

Preparation of Polyamide-Imides by Direct Polycondensation with Triphenyl Phosphite.

V. Aliphatic-Aromatic Polyamide-Imides Based on *N,N'*-Bis(ω -Carboxyalkyl)benzophenone-3,3',4,4'-Tetracarboxylic Diimides

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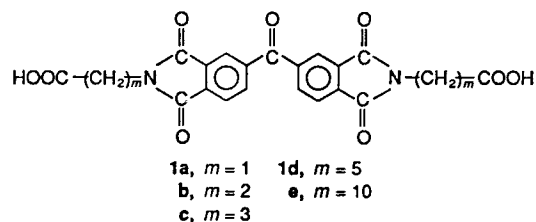
SYNOPSIS

Five diimide-dicarboxylic acids were prepared from benzophenone-3,3',4,4'-tetracarboxylic dianhydride and glycine, β -alanine, 4-aminobutyric acid, 6-aminocaproic acid, and 11-aminoundecanoic acid. New aromatic-aliphatic polyamide-imides were prepared by the direct polycondensation of these diacids with aromatic diamines using triphenyl phosphite in *N*-methyl-2-pyrrolidone (NMP)-pyridine solution in the presence of calcium chloride. The resulting polymers were characterized by inherent viscosity, infrared spectra, elemental analyses, solubility, differential scanning calorimetry (DSC), thermogravimetry, and wide-angle x-ray diffraction measurements.

INTRODUCTION

In 1975 Yamazaki et al.¹ reported an elegant procedure for the synthesis of aromatic polyamides which involves the direct polycondensation of aromatic amino acids or aromatic diamines with aromatic diacids in the presence of an aryl phosphite and an organic base. After them, other researchers²⁻⁵ followed the same system to obtain several novel polyamides and copolyamides. Recently, we have successfully applied the triphenyl phosphite means to the preparation of various polyamide-imides containing trimellitimide and pyromellitimide units.⁶⁻⁹ In the present work, five diimide-diacids **1a-e** were obtained from benzophenone-3,3',4,4'-tetracarboxylic dianhydride and the corresponding ω -amino acids and these were

then directly polycondensed with aromatic diamines by means of triphenyl phosphite preparing several novel aliphatic-aromatic polyamide-imides. These polymers were characterized and the relationships between the properties and their molecular structure were investigated.



EXPERIMENTAL

Materials

Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) was purchased from Aldrich Co. and was recrystallized from boiling acetic anhydride. Glycine (Hanawa), β -alanine (Sigma), 4-aminobutyric acid

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Table I. Yields and Properties of the Diacids 1a–d Prepared from Benzophenone-3,3',4,4'-Tetracarboxylic Dianhydride and Various Amino Acids

Diacid (<i>m</i>)	Yield (%)	mp (°C)	Formula (Mol. wt.)	Elemental Analysis			
				Calcd	Found		
				C	H	N	
1a (1)	85	251–252	C ₂₁ H ₁₂ N ₂ O ₉ (436.33)	Calcd	57.80	2.77	6.42
				Found	57.50	2.74	6.42
1b (2)	87	245–246	C ₂₃ H ₁₆ N ₂ O ₉ (464.39)	Calcd	59.48	3.47	6.03
				Found	59.42	3.51	5.98
1c (3)	83	218–219	C ₂₅ H ₂₀ N ₂ O ₉ (492.44)	Calcd	60.68	4.09	5.69
				Found	61.19	3.82	5.60
1d (5)	75	189–190	C ₂₉ H ₂₈ N ₂ O ₉ (548.55)	Calcd	63.49	5.14	5.10
				Found	63.59	5.13	5.28
1e (10)	73	148–149	C ₃₉ H ₄₈ N ₂ O ₉ (688.81)	Calcd	68.00	7.02	4.06
				Found	67.89	7.01	4.02

Table II. Preparation of Polyamide-imides from Diacids 1a–e and Diamines 2a–e

Formula (<i>m</i> , R) ^a	Monomer concentration ^b		Polymer	
	mol/L	(wt %)	Yield (%)	η_{inh}^d (dL/g)
3a ^d (1, R1)	0.10	6.4	99	1.14
3b (2, R1)	0.15	9.9	99	1.75
3c (3, R1)	0.15	10.3	99	1.22
3d (5, R1)	0.15	11.1	99	insol.
3e (10, R1)	0.15	13.2	97	0.88
4a (1, R2)	0.10	6.4	99	0.83
4b (2, R2)	0.15	9.9	99	1.13
4c (3, R2)	0.15	10.3	98	0.64
4d (5, R2)	0.15	11.1	99	1.33
4e (10, R2)	0.15	13.2	97	0.84
5a (1, R3)	0.10	7.3	99	1.04
5b (2, R3)	0.15	11.2	99	1.78
5c (3, R3)	0.15	11.6	98	1.02
5d (5, R3)	0.15	12.5	99	1.30
5e (10, R3)	0.15	14.6	98	0.94
6a (1, R4)	0.10	6.3	99	0.83
6b (2, R4)	0.15	9.8	99	1.54
6c (3, R4)	0.15	10.2	98	0.81
6d (5, R4)	0.15	11.1	99	insol.
6e (10, R4)	0.15	13.2	96	0.65
7a (1, R5)	0.10	5.4	99	0.85
7b (2, R5)	0.15	8.5	99	1.19
7c (3, R5)	0.15	8.9	98	1.20
7d (5, R5)	0.15	9.7	99	insol.
7e (10, R5)	0.15	11.8	96	0.61

^a *m*: Number of methylene groups in the repeat unit; R: substituent in diamine.^b Conditions: diacid = diamine = 2.5 mmol, TPP = 5.2 mmol, NMP/Py = 4/1 by volume, CaCl₂ = 12 wt %, temperature = 100°C, time = 3 h.^c Measured at a concentration of 0.5 g/dL at 30°C in DMAc containing 5 wt % LiCl.^d ANAL. Calcd for (C₃₃H₂₀N₄O₈)_n: C, 66.00; H, 3.35; N, 9.33%; Found: C, 65.87; H, 3.50; N, 9.23%.

(TCI), 6-aminocaproic acid (TCI), and 11-aminoundecanoic acid (Sigma) were used without purification. *p*-Phenylenediamine (Wako) was vacuum distilled before use. 3,4'-Oxydianiline was supplied by Teijin Co. (Tokyo, Japan) and was used without purification. All other diamines and triphenyl phosphite were purchased from Tokyo Kasei Kogyo Co. The phosphite was purified by vacuum distillation. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180°C for 10 h. NMP and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Synthesis of *N,N'*-Bis(ω -Carboxyalkyl)benzophenone-3,3',4,4'-Tetracarboxylic Diimides (1a-e)

BTDA (0.2 mol) and an ω -amino acid (0.4 mol) were heated in 250–300 mL of dry dimethylformamide (DMF) to 60°C for 1 h. About 80 mL of toluene was added, and the mixture was further heated at reflux until the stoichiometric amount of water was recovered. Toluene was distilled off and the solution was poured into ice water; the precipitated crude diacids were isolated by filtration and recrystallized from DMF–water. Yields and properties of the diacids 1a–e are summarized in Table I.

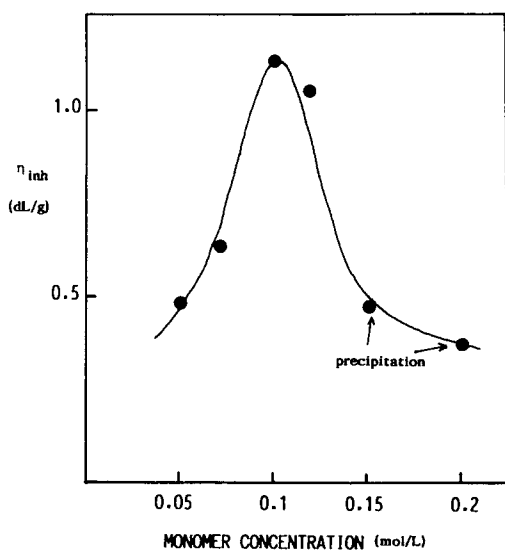


Figure 1. Effect of monomer concentration on the inherent viscosity of polyamide-imide 3a from diacid 1a and diamine 2a.

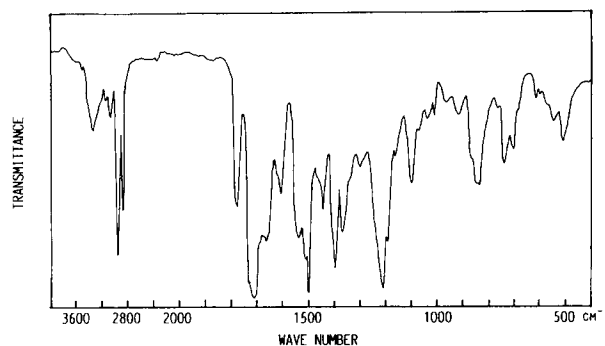


Figure 2. IR spectrum of polyamide-imide 5e.

Polymerization

A diacid (1a–e) (2.5 mmol), an aromatic diamine (2a–e) (2.5 mmol), 1.6 g (5.2 mmol) of triphenyl phosphite, and 12 wt % (1.2–1.6 g) of CaCl_2 were added to a mixture of NMP and pyridine (4 : 1 by volume). The each monomer concentrations ranged from 0.1 to 0.15 mol/L. The reaction mixture was heated with stirring at 100°C for 3 h under nitrogen. The viscous 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. Yields and inherent viscosities of the polymers are summarized in Table II.

Measurements

Inherent viscosities were determined in dimethylacetamide (DMAc) containing dissolved 5 wt % LiCl at 30°C in a Cannon-Fenske viscometer. IR spectra were recorded on a Jasco A-202 Infrared Spectrophotometer. The thermal properties were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) in the DuPont devices 1090B at 20°C/min under nitrogen flow. The x-ray diffraction patterns were obtained for film specimens on a Rigaku Geiger D-Max IIIa x-ray diffraction apparatus with nickel-filtered $\text{CuK}\alpha$ radiation (30 kV, 15 mA).

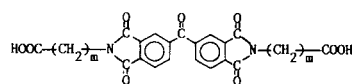
RESULTS AND DISCUSSION

Polymer Synthesis

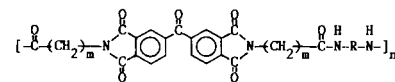
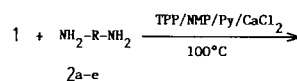
The imide-containing diacids 1a–e were prepared by condensation of BTDA with the corresponding ω -amino acids. The complete cyclization of the in-

intermediate amic acids was achieved by toluene-water azeotropic distillation. Yields, melting points, and elemental analyses of these diacids are summarized in Table I.

The recrystallized diacids **1a-e** were condensed directly with the diamines **2a-e** in the mixture of NMP and pyridine (4 : 1 by volume) in the presence of triphenyl phosphite (TPP) and CaCl₂ at 100°C for 3 h [eq. (1)]. All polyamide-imides were isolated as yellowish materials with almost quantitative yields. Their inherent viscosities are summarized in Table II. Unfortunately, no information was available on some poly(amide-imide)s with five methylenes in the repeated unit because they are insoluble in all common solvents that do not degrade the polymers. The relatively high inherent viscosities suggest that the molecular weights are high enough for potential technical applications. In agreement with this conclusion, tough films could be cast from solution.



1a, m = 1 1d, m = 5
b, m = 2 e, m = 10
c, m = 3



3, 4, 5, 6, 7 (1)

2a: R = R1 = 3a-e: m = 1, 2, 3, 5, 10; R = R1
b: R = R2 = 4a-e: m = 1, 2, 3, 5, 10; R = R2
c: R = R3 = 5a-e: m = 1, 2, 3, 5, 10; R = R3
d: R = R4 = 6a-e: m = 1, 2, 3, 5, 10; R = R4
e: R = R5 = 7a-e: m = 1, 2, 3, 5, 10; R = R5

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

Polymer	Solvent ^b								Conc. H ₂ SO ₄
	DMF	DMAc	NMP	DMI	HMPT	DMSO	<i>m</i> -Cresol	Pyridine	
3a	s	s	s	s	—	s	s	—	s
3b	+	+	+	+	sh	+	+	—	s
3c	—	+	+	+	+h	—	s	—	s
3d	—	—	s	s	—	s	s	—	s
3e	+h	+h	+	+	+	+h	+	+	s
4a	+h	+	+	+	+h	—	s	—	+
4b	+	+	+	+	+h	+	+	+	+
4c	+h	+	+h	+	s	—	s	+h	s
4d	+	+	+	+	+	+	+	+	s
4e	+	+	+	+	+h	+	+	+	s
5a	—	+	+	+	—	+	s	—	+
5b	+	+	+	+	+	+	+	+	+
5c	s	s	s	s	s	s	s	s	s
5d	+	+	+	+	—	+	+	+	s
5e	+	+	+	+	+	sh	+	+	s
6a	+	+	+	+	—	+	+h	—	+
6b	+	+	+	s	sh	+	+	—	+
6c	—	—	—	—	—	—	s	s	+
6d	s	s	s	s	—	+	+	+	+
6e	+	+	+	+	+	+h	+	+	+
7a	—	—	—	—	—	—	—	—	s
7b	+	+	+	+	sh	+	+	—	+
7c	—	—	—	+	—	—	s	—	+
7d	—	—	—	—	—	—	s	—	s
7e	+h	+h	+	+	+	+h	+	+h	+

^a Solubility: +, soluble at room temperature; s, swelling at room temperature; +h, soluble on heating; sh, swelling on heating; —, insoluble.

^b DMF (dimethylformamide); DMAc (dimethylacetamide); NMP (*N*-Methyl-2-pyrrolidone); DMI (1,3-dimethyl-2-imidazolidone); HMPT (hexamethylphosphoric triamide); DMSO (dimethylsulfoxide).

The reactant concentration plays a significant role on the attainment of high molecular weight for polymers synthesized by the phosphorylation reaction. Taking the reaction of diacid **1a** and 4,4'-oxydianiline (**2a**) as an example, the dependence upon monomer concentration exhibits a pronounced maximum, as shown in Figure 1. A maximum of viscosity was observed at the concentration of about 0.1 mol/L. We found that the polymer precipitates from the reaction medium for concentration of 0.15 mol/L and above. This explains the lower inherent viscosities observed for the higher monomer concentrations. By using the concentration of 0.1 mol/L in the polycondensation of diacid **1a** and each diamine, polymers of high η_{inh} above 0.83 dL/g and of nearly quantitative yields were obtained. For other cases using **1b–e** as monomers, an increase of

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

Polymer	T_g^a (°C)	Temperature (°C) with following wt loss ^b			Residual wt % at 800°C
		5%	10%	30%	
3a	235	405	446	610	55.9
3b	232	390	411	600	51.7
3c	198	402	426	638	62.3
3d	195	440	459	610	62.5
3e	132	445	462	495	36.3
4a	226	407	430	601	50.9
4b	224	399	415	595	51.0
4c	188	415	438	600	60.7
4d	170	440	458	506	46.2
4e	126	440	463	495	39.1
5a	230	411	435	598	53.8
5b	221	400	420	575	51.0
5c	178	400	425	596	61.3
5d	158	435	455	498	44.2
5e	122	445	460	493	35.0
6a	233	408	435	550	51.2
6b	221	382	406	532	50.0
6c	195	410	437	605	62.8
6d	187	428	450	565	60.5
6e	136	441	463	494	36.4
7a	250	416	436	513	48.3
7b	237	388	406	580	51.8
7c	209	405	425	616	58.0
7d	200	440	460	520	59.1
7e	125	436	455	487	32.5

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

^b Thermogravimetric analyses conducted at a heating rate of 20°C/min in nitrogen.

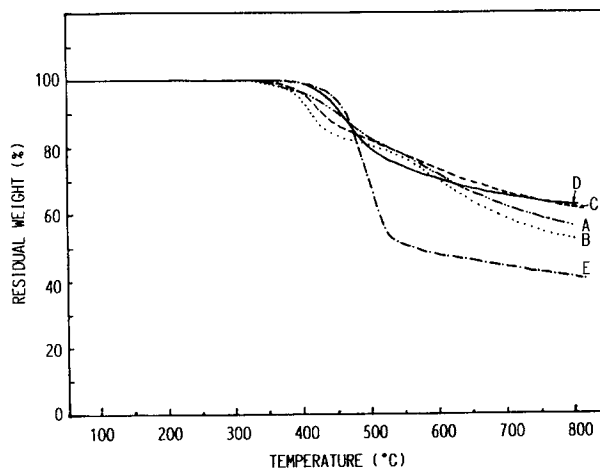


Figure 3. TG curves of polymers (A) **3a**, (B) **3b**, (C) **3c**, (D) **3d**, and (E) **3e**, with heating rate of 20°C/min in nitrogen.

monomer concentration to 0.15 mol/L could proceed the polymerization smoothly without precipitation of polymers. This can be attributable to the increased solubility of the resulting polymers due to the presence of more flexible structure.

The polymers were characterized by infrared spectra and elemental analysis. The infrared spectra showed characteristic imide bands at 1780 and 1720 cm^{-1} due to symmetrical and asymmetrical carbonyl stretching vibrations and at 1100 and 740 cm^{-1} possibly due to ring carbonyl deformations. Bands of amide groups appear at approximately 3300, 1660, and 1540 cm^{-1} . A typical IR spectrum for the representative polyamide-imide **5e** is shown in Figure 2. The results of elemental analysis are in exceptionally good agreement with the polymer structures.

Properties of Polymers

The qualitative solubilities of the polyamide-imides are listed in Table III. The series of **4a–e** derived from 3,4'-oxydianiline (**2b**) showed better solubility due to the existence of an unsymmetrical 3,4'-diphenyl ether along with the polymer chain, and those polyamide-imides derived from *p*-phenylenediamine (**2e**) showed less solubility due to the more rigid nature of their polymer backbones. However, no clear relationship was found between the solubility and the number of methylene units. It is of interest to note that not all the polyamide-imides are soluble in concentrated sulfuric acid. This phenomenon is quite different from that observed from the polyamide-imides based on trimellitimide or pyromellitimide. In general these polyamide-imides based

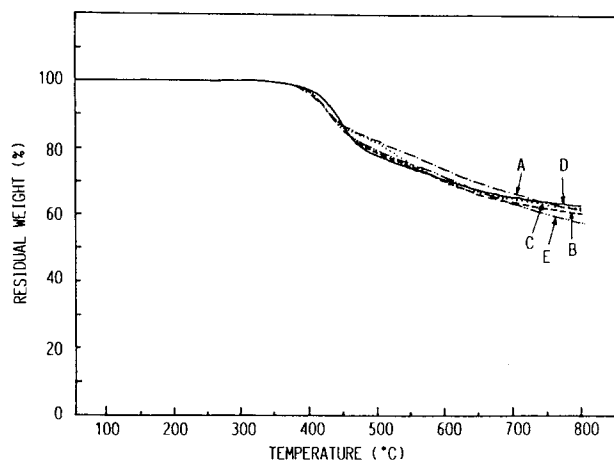


Figure 4. TG curves of polymers (A) **3c**, (B) **4c**, (C) **5c**, (D) **6c**, and (E) **7c**, with a heating rate of 20°C/min in nitrogen.

on benzophenonetetracarboxylic diimide showed better solubility than their homologs with pyromellitimide units while less solubility than that with trimellitimide units as described in the Parts I-IV.⁶⁻⁹

Table IV summarizes the data of DSC and thermogravimetric analyses of all the polyamide-imides. DSC measurements conducted at a heating rate of 20°C/min revealed glass transition temperatures (T_g) in the range 122–250°C. As expected, the T_g 's increase with decreasing length of the flexible aliphatic chains. The low degrees of crystallinity developed are the main cause of not being able to observe well-defined melting points by DSC. To confirm further the crystalline characteristics of these polymers they have been subjected to x-ray diffraction determinations. Almost all the polyamide-imides showed amorphous patterns, which can be explained by the unsymmetrical structure probably due to the presence of benzophenone units.

The thermal stability of the polyamide-imides

was characterized by means of thermogravimetric analyses conducted at a heating rate of 20°C/min in nitrogen. Typical TG curves are illustrated in Figures 3 and 4. The polyamide-imides with 10 or 5 methylenes start to lose weight at higher temperatures than those with 1–3 methylenes, possibly due to better packing of polymer chains in the case of longer aliphatic carbons. The nature of the diamine seems not to affect the thermal stability significantly. As shown in Table IV, the decomposition temperatures at which 10% weight loss was observed for all polyamide-imides were recorded above 400°C. The thermostability of these polymers is certainly lower than that of fully aromatic ones. Table IV also lists the char yields of polyamide-imides at 800°C under nitrogen. As expected, the lowest values correspond to the polymers containing 10 methylene units.

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