

Synthesis and Characterization of Oxyethylene Containing Polyamide-imides*

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Synopsis

Two nonlinear dihydrazides, namely 1,2-bis(3-hydrazinocarbonylphenoxy)ethane and bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether, were synthesized by the acylation reaction of hydrazine hydrate with the corresponding aromatic esters and were characterized by IR, ¹³C-NMR, and mass spectroscopy. These dihydrazides were each polycondensed with dianhydrides, benzophenonetetracarboxylic dianhydride (BTDA), and pyromellitic dianhydride (PMDA) to obtain poly(amic acid) with η_{inh} 0.60–0.85 dL/g in dimethylacetamide solution. These poly(amic acid)s were soluble in polar aprotic solvents like dimethylacetamide (DMAc), dimethyl formamide (DMF) and could be cast into transparent, tough, and flexible films that were cyclodehydrated to obtain amorphous, thermally stable polyamide-imides. The polymers were characterized by IR spectroscopy, X-ray diffraction, and thermogravimetric analysis.

INTRODUCTION

Studies in high-performance polymers, like polyamides, polyamide-imides, and polyimides, which are well known for their high thermal stability, reveal that rigid crystalline structures of high symmetry account for their high softening point, poor solubility in organic solvents, and poor processability. It is highly desirable that these polymers be soluble to facilitate processing and be solvent resistant in use. As an approach to improve the polymer processing characteristics, emphasis is placed on the synthesis of thermally stable polymers by the insertion of flexibilizing groups such as, oxyethylene, ether, sulfone, and so on into the polymer backbone, and by the disturbance of rigid crystalline structure of the polymer to improve their solubility in organic solvents without much sacrifice in thermal stability.^{1–4} Condensation type polyamide-imides containing oxyethylene linkages are reckoned to possess good thermal stability, toughness, and ease of processability and be intermediate between polyamides and polyimides in properties.^{5–10}

Polyamide-imides can be prepared by a variety of routes,^{11–21} while those containing N–N linkages are prepared by the reaction of tetracarboxylic dianhydrides and dihydrazides.^{22–25} In this study we report the synthesis and characterization of two nonlinear dihydrazides containing oxyethylene moiety, viz., 1,2-bis(3-hydrazinocarbonylphenoxy)ethane and bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether, by the convenient acylation reaction of hydrazine hydrate with corresponding aromatic diesters, the most common acylating agent²⁶

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and their characterization by IR, ^{13}C -NMR, and mass spectra. Further we describe their polycondensation with dianhydrides BTDA and PMDA to give four new polyamide-imides containing oxyethylene linkages, with a view to study the improvement in solubility in organic solvents. The polyamide-imides were characterized by IR spectroscopy, X-ray diffraction, and thermogravimetric analysis.

We synthesized 1,2-bis(4-hydrazinocarbonylphenoxy)ethane and bis[2-(4-hydrazinocarbonylphenoxy)ethyl] ether, the para-analogues, also, but owing to their insolubility, these were not pursued further.²⁸

EXPERIMENTAL

N,N-Dimethylacetamide (DMAc) was fractionally distilled under reduced pressure after it was stood over P_2O_5 for 24 h. 1,2-Dibromoethane, 2-chloroethyl ether, thionyl chloride, and hydrazine hydrate were distilled prior to use. Benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA) were sublimed prior to use. Other chemicals were of laboratory reagent grade and were used as such.

Synthesis of 1,2-bis(3-Hydrazinocarbonylphenoxy)ethane (4a)

Preparation of 2,3-bis(3-Carboxyphenoxy)ethane (1a), the Diacid

To a well-stirred solution of 3-hydroxybenzoic acid (13.8 g, 0.1 mol) and sodium hydroxide (8.0 g, 0.2 mol) in 50 mL water under reflux, was added 1,2-dibromoethane (9.2 g, 0.05 mol) dropwise over 1 h. The reaction mixture was maintained in that condition for 10 h. Next, sodium hydroxide (2.0 g, 0.05 mol) was added and refluxed further for 1 h. The reaction mixture was cooled, dissolved in water, filtered, and acidified with 10% hydrochloric acid to give **1a**. Yield: 7.59 g (55%), mp 289–290°C; lit.²⁷ 291–293°C.

Preparation of 1,2-bis(3-Carbethoxyphenoxy)ethane (3a), the Diethyl Ester

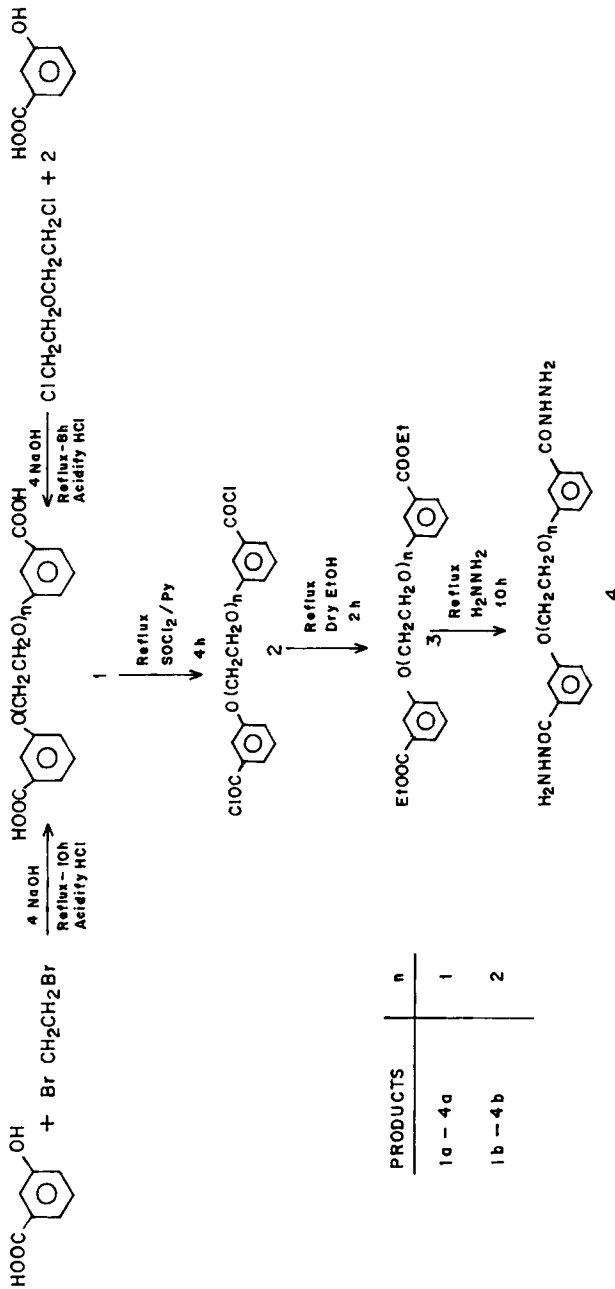
1a (3.02 g, 0.01 mol), thionyl chloride (23.8 g, 0.2 mol), and one drop of pyridine were refluxed for 4 h. Removal of excess thionyl chloride under reduced pressure and recrystallization from a mixture of pet ether–benzene gave pure 1,2-bis(3-chlorocarbonylphenoxy)ethane (**2a**), the diacylchloride. Yield: 2.78 g (92%), mp 100°C.

2a (3.39 g, 0.01 mol) was refluxed with 100 mL dry ethanol for 2 h, and recrystallization from ethanol gave **3a**. Yield: 3.25 g (96%), mp 79°C.

Preparation of 1,2-bis(3-Hydrazinocarbonylphenoxy)ethane (4a), the Dihydrazide

To a solution of **3a** (3.58 g, 0.01 mol) in 50 mL dry ethanol was added hydrazine hydrate (12.8 g, 0.04 mol) and refluxed for 10 h. The solid that separated out was recrystallized from ethanol–DMAc mixture to yield **4a** in pure form. Yield: 2.79 g (78%), mp 210°C:

ANAL: Calcd: C, 58.18%; H, 5.45%, N, 16.97%. Found: C, 58.00%; H, 4.98%; N, 16.62%.



Scheme 1. Synthesis of oxyethylene containing dihydrazides.

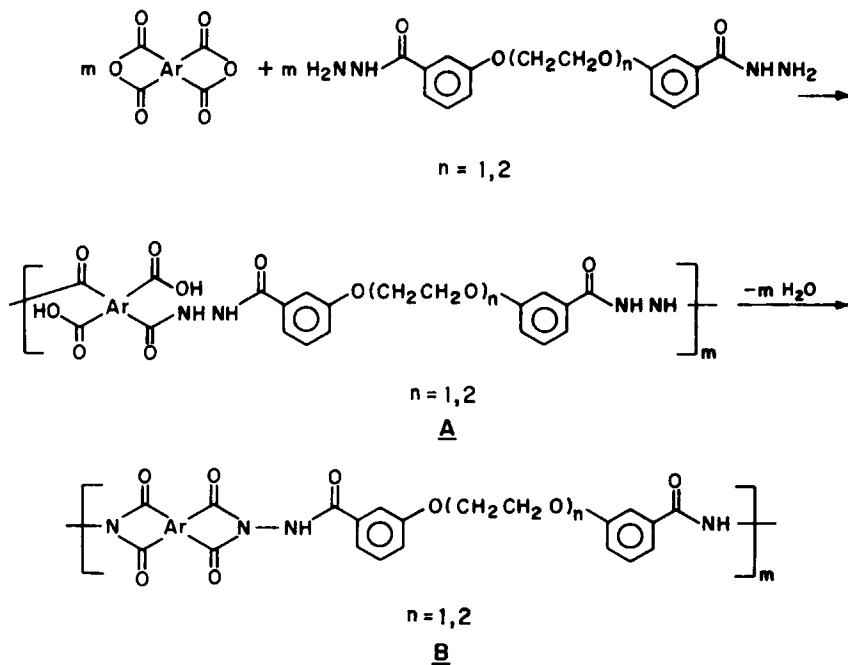
Synthesis of bis[2-(3-Hydrazinocarbonylphenoxy)ethyl] ether (4b)

Preparation of bis[2-(3-Carboxyphenoxy)ethyl] Ether (1b), the Diacid

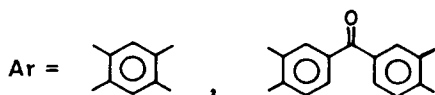
To a well-stirred solution of 3-hydroxybenzoic acid (13.8 g, 0.1 mol) and sodium hydroxide (8.0 g, 0.2 mol) in 50 mL water under reflux, 2-chloroethyl ether (7.15 g, 0.05 mol) was added over 1 h. The reaction mixture was maintained in that condition for 8 h. Next, sodium hydroxide (2.0 g, 0.05 mol) was added and refluxed further for 1 h. The reaction mixture was cooled, dissolved in water, filtered and acidified with 10% hydrochloric acid to give **1b**. Yield: 8.0 g (64.5%), mp 225°C; lit.²⁷ 226–228°C.

Preparation of bis[2-(3-Carboxyphenoxy)ethyl] Ether (3b), the Diethyl Ester

1b (3.46 g, 0.01 mol), thionyl chloride (24.0 g, 0.2 mol), and one drop of pyridine was refluxed for 4 h. Removal of excess thionyl chloride under reduced pressure and recrystallization from pet ether–benzene mixture gave bis[2-(3-chlorocarbonylphenoxy)ethyl] ether (**2b**), the diacylchloride. Yield: 3.3 g (95%), mp 70°C.



Where,



Scheme 2.

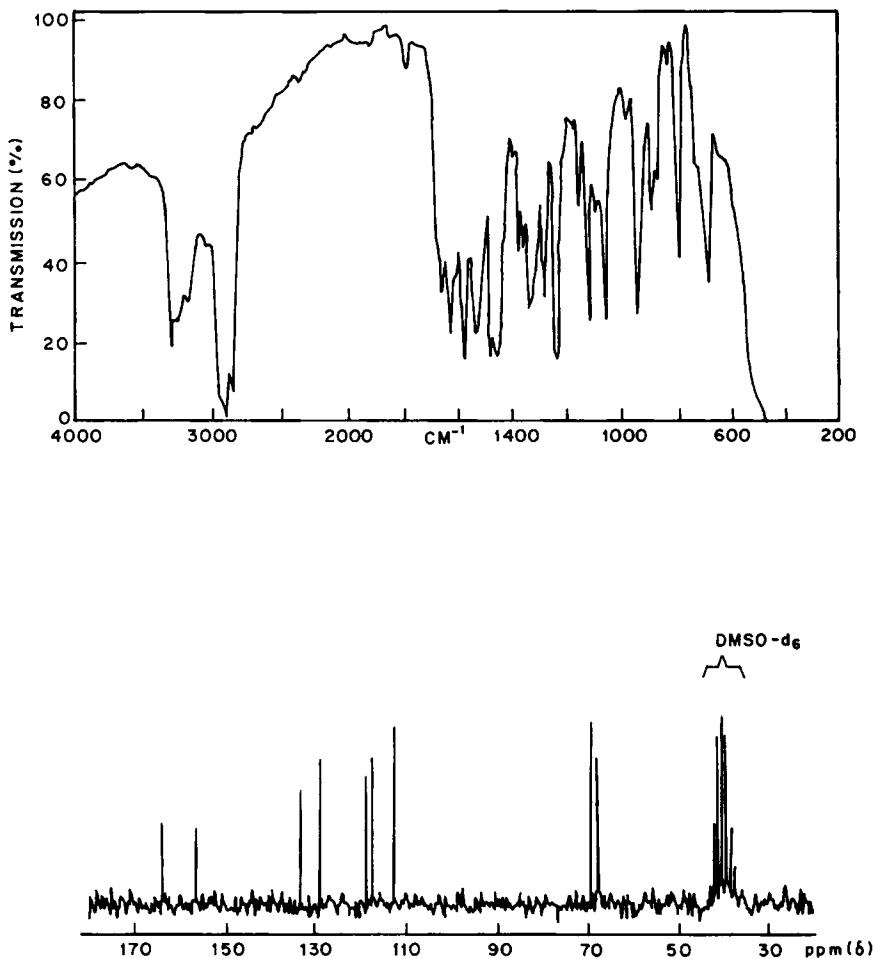


Fig. 1. IR and ^{13}C -NMR spectra of bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether.

2b (3.88 g, 0.01 mol) was refluxed for 2 h in 100 mL dry ethanol. Recrystallization from ethanol gave **3b**. Yield: 3.37 g (88%), mp 56°C.

Preparation of bis[2-(3-Hydrazinocarbonylphenoxy)ethyl] Ether (4b), the Dihydrazide

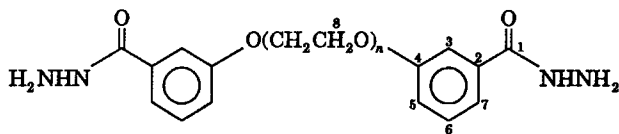
To a solution of **3b** (4.02 g, 0.01 mol) in 100 mL ethanol was added hydrazine hydrate (12.8 g, 0.04 mol) and refluxed for 10 h. The solid that separated out was recrystallized from water-DMAC mixture to give **4b** in pure form. Yield 3.4 g (85%), m.p. 144–145°C:

ANAL: Calcd: C, 57.75%; H, 5.88%; N, 14.97%. Found: C, 56.98%; H, 5.39%; N, 14.67%.

Polymerization

As an illustration we report the polymerization of dihydrazide **4a** with PMDA. The other three polymers were prepared similarly (Scheme 2).

TABLE I
 ^{13}C -NMR Spectral Values of Dihydrazides



$n = 1, 2$

Carbon no.	Diacylhydrazide 4a ($n = 1$) (ppm) δ	Diacylhydrazide 4b ($n = 2$) (ppm) δ
1	165.61	166.91
2	134.87	135.00
3	129.48	130.39
4	158.33	159.12
5	112.90	113.56
6	117.65	118.50
7	119.60	120.06
8	66.57	68.13
9		69.62

Preparation of Polyamide-imide **IB** and Poly(amic Acid) **IA**

A mixture of dihydrazide **4a** (3.30 g, 0.01 mol) and 100 mL DMAC containing 0.5 g LiCl was heated to 90°C and then cooled to 10°C after dissolution. To this clear solution, maintained at 10°C , was added with stirring PMDA (2.18 g, 0.01 mol) in small portions of 20 mg over a period of 1 h. The reaction mixture became viscous as the solid dissolved. It was stirred for 2 h at 10°C . The entire experiment was conducted under a slow stream of dry nitrogen. The poly(amic acid) gave inherent viscosity of 0.85 dL/g in DMAC at 30°C .

The poly(amic acid) **IA** was precipitated by pouring one-third of the reaction mixture into a large excess of water. It was washed with water, filtered, and dried in vacuum, when white flakes of polymer were obtained.

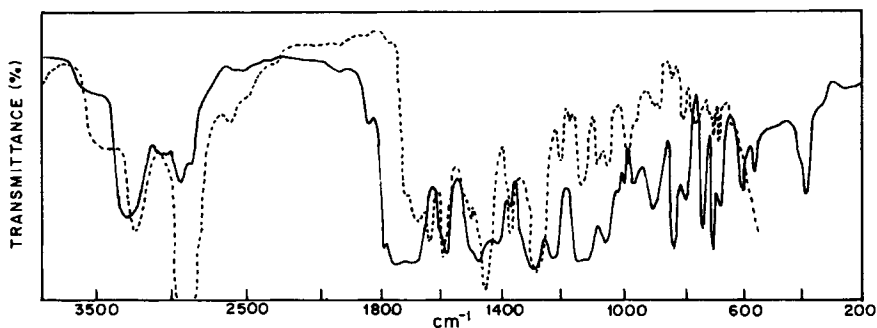


Fig. 2. IR spectrum of poly(amic acid) **III A** and polyamide-imide **III B**.

TABLE II
Preparation of Poly(amic acid)s and Their Inherent Viscosities

Polymer	Dihydrazide (g)		Dianhydride (g)		LiCl (g)	DMAc (mL)	Reaction condition		η_{inh} of ^a poly(amic acid) (dL/g)
	4a	4b	PMDA	BTDA			°C	h	
IB	3.30	—	2.18	—	0.5	100	10	2	0.85
IIB	3.30	—	—	3.22	0.5	100	10	2	0.81
IIIB	—	3.7	2.18	—	—	100	10	1.5	0.84
IVB	—	3.7	—	3.22	—	100	10	1.5	0.65

^a Measured at a concentration of 0.5 g/100 mL in DMAc at 30°C.

Preparation of Polyamide-Imide IB by Imidization Reaction

1. By chemical cyclization: To one-third of the reaction mixture was added 2 mL acetic anhydride and 2 mL pyridine at room temperature and swirled for 5 min and allowed to stand for 2 h. During this period, the solution developed a yellow tinge. Polymer **IB** formed in solution was precipitated with methanol, filtered, and washed with methanol. Yellow flakes a polyamide-imide were obtained and were dried at 100°C in vacuum for 3 h.
2. Thermal cyclization: The remaining reaction mixture was poured on a glass plate and the solvent was removed under vacuum. The tough film obtained was cyclized by heating in vacuum at 250°C for 3 h.

Alternately, polyamide-imide was prepared by heating the precipitated poly(amic acid) at 250°C for 3 h in high vacuum.

RESULTS AND DISCUSSION

Due to their high softening point and insolubility in common organic solvents, polyamide-imides could not be widely exploited commercially. Of the various approaches that attempted to improve their solubility, introduction of flexible linkages, such as ether, sulfone, etc., in the polymer backbone met with some

TABLE III
Solubility of Polyamide-imides

Polyamide-imides	Solubility in different solvents ^a							
	Concn H ₂ SO ₄	HMPA	NMP	DMAc	DMAc + 5% LiCl	DMF	DMSO	<i>m</i> -Cresol
IB	++	+	+	—	+	—	—	—
IIB	++	+	+	—	+	—	—	—
IIIB	++	+	+	+	+	—	—	—
IVB	++	+	+	+	+	—	—	—

^a ++ = Soluble; + = slightly soluble on heating; — = insoluble.

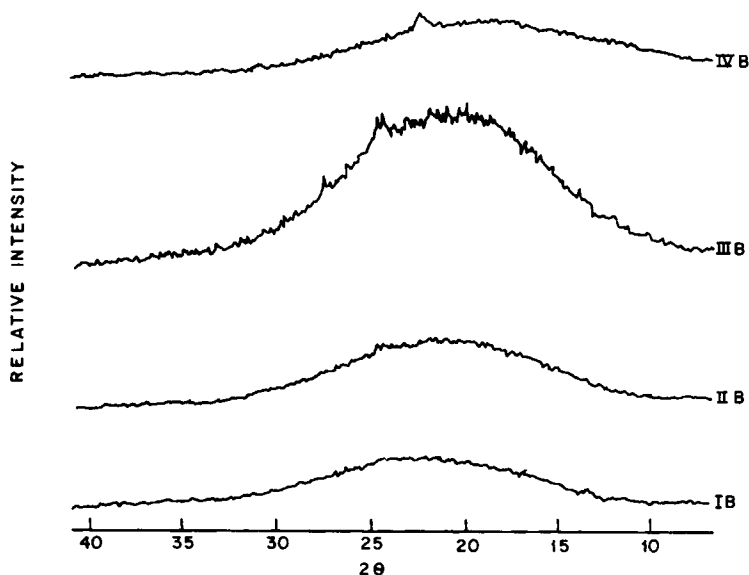


Fig. 3. X-ray diffraction patterns of polyamide-imides.

success. In the present work, four new polyamide-imides containing oxyethylene linkages were prepared by the polycondensation of dihydrazides with BTDA and PMDA with a view to improve their solubility. These were characterized by IR spectroscopy, X-ray diffraction, and thermogravimetric analysis.

The dihydrazides containing oxyethylene linkage were synthesized by the facile acylation reaction of hydrazine hydrate with diethyl esters of corresponding diacids as illustrated in Scheme 1 and characterized by IR, $^{13}\text{C-NMR}$, and mass spectroscopy. IR spectra of dihydrazides (e.g. **4B**, Fig. 1) show peaks at 3260, 1650, and 1240 cm^{-1} characteristic of N—H, C=O, and C—O—C groups, respectively. The presence of molecular ion peaks at 330 and 374 in mass spectra of dihydrazides **4a** and **4b**, respectively, and $^{13}\text{C-NMR}$ spectra (Table I) confirmed the structure of dihydrazides.

Synthesis of polyamide-imides by polycondensation of dianhydrides and dihydrazides involves two steps—the ring opening polyaddition reaction of the dianhydride with dihydrazide to form the poly(amic acid) **A** and the subsequent imidization to polyamide-imide **B** containing both amide and imide units. Ring opening polyaddition reaction of dianhydride with dihydrazide was carried out at low temperature in polar solvents in a slow stream of dry nitrogen.

Dihydrazide **4b** was freely soluble in DMAc. However, owing to its low solubility in DMAc, dihydrazide **4a** was dissolved in DMAc containing 5% LiCl. The solution of both these dihydrazides were reacted with PMDA and BTDA at 10°C to give poly(amic acid) **A**, which could be isolated by adding water. Alternatively, transparent, tough, and flexible films could be obtained by evaporation of solvent after casting.

Cyclodehydration of the poly(amic acid) **A** to polyamide-imide **B** could be achieved both chemically as well as thermally. In the present work both methods were used. In chemical cyclization DMAc solution of poly(amic acid) **A** was treated with acetic anhydride and pyridine, when a yellow-colored solution was

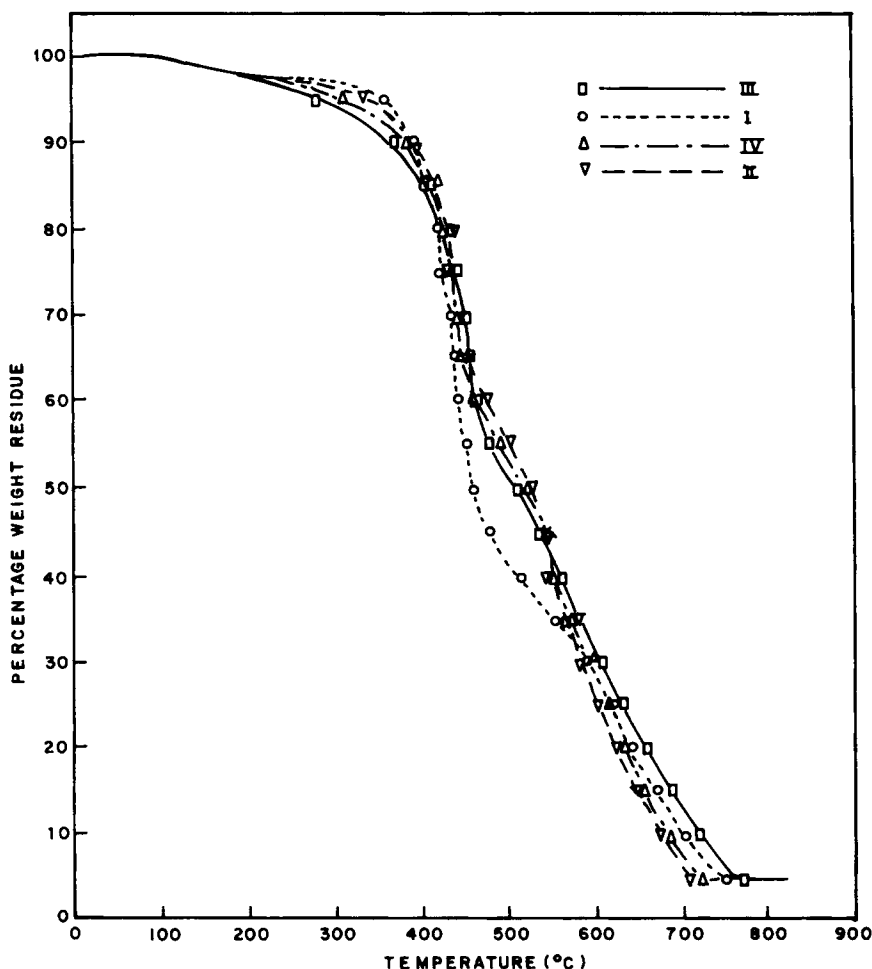


Fig. 4. TGA curves of polyamide-imides in air at a heating rate of 10°C/min.

obtained from which yellow flakes of polyamide-imide **B** were precipitated by addition of methanol. In thermal cyclization the cast film of poly(amic acid) was heated in vacuum at 250°C to give a tough, pale yellow film. Polyamide-imides thus obtained by both methods showed similar IR and absence of amic acid bands.

The IR spectra of poly(amic acid) **A** (e.g., **IIIA**, Fig. 2) showed characteristic peaks at 3300 cm^{-1} for N-H stretching, 1700 and 1660 cm^{-1} for C=O stretching of carboxylic acid and C=O stretching of amide, respectively, and 1230 cm^{-1} for C-O-C stretching. The IR spectra of polyamide-imides (e.g., **IIIB**, Fig. 2) showed characteristic strong absorptions at 1795 and 1745 cm^{-1} (imide-I), 1705 cm^{-1} (for C=O of amide), 1380 cm^{-1} (imide-II), 1230 cm^{-1} (for C-O-C), 1150 cm^{-1} (imide-III), and 718 cm^{-1} (imide-IV). Imide-I band is attributed to the stretching vibrations of two carbonyls that are weakly coupled. Imide-II, -III, and -IV bands are assigned to axial, transverse, and out-of-plane vibrations of the cyclic imide structure.

TABLE IV
Percent Weight Loss of Polyamide-imides at Different Temperatures (°C)^a

Polymer	IB	IIB	IIIB	IVB
IDT ^b	340	340	320	360
T _{% wt loss}				
10	365	370	335	370
20	395	400	380	415
30	415	420	405	435
50	445	520	480	520

^a Heating rate 10°/min.

^b Initial decomposition temperature.

Inherent viscosities of the polymers were determined at the poly (amic acid) stage in DMAc at 30°C by diluting the solutions to a concentration of 0.5 g/100 mL. It varied from 0.60 to 0.85 dL/g (Table II). The polyamide-imides once precipitated from DMAc solution do not dissolve in many organic solvents. They swell in 1-methyl-2-pyrrolidone (NMP) and hexamethylphosphoramide (HMPA) and dissolved slightly on heating (Table III). However, these polymers were soluble in concentrated sulfuric acid accompanied with degradation as evidenced by their low viscosities in it.

The polyamide-imides were amorphous in nature as evidenced by their X-ray diffraction patterns taken by the powder method using nickel-filtered CuK α radiations on Phillips X-ray unit (Phillips generator, PW-1730). Figure 3 shows the X-ray diffraction patterns of these polyamide-imides.

The thermal stability of the polymers **IB** to **IVB** was studied by thermogravimetric analysis (TGA) on Netzsch 409 Thermal Analyzer. Thermograms were obtained by heating the samples in air at a heating rate of 10°C/min (Fig. 4). A weight loss of 3% up to 300°C in all these polymers may be attributed to the absorbed moisture. Initial decomposition temperature (IDT) for these polymers was in the range 320–360°C. The results of thermogravimetric analysis are incorporated in Table IV.

CONCLUSION

Two new nonlinear dihydrazides, namely 1,2-bis(3-hydrazinocarbonylphenoxy)ethane and bis[2-(3-hydrazinocarbonylphenoxy)ethyl] ether, containing oxyethylene linkages, were synthesized and characterized by IR, ¹³C-NMR, and mass spectroscopy. Four new polyamide-imides containing oxyethylene linkages were prepared by the polycondensation of these dihydrazides and dianhydrides BTDA and PMDA. Poly(amic acid) was soluble in DMAc and could be cast into a tough film, but the polyamide-imides were insoluble. These polyamide-imides showed good thermal stability. Introduction of oxyethylene linkages imparts partial solubility improvement. However, greater modification is needed for complete solubility.

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28. Unpublished results during the course of the present work.

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