiCl was 1.85 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

ANAL. Calcd for $(\text{C}_{24}\text{H}_{17}\text{N}_3\text{O}_5)_n$ (427.40)_n: C, 67.44%; H, 4.01%; N, 9.83%. Found: C, 67.59%; H, 4.09%; N, 9.72%.

IR (film): 3298, 1665, and 1545 cm^{-1} (amide), 1775 and 1717 cm^{-1} (imide ring, symmetrical and asymmetrical C=O stretching), 727 cm^{-1} (imide ring deformation).

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

Measurements

The inherent viscosities were measured with a Cannon-Fenske viscometer thermostated at 30°C. Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by means of gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: DMF containing 0.01 mol/L of lithium bromide). 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. ¹H- and ¹³C-NMR spectra were obtained with Jeol EX-400 NMR spectrometer, working at 400 and 100 MHz, respectively.

The DSC traces were measured on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller at the rate of 20°C/min in flowing nitrogen (30 cm³/min). Thermogravimetry (TG) was done on a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing

nitrogen or air (50 cm³/min) at a heating rate of 20°C/min.

The wide-angle X-ray scattering measurements were performed at room temperature (about 25°C) in film specimens of about 0.1 mm thick on a Rigaku Geiger Flex D-Max III_a X-ray diffractometer, using Ni-filtered CuK_α radiation (operating at 40 kV and 15 mA). The intensity, measured at a scanning rate of 2°/min, was recorded for the angular range 5–40° (2θ).

Tensile measurements were performed at room temperature for all films on an Instron Universal Tester Model 1130. Film dimensions were 0.5 × 6 cm, with about 0.1 mm thick. Data of an average of at least five individual determinations were used.

RESULTS AND DISCUSSION

Synthesis of Imide-Diacid Monomer

Seven imide ring-preformed dicarboxylic acids II-1-5, II-10, and II-11 were synthesized from trimellitic anhydride and ω-amino acids containing different numbers of methylene groups. The melting points, yields, and elemental analyses of all imide-diacids are listed in Table I. The yields of these imide-diacids were high, and the results of elemental analyses and characteristic absorptions on the IR spectra agree well with the proposed structures. The IR spectra exhibited obviously the characteristic absorptions of imide ring and carboxyl groups.

The structures of imide-diacids were also confirmed by ¹H- and ¹³C-NMR spectra. Their num-

bered formula appear in Figure 1. Figure 2 shows the ¹H- and ¹³C-NMR spectra of the representative imide-diacid II-2 and the assignment to all carbons and protons. All expected absorptions are observed. In the ¹H-NMR spectrum, the absorption signals of aromatic protons appear in the range of δ 7.97–8.34 ppm, the methylene protons give triplet resonances centred at 2.64 and 2.83 ppm, and the hump around 13.0 ppm is peculiar to the carboxyl protons. Furthermore, in the ¹³C-NMR spectrum, most carbon atoms gave separate and assignable resonances. In the carbonyl region, the aliphatic carboxylic acid appears at 172.2 ppm, the aromatic carboxylic acid at 165.8 ppm, and the phthalimide group gives one signal (coinciding accidentally) at 166.9 ppm. The aromatic carbon atoms exhibit six peaks in the range of 123.0–136.2 ppm, and the absorptions at 32.3 and 33.8 ppm correspond to the methylene carbons. The proton and carbon-13 chemical shifts of all the imide-diacids are summarized in Table II and Table III, respectively.

Polymer Synthesis

In the present study, poly (amide-imide)s were prepared in two cases, and the effect of structural changes on the properties of polymers was discussed. These polymers were directly polycondensed from the imide-diacids and the diamines using triphenyl phosphite and pyridine as the condensing agents. Almost all the reactions proceeded readily in homogeneous solutions, and gave quantitative yields of poly (amide-imide)s. Inherent viscosities of IV-2 and IV-5 series poly (amide-imide)s are sum-

Table I. Melting Points, Yields, and Elemental Analyses of Imide-Diacids

Imide-Diacid	mp (°C)	Yield (%)	Formula (MW)	Elemental Analyses			
				(% C)	(% H)	(% N)	
II-1	268	84.0	C ₁₁ H ₇ NO ₆ (249.17)	Calcd:	53.02	2.83	5.62
				Found:	53.02	2.59	5.57
II-2	247	74.7	C ₁₂ H ₉ NO ₆ (263.20)	Calcd:	54.76	3.45	5.32
				Found:	54.71	3.55	5.13
II-3	210	80.0	C ₁₃ H ₁₁ NO ₆ (277.23)	Calcd:	56.31	4.00	5.05
				Found:	56.08	3.95	5.15
II-4	228	75.7	C ₁₄ H ₁₃ NO ₆ (291.25)	Calcd:	57.73	4.50	4.81
				Found:	57.74	4.58	4.86
II-5	204	74.0	C ₁₅ H ₁₅ NO ₆ (305.28)	Calcd:	59.01	4.95	4.59
				Found:	58.72	4.87	4.75
II-10	162	78.8	C ₂₀ H ₂₅ NO ₆ (375.41)	Calcd:	63.98	6.71	3.73
				Found:	63.83	6.84	3.83
II-11	168	76.9	C ₂₁ H ₂₇ NO ₆ (389.44)	Calcd:	64.76	6.99	3.60
				Found:	64.65	6.88	3.79

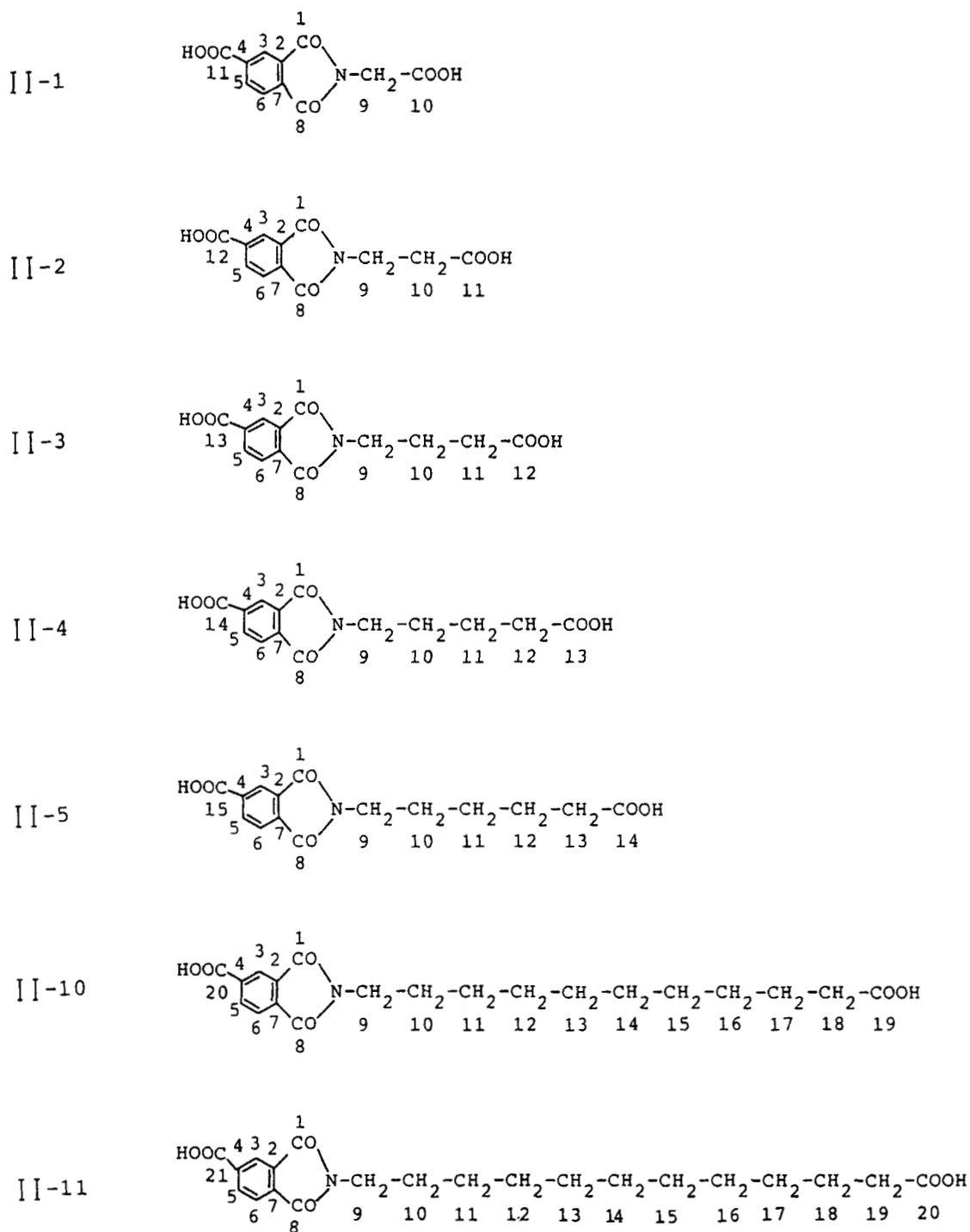


Figure 1. Numbered formula for imide-diacids.

marized in Table IV. \bar{M}_w , \bar{M}_n , and \bar{M}_w/\bar{M}_n determined by GPC are also listed in Table IV. In these GPC measurements, the solution of DMF containing 0.01 mol/L of lithium bromide was used as the eluent, and polystyrene was used as the standard. Possibly due to high crystallinity or too high mo-

lecular weights, some of IV-2 and IV-5 poly (amide-imide)s were insoluble in the eluent so that their molecular weight data were not detectable by GPC. Anyway, observed from the inherent viscosity values, these polymers should have high molecular weights. The electron-rich oxygen atom made the

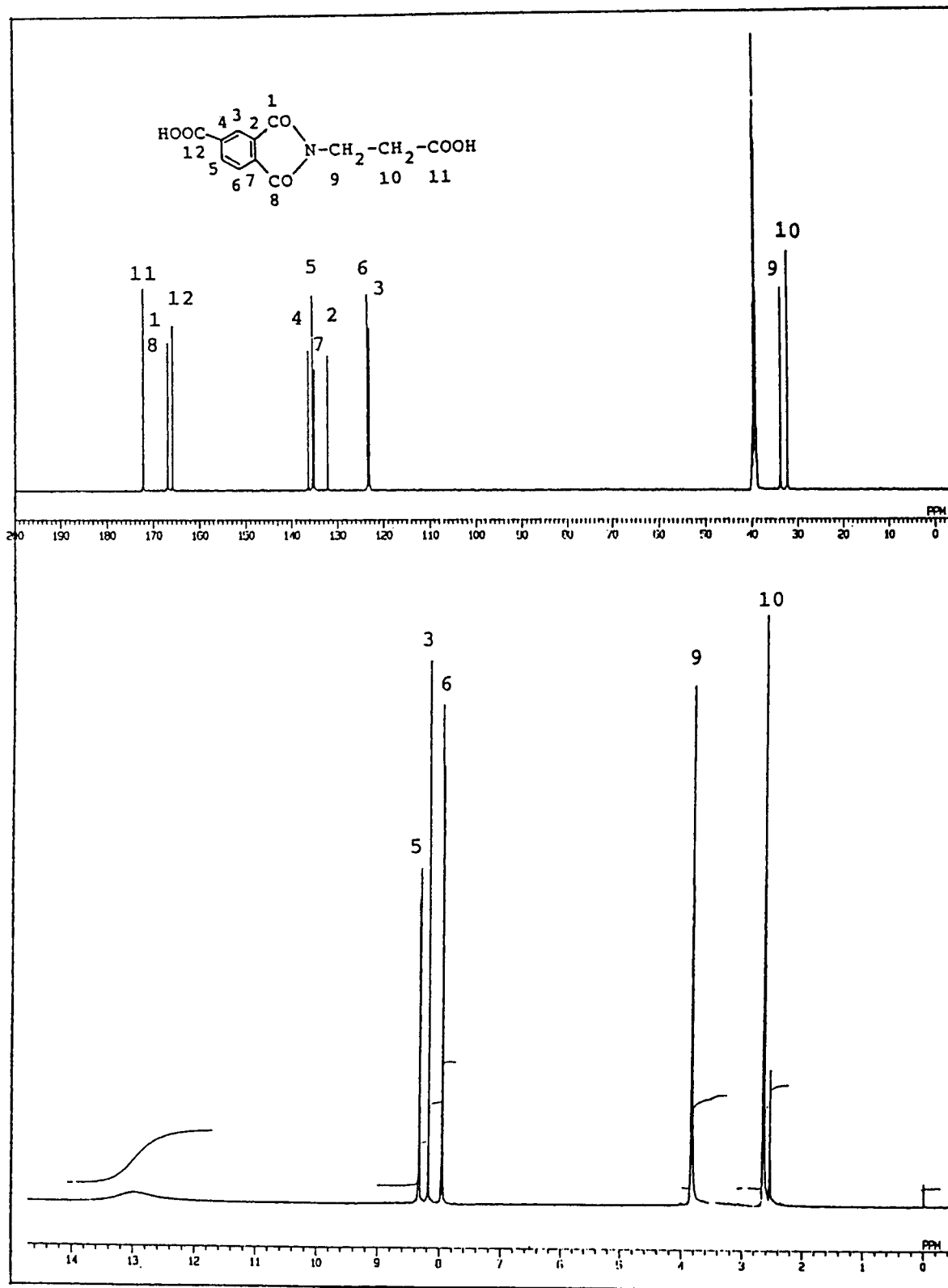


Figure 2. (A) ^{13}C - and (B) ^1H -NMR spectra of imide-diacid II-2 in $\text{DMSO}-d_6$.

Table II. Proton Chemical Shifts^a (δ in ppm) and Assignments of Imide-Diacids^b

Atom No.	II-1	II-2	II-3	II-4	II-5	II-10	II-11
1	—	—	—	—	—	—	—
2	—	—	—	—	—	—	—
3	8.28	8.18	8.20	8.20	8.18	8.20	8.20
4	—	—	—	—	—	—	—
5	8.41	8.34	8.35	8.35	8.34	8.35	8.35
6	8.05	7.97	7.97	7.98	7.95	7.97	7.97
7	—	—	—	—	—	—	—
8	—	—	—	—	—	—	—
9	4.36	3.83	3.64	3.58	3.58	3.58	3.57
10	—	2.64	1.85	1.63			
11	—	—	2.28	1.51	1.2-1.7		
12	—	—	—	2.26			
13	—	—	—	—	2.23	1.2-1.6	
14	—	—	—	—	—		1.2-1.6
15	—	—	—	—	—		
16	—	—	—	—	—		
17	—	—	—	—	—		
18	—	—	—	—	—	2.18	
19	—	—	—	—	—	—	2.18
20	—	—	—	—	—	—	—
21	—	—	—	—	—	—	—

^a External reference TMS = 0.00 ppm.^b Atoms numbered according to Figure 1.**Table III.** Carbon-13 Chemical Shift^a (δ in ppm) and Assignments of Imide-Diacids^b

Atom No.	II-1	II-2	II-3	II-4	II-5	II-10	II-11
1	166.5	166.9	167.3	167.2	167.2	169.2	167.1
2	131.9	132.1	132.2	132.1	132.1	132.0	132.0
3	123.9	123.0	123.4	123.4	123.3	123.3	123.3
4	136.8	136.3	136.2	136.3	136.2	136.3	136.2
5	135.8	135.3	135.2	135.2	135.2	135.2	135.2
6	123.5	123.4	123.0	123.0	123.0	123.0	122.9
7	134.7	134.9	135.1	134.9	134.9	134.9	134.9
8	166.5	166.9	167.3	167.2	167.2	167.2	167.1
9	38.9	33.8	37.2	37.4	37.6	37.7	37.6
10	168.8	32.3	23.3	27.4	27.6	28.9	28.9
11	165.8	172.2	31.0	21.8	25.8	28.6	28.7
12	—	165.8	173.9	33.1	24.1	26.3	27.8
13	—	—	165.9	174.3	33.5	24.5	24.5
14	—	—	—	165.9	174.4	24.5	24.5
15	—	—	—	—	165.8	24.5	24.5
16	—	—	—	—	—	27.8	26.2
17	—	—	—	—	—	28.7	28.5
18	—	—	—	—	—	33.7	28.8
19	—	—	—	—	—	174.5	33.6
20	—	—	—	—	—	165.9	174.4
21	—	—	—	—	—	—	165.8

^a Internal reference DMSO = 39.50 ppm.^b Atoms numbered according to Figure 1.

Table IV. Inherent Viscosities, Molecular Weights, and Polydispersities of Poly(amide-Imide)s

Polymer	η_{inh}^b (dL/g)	\bar{M}_w^c ($\times 10^{-4}$)	\bar{M}_n^c ($\times 10^{-4}$)	\bar{M}_w/\bar{M}_n
IV _a -2	1.10	—	—	—
IV _b -2	1.18	—	—	—
IV _c -2	1.85	22.86	10.17	2.25
IV _d -2	1.10	9.93	4.61	2.16
IV _e -2	1.66	22.38	9.47	2.36
IV _f -2	1.75	23.48	11.78	1.99
IV _g -2	0.88	11.09	4.95	2.24
IV _h -2	0.94	—	—	—
IV _i -2	0.70	—	—	—
IV _j -2	1.40	20.49	8.49	2.41
IV _k -2	1.13	20.87	9.41	2.22
IV _l -2	1.30	23.54	9.70	2.43
IV _m -2	0.96	9.63	4.12	2.34
IV _n -2	1.05	16.07	9.35	1.72
IV _o -2	0.71	8.51	4.11	2.07
IV _a -5	1.64	—	—	—
IV _b -5	0.97	10.94	5.46	2.00
IV _c -5	1.80	—	—	—
IV _d -5	1.16	9.48	4.29	2.21
IV _e -5	1.75	—	—	—
IV _f -5	1.71	22.72	9.97	2.28
IV _g -5	1.28	20.47	7.99	2.56
IV _h -5	0.90	—	—	—
IV _i -5	0.82	—	—	—
IV _j -5	1.41	19.84	8.46	2.34
IV _k -5	1.04	14.25	6.52	2.18
IV _l -5	1.34	16.40	7.36	2.23
IV _m -5	0.91	10.45	5.46	1.91
IV _n -5	0.99	12.71	4.88	2.60
IV _o -5	0.79	6.31	2.70	2.33
IV _a -1	1.78	21.32	8.40	2.54
IV _a -2	1.10	—	—	—
IV _a -3	1.40	—	—	—
IV _a -4	0.93	—	—	—
IV _a -5	1.64	—	—	—
IV _a -10	1.10	—	—	—
IV _a -11	1.29	—	—	—
IV _c -1	2.15	23.23	9.02	2.58
IV _c -2	1.84	22.86	10.17	2.25
IV _c -3	1.41	16.27	7.48	2.17
IV _c -4	1.07	8.85	3.94	2.24
IV _c -5	1.80	—	—	—
IV _c -10	1.69	—	—	—
IV _c -11	1.43	—	—	—

^a Polymerization was carried out with 2.5 mmol each monomer, 1.6 mL of TPP, 1.5 mL of pyridine, and 0.8 g of CaCl₂ in 5 mL of NMP at 105°C for 3 h under nitrogen.

^b Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % of LiCl dissolved, at 30°C.

^c Determined by GPC.

para-amino group on the benzene ring have more nucleophilic reactivity than the *meta*-amino group; therefore, for example, polymers IV_c-2 and IV_c-5

derived from *p,p'*-diamine III_c had higher molecular weights than IV_d-2 and IV_d-5 from *p,m'*-diamine III_d. Furthermore, the electron-withdrawing sulfonyl group would reduce the reactivity of amino group, so polymers IV_m-2 and IV_m-5 showed relatively lower average molecular weights. The \bar{M}_w/\bar{M}_n values of IV -2 and IV -5 series polymers, a measure of molecular weight distribution, were in the range of 1.72–2.60.

Inherent viscosities and average molecular weights of IV_a and IV_c series poly(amide-imide)s are also summarized in Table IV. In IV_a series polymers, only polymer IV_a-1 was soluble in the eluent, and calculated from the GPC curve its \bar{M}_w was about 213,000, and \bar{M}_w/\bar{M}_n was 2.54. Due to the presence of rigid *p*-phenylene unit and less polar aliphatic chains, polymers with longer aliphatic chains (that is, $m \geq 2$) were insoluble in the eluent so that data of their average molecular weights could not be obtained. However, it is believed that the IV_a series polymers have high molecular weights according to their high inherent viscosity values. The polymers derived from 4,4'-oxydianiline (III_c) had higher solubility than IV_a series polymers. Polymers IV_c-1–4 were soluble in the eluent, and their \bar{M}_w and \bar{M}_w/\bar{M}_n values were recorded in the range of 88,000–232,000 and 2.17–2.56, respectively. In IV_c series polymers, the polymers with $m \geq 5$ were insoluble in the eluent, possibly also due to the decrease of polarity of polymer chain, so that no data of molecular weight was presented.

Figure 3 shows the representative FTIR spectrum of polymer IV_c-2. The IR spectrum showed characteristic absorptions for the imide ring at 1775 and 1717 cm⁻¹, peculiar to the symmetrical and asymmetrical carbonyl stretching vibration, and at 1100 and 727 cm⁻¹, due to imide ring deformation. Characteristic absorption bands of amide groups appear at 3298, 1665, and 1545 cm⁻¹.

Properties of Polymers

Solubility

The solubility behavior of IV -2 and IV -5 series poly(amide-imide)s is shown in Table V. Except for polymers IV_a-2, IV_h-2, IV_a-5, and IV_h-5, almost all the polymers showed excellent solubility in DMSO, *m*-cresol, and amide-type polar solvents such as DMF, DMAc, and NMP. Incorporation of *p*-phenylene and 4,4'-biphenylene into the polymer backbones led to a decrease in solubility. For example, polymers IV_a-2, IV_a-5, and IV_h-5 were soluble only in NMP, and IV_h-2 was insoluble in all the tested organic solvents. The poor solubility of

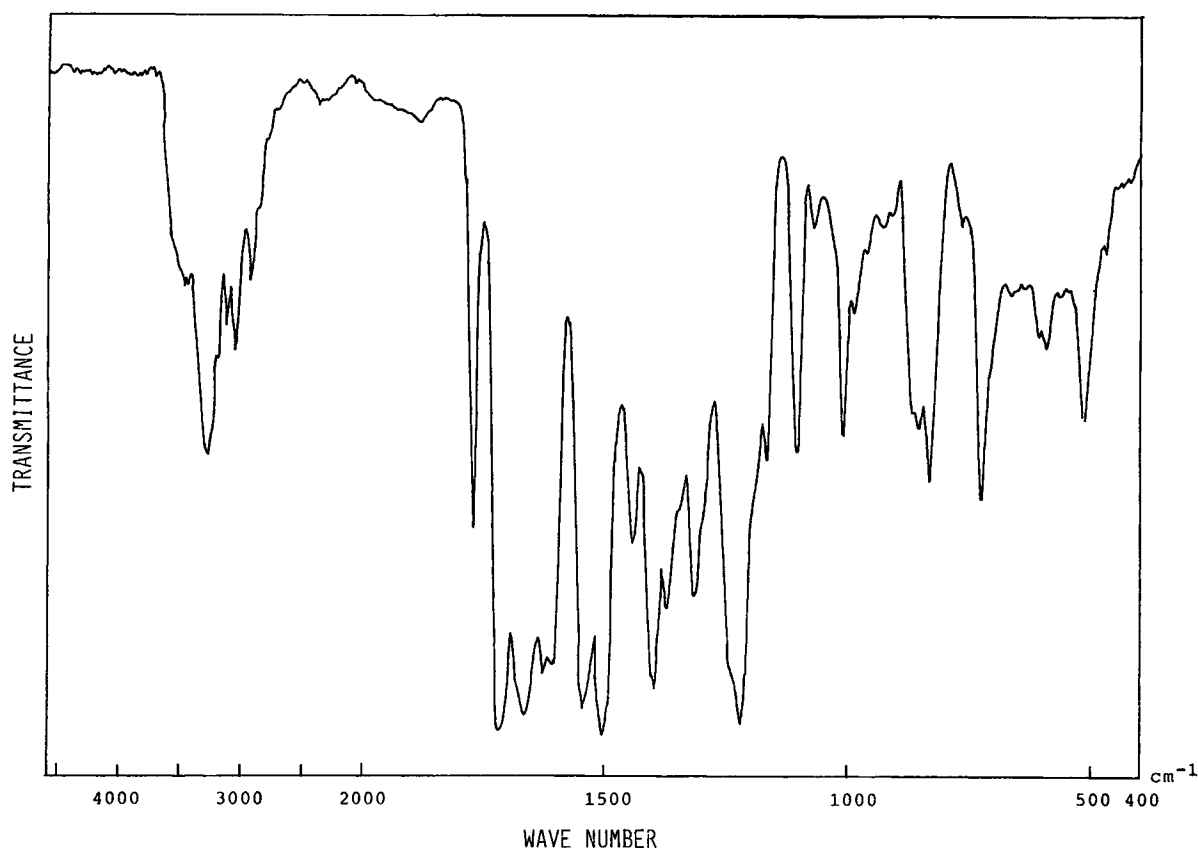


Figure 3. FTIR spectrum of poly(amide-imide) IV_c -2.

these polymers may be attributable to their high crystallinity. This will be evidenced by DSC and X-ray diffraction measurements later.

Table V also shows the solubility behavior of IV_a and IV_c poly(amide-imide)s series. Obviously, the polymers derived from *p*-phenylenediamine (III_a) revealed less solubility because of the more rigid nature of *p*-phenylene unit. Increasing the length of aliphatic chain in the repeating unit of these poly(amide-imide)s decreased the solubility in polar solvents such as DMF, DMAc, and DMSO, probably due to the decreased polarity and high crystallinity of their polymer chains. Long aliphatic chains favor the zig-zag packing and possibly better match of hydrogen bonding between polymer chains, and, hence, increase the crystallinity. This can be further confirmed by X-ray diffraction. However, the poly(amide-imide)s containing longer aliphatic chains behaved as nylons and showed good solubility in *m*-cresol.

In addition, all the poly(amide-imide)s are soluble in concentrated sulfuric acid, but they are insoluble in common organic solvents like benzene, acetone, tetrahydrofuran, chloroform, etc.

Crystallinity

To further confirm the crystalline characteristics of these polymers, they have been subjected to X-ray diffraction determination. The polymer samples of IV -2 and IV -5 series poly(amide-imide)s were determined in a powder (IV_h -2) or film form (for the other polymers). X-ray diffractograms of some representative polymers are shown in Figure 4. Polymers IV_a -2, IV_h -2, IV_i -2, and IV_h -5 showed highly crystalline diffraction patterns. This result is consistent with the results of solubility test, and this is reasonable because it is in agreement with the general rule that solubility decreases with increasing crystallinity.

All the IV_c series poly(amide-imide)s could be cast into tough films from DMAc or NMP. Figure 5 presents the X-ray diffractograms of all IV_c series polymer films. Polymers with longer aliphatic chain (e.g., $m \geq 5$) in the repeating unit gradually revealed strong reflection peaks around 20° . In particular, polymers IV_c -10 and IV_c -11 with 10 and 11 methylene groups in the repeating unit showed a very strong diffraction peak. This implies that those

Table V. Solubility of Poly(amide-Imide)s^a

Polymer	Solvents ^b					
	DMAc	NMP	DMF	DMSO	<i>m</i> -Cresol	H ₂ SO ₄
IV _a -2	-	+	-	-	-	+
IV _b -2	+	+	-	+	-	+
IV _c -2	+	+	+	+	+	+
IV _d -2	+	+	+	+	+	+
IV _e -2	+	+	+	+	+	+
IV _f -2	+	+	+	+	+	+
IV _g -2	+	+	+	+	+	+
IV _h -2	-	-	-	-	-	+
IV _i -2	+	+	-	+	-	+
IV _j -2	+	+	+	+	+	+
IV _k -2	+	+	+	+	+	+
IV _l -2	+	+	+	+	+	+
IV _m -2	+	+	+	+	+	+
IV _n -2	+	+	+	+	+	+
IV _o -2	+	+	+	+	+	+
IV _a -5	-	+	-	-	-	+
IV _b -5	+	+	+	+	+	+
IV _c -5	+h	+	-	+h	+	+
IV _d -5	+	+	+	+	+	+
IV _e -5	+	+	-	+h	+	+
IV _f -5	+	+	+	+	+	+
IV _g -5	+	+	+	+	+	+
IV _h -5	-	+	-	-	-	+
IV _i -5	+	+	-	+-	+	+
IV _j -5	+	+	+	+	+	+
IV _k -5	+	+	+	+	+	+
IV _l -5	+	+	+	+	+	+
IV _m -5	+	+	+	+	+	+
IV _n -5	+	+	+	+	+	+
IV _o -5	+	+	+	+	+	+
IV _a -1	+	+	+	+	-	+
IV _a -2	-	+	-	-	-	+
IV _a -3	-	+	-	+	-	+
IV _a -4	+	+	-	+	+	+
IV _a -5	-	+	-	-	-	+
IV _a -10	-	+	-	-	+	+
IV _a -11	-	+	-	-	+-	+
IV _c -1	+	+	+	+	-	+
IV _c -2	+	+	+	+	+	+
IV _c -3	+	+	+	+	+	+
IV _c -4	+	+	+	+	+	+
IV _c -5	+h	+	-	+h	+	+
IV _c -10	+h	+	-	+-	+	+
IV _c -11	-	+	-	-	+	+

^a Solubility: (+) soluble, (-) insoluble, (+-) partially soluble at room temperature, and (+h) soluble on heating.

^b (DMAc) *N,N*-dimethylacetamide, (DMF) *N,N*-dimethylformamide, (NMP) *N*-methyl-2-pyrrolidone, and (DMSO) dimethylsulfoxide.

poly(amide-imide)s with longer polymethylene chain have higher crystallization tendency, and the tendency is also in agreement with the solubility behavior.

Mechanical Properties

In the IV -2 and IV -5 series poly(amide-imide)s, except for polymer IV_a and those derived from di-

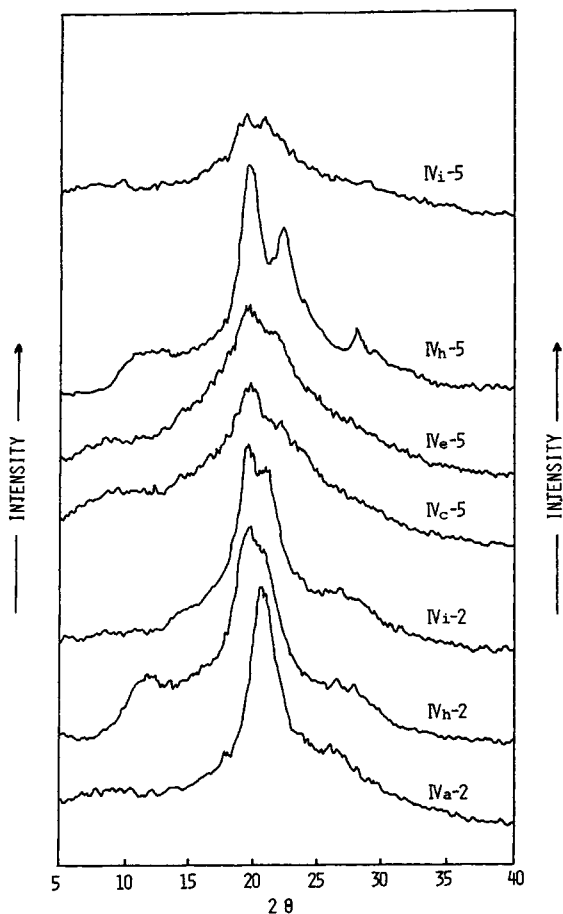


Figure 4. Wide-angle X-ray diffractograms of some poly(amide-imide)s.

amines **III_h** and **III_i**, almost all the polymers could be cast into flexible films from their polymer solutions of NMP or DMAc. Their tensile properties are compiled in Table VI. Flexible films, polymers derived from diamines 1,4- (**III_e**) or 1,3-bis(4-aminophenoxy)benzene (**III_f**), and 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (**III_j**), such as **IV_e-2**, **IV_f-2**, **IV_j-2**, **IV_f-5**, and **IV_j-5**, exhibited yield points and moderate elongation to break on their stress-strain curves, indicating that they were tough materials. The use of flexible arylene ether linkage and isopropylidene groups to connect the benzene rings may be one of the major reasons. Surprisingly, polymers **IV_i-2** and **IV_i-5** derived from the four-ring trioxy-linked diamine **III_i** behaved as those derived from 4,4'-biphenylene-containing diamine **III_h** being highly crystalline, so that they could not be cast into flexible films. The close proximity of isopropylidene linkages, for example, in the cases of polymers derived from **III_n** and **III_o**, causes a decrease in elongation. Moreover, more crowded molecular conformation, such as diamine moieties of **III_g**, **III_l**, and

III_o, made polymer chains unfavorable to be well packed, therefore, the polymers such as **IV_g-2**, **IV_i-2**, **IV_o-2**, **IV_l-5**, and **IV_o-5** possessed lower elongation to break, i.e., decreased toughness.

The tensile properties of **IV_a** and **IV_c** series poly(amide-imide)s are also summarized in Table VI. In **IV_c** series derived from 4,4'-oxydianiline (**III_c**), the polymers containing methylene groups of $m \leq 5$ in the repeating unit could be cast into transparent and tough films; however, the cast films of polymer **IV_c-10** ($m = 10$) and **IV_c-11** ($m = 11$) were opaque and showed low elongation rate, possibly due to higher crystallinity.

Thermal Properties

The thermal properties of all polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Table VII compiles the thermal behavior data of both **IV-2** and **IV-5** series poly(amide-imide)s. Glass transition temperatures (T_g s) and melting points of these

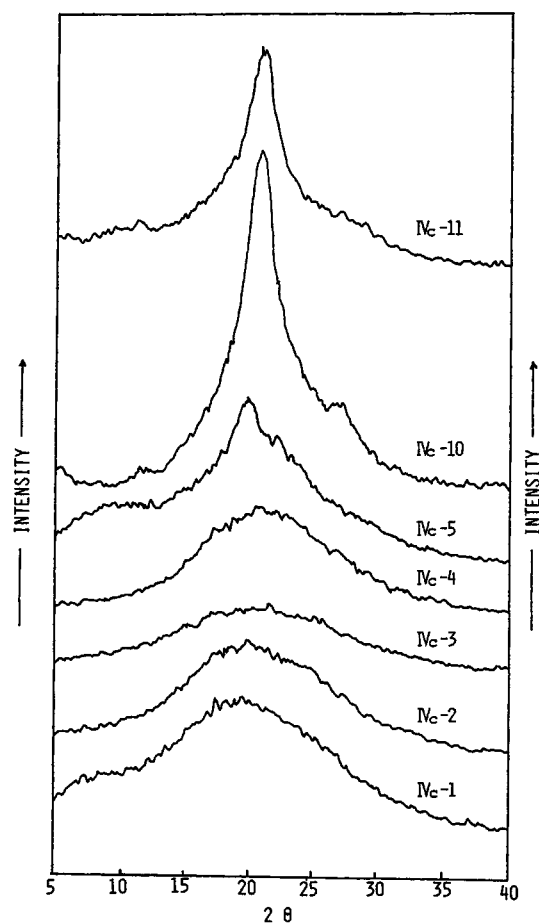


Figure 5. Wide-angle X-ray diffractograms of the **IV_c** series poly(amide-imide)s.

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

Polymer	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
IV _a -2	—	—	—	—
IV _b -2	—	103	7	2.62
IV _c -2	80	68	19	2.18
IV _d -2	86	65	14	2.35
IV _e -2	95	85	57	2.43
IV _f -2	91	70	43	2.23
IV _g -2	—	75	4	2.45
IV _h -2	—	—	—	—
IV _i -2	—	—	—	—
IV _j -2	75	62	55	1.84
IV _k -2	78	71	17	1.53
IV _l -2	73	69	7	2.26
IV _m -2	77	68	23	1.84
IV _n -2	74	67	10	1.37
IV _o -2	—	59	6	1.39
IV _a -5	80	70	12	1.73
IV _b -5	94	84	10	2.54
IV _c -5	62	58	15	1.49
IV _d -5	98	74	17	2.50
IV _e -5	90	75	18	2.29
IV _f -5	73	52	55	2.02
IV _g -5	84	70	19	2.07
IV _h -5	—	—	—	—
IV _i -5	—	—	—	—
IV _j -5	69	55	33	1.95
IV _k -5	65	60	13	1.19
IV _l -5	—	68	7	1.89
IV _m -5	—	78	10	2.03
IV _n -5	73	69	11	1.06
IV _o -5	—	51	5	1.47
IV _a -1	85	82	46	2.46
IV _a -2	—	—	—	—
IV _a -3	84	72	16	2.07
IV _a -4	—	—	—	—
IV _a -5	80	70	12	1.73
IV _a -10	—	—	—	—
IV _a -11	—	65	10	1.52
IV _c -1	80	68	56	1.94
IV _c -2	80	68	19	2.18
IV _c -3	81	66	40	1.97
IV _c -4	62	45	32	1.80
IV _c -5	62	58	15	1.49
IV _c -10	—	47	5	1.06
IV _c -11	—	60	8	1.63

polymers were characterized by means of DSC measurements with a heating rate of 20°C/min in nitrogen. In the first heating traces of DSC, most polymers of IV-2 series exhibited obvious melting endothermic peaks. This suggests that the as-polymerized polymers of this series have higher crystallinity than IV-5 series. Except for IV_i-2 and IV_n-5, quenching from the elevated temperatures of about 400°C to room temperature, the endothermic peaks

disappeared, and only glass transition shifts were observed on the second heating traces. Generally, the T_g s of IV-2 series polymers were higher than those of corresponding IV-5 ones. Incorporation of ether linkage into the polymer backbones increased the flexibility of polymers and, hence, decreased T_g s of polymers. Although the introduction of isopropylidene and hexafluoroisopropylidene bridging moieties into the polymer backbones also could in-

Table VII. Thermal Properties of Poly(amide-Imide)s

Polymer	T_g^a (°C)	Range of Melt Endotherm ^b (°C)	Melt Max. (°C)	T_d (°C) ^c		Char Yield ^d (wt %)
				In Air	In N ₂	
IV _a -2	no ^e	345-420 (s)	397	396	400	58.5
IV _b -2	243	315-370 (b)	—	384	377	50.3
IV _c -2	213	350-370 (s)	365	400	402	51.3
IV _d -2	206	300-385 (b)	—	395	393	52.1
IV _e -2	193	350-380 (s)	370	412	407	46.6
IV _f -2	193	285-320 (s)	310	413	415	53.3
IV _g -2	205	350-400 (b)	—	416	418	40.9
IV _h -2	206	375-405 (s)	400	426	431	53.1
IV _i -2	175	315-335 (s)	313	415	410	48.8
		335-360 (s)	348			
IV _j -2	222	315-380 (b)	—	424	425	53.4
IV _k -2	195	—	—	443	443	48.6
IV _l -2	217	270-400 (b)	—	425	437	57.7
IV _m -2	240	320-380 (b)	—	419	423	52.9
IV _n -2	208	320-400 (b)	—	438	447	51.1
IV _o -2	170	320-360 (b)	—	448	422	44.0
IV _a -5	185	—	—	428	428	56.5
IV _b -5	192	—	—	436	433	53.6
IV _c -5	177	—	—	445	434	54.6
IV _d -5	172	—	—	437	430	61.0
IV _e -5	172	—	—	452	450	39.8
IV _f -5	171	—	—	449	444	52.0
IV _g -5	178	—	—	451	443	45.2
IV _h -5	190	320-345 (s)	334	444	466	40.6
		345-375 (s)	360			
IV _i -5	170	275-300 (s)	293	442	441	48.4
IV _j -5	182	—	—	465	457	41.8
IV _k -5	195	—	—	471	458	45.7
IV _l -5	212	—	—	452	449	54.7
IV _m -5	214	—	—	451	451	50.8
IV _n -5	182	—	—	461	472	35.8
IV _o -5	148	—	—	437	438	50.3
IV _a -1	313	—	—	415	440	51.5
IV _a -2	no	345-420 (s)	397	396	400	58.5
IV _a -3	222	358-435 (s)	394	416	414	55.7
IV _a -4	212	355-384 (s)	368	405	412	50.7
IV _a -5	185	—	—	428	428	56.5
IV _a -10	155	278-325 (s)	310	440	427	46.8
IV _a -11	144	260-302 (s)	294	441	427	41.8
		302-332 (s)	319			
IV _c -1	261	—	—	416	436	50.7
IV _c -2	213	350-370 (s)	365	400	402	51.3
IV _c -3	212	—	—	429	422	54.2
IV _c -4	208	—	—	409	406	52.9
IV _c -5	177	—	—	445	434	54.6
IV _c -10	153	236-275 (s)	264	454	434	45.4
IV _c -11	129	225-281 (s)	263	449	441	42.5

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

^b Endotherm peaks on the first heating DSC traces; (s) sharp peak.

^c Temperature at which 10% weight loss was recorded with thermogravimetry (TG) at a heating rate of 20°C/min.

^d Char yield at 800°C in nitrogen.

^e Difficult to judge.

crease the flexibility of polymers, the T_g s were higher than those of the corresponding oxy-bridge containing polymers. This may be attributed to the fact that the lowering effect caused by increased flexibility was partially offsetted by the steric hindrance effect of $-\text{CH}_3$ and $-\text{CF}_3$ groups. The T_g s of poly(amide-imide)s derived from isomeric diamines such as 1,2-, 1,3-, and 1,4-bis(4-aminophenoxy)benzene did not display significant difference, but the 1,2- (ortho) substituted diamine derived polymers showed slightly higher T_g s because of the dipolar effect from the close proximity of oxy bridges. In the diamines derived from bisphenols, diamines **III_m** and **III_l** derived polymers had higher T_g s due to the presence of polar sulfonyl groups in the former and the pendant bulky phenyl group in the latter. The DSC experiment performed on polymer **IV_i-2**, one of these crystalline polymers, is shown in Figure 6. Two closely neighboring endotherms were observable in the first heating trace. After quenching, a clear glass transition around 175°C, a crystallization exotherm maximum at 268°C, and only one endotherm at 335°C were detectable in the second heating trace. This result excludes the existence of a mesophase between both endotherms and also indicates that polymer **IV_i-2** has a high crystallization tendency, which is in agreement with the result of

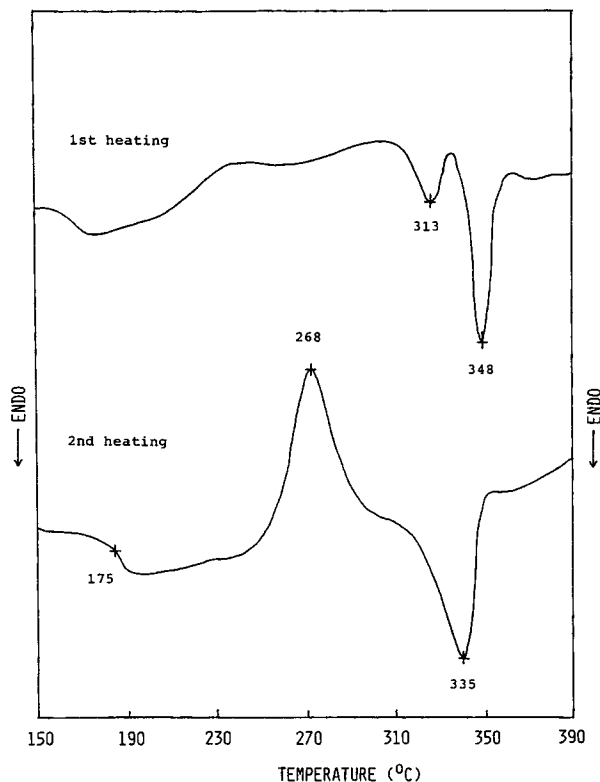


Figure 6. DSC curves of poly(amide-imide) **IV_i-2**, with a heating rate of 20°C/min in nitrogen.

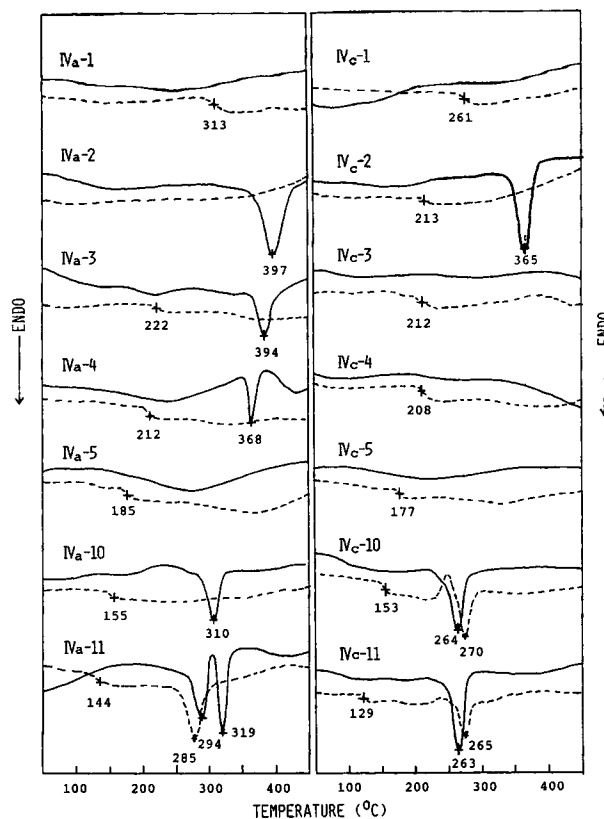


Figure 7. DSC traces (with a heating rate of 20°C/min) of the **IV_a** and **IV_c** series of poly(amide-imide)s. (—) first heating and (---) second heating.

X-ray diffraction measurement. As expected, these polymers with aliphatic chains in the main chains were less thermal resistant than wholly aromatic polymers, and the 10% weight loss temperature was recorded in the range of 384–465°C in air and 377–472°C in nitrogen.

Figure 7 presents the DSC patterns of all **IV_a** and **IV_c** series poly(amide-imide)s. As mentioned above, quenching from the elevated temperatures to room temperature in air yields more amorphous samples so that in almost all cases the T_g s could be more easily measured in the second heating traces of DSC. As expected, the T_g s show an obvious tendency to decrease with increasing length of the aliphatic chains. Moreover, among **IV_a** and **IV_c** series polymers, the **IV_a** series polymers derived from *p*-phenylenediamine revealed higher T_g s, and most polymers of this series exhibited sharp melt endothermic peaks in the first heating traces, possibly on account of the rigid nature of *p*-phenylene unit. In **IV_c** series polymers, well-defined melt endothermic peaks of the polymers with shorter aliphatic chain (e.g., $m \leq 5$) could not be detected by DSC, probably due to a low degree of crystallinity. However, polymer **IV_c-2** with two methylene groups (i.e.,

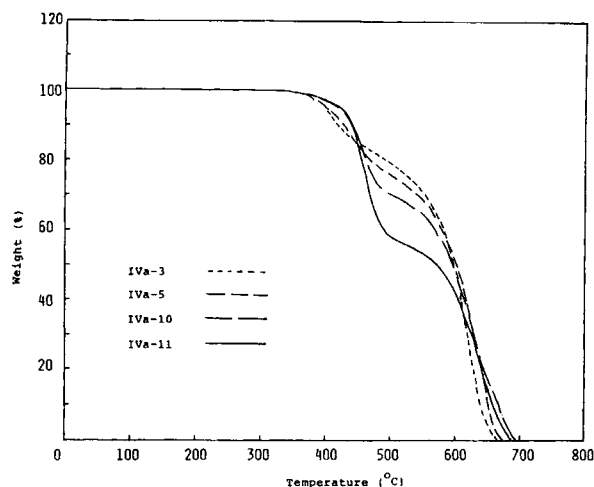


Figure 8. TG curves of some typical poly(amide-imide)s, with a heating rate of 20°C/min in air.

$m = 2$) in the repeating unit showed a sharp melt endothermic peak. This implies that the degree of crystallinity is related to the extended zigzag conformation of polymer chains and matching of hydrogen bonding between neighboring polymer chains. In both IV_a and IV_c series, the methylene groups $m < 5$ crystallized so slowly that after quenching in air the melt endothermic peaks disappeared in the second heating traces. Thus, it appears that the initial crystallinity results from the presence of solvent and the way these polymers were precipitated. The polymers with longer aliphatic chains (e.g., $m = 10$ and 11) in the repeating unit such as IV_a -11, IV_c -10, and IV_c -11 displayed clear melting endotherms in the second heating DSC traces in addition to glass transition shifts. The as-precipitated polymer sample of IV_a -11 showed two melt endotherms in the first heating traces because of the existence of different crystalline domains.

In Figure 8, TG thermograms of poly(amide-imide)s IV_a -3, 5, 10, and 11 are compared. Obviously, polymers IV_a -10 and IV_a -11 showed evidently higher initial decomposition temperatures owing to higher crystallinity. All the thermal behavior data of all the IV_a and IV_c series polymers are also summarized in Table VII.

CONCLUSIONS

1. High-molecular-weight poly(amide-imide)s containing different lengths of $-(CH_2)_m-$ segment were easily prepared from imide ring-preformed dicarboxylic acids, which were obtained from the condensation of the trimellitic anhydride and ω -amino acids, with various aromatic diamines by means of tri-

phenyl phosphite/pyridine promoted polycondensation reaction. Transparent and tough films were obtained from most of the poly(amide-imide)s by solution cast.

2. Those poly(amide-imide)s derived from *p*-phenylenediamine (III_a), 4,4'-bis(4-aminophenoxy)diphenyl (III_h), and 4,4'-bis(4-aminophenoxy)diphenyl ether (III_i) are crystalline and show less solubility in organic solvents.
3. Some conclusions may be withdrawn from the study of the diamine structure on the glass transition temperature (T_g). Oxy bridges increased chain flexibility and caused a T_g lowering. Isopropylidene or perfluoroisopropylidene also increased chain flexibility but were less effective in reducing the T_g s. Highly dipolar bridging groups, such as sulfonyl, and bulky pendant phenyl groups impact higher T_g . The effect of isomeric attachment in the bis(4-aminophenoxy)benzenes showed that the polymers with *meta* catenation revealed comparable T_g s with those with *para* catenation; however, the *ortho*-polymers exhibited slightly higher T_g s than *para*- or *meta*-ones.
4. Increasing the number of $-CH_2-$ units introduced in the polymer chain led to an increase in crystallinity and a decrease in T_g and solubility in polar amide-type solvents.

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