Synthesis and Characterization of Polyester–Imides from Imidodicarboxylic Acid Monomers and Ethylene Glycol*

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SYNOPSIS

Two monoimidodicarboxylic acids and four diimidodicarboxylic acids were synthesized from trimellitic anhydride and amino compounds, viz., glycine, p-aminobenzoic acid, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl methane, and 4,4'-diaminodiphenyl sulfide, and characterized by IR and ^{1}H-NMR spectroscopies and melting-point determination. These functional monomers were condensed in N-methyl-2-pyrrolidone solvent with ethylene glycol by a transesterification reaction to obtain the novel polyester–imides with backbones of alternate imide–ester linkages or imide–imide–ester–ester linkages with $-SO_2-$, $-O-$, $-CH_2-$, or $-S-S-$ bridges in between. All the polymers were characterized by IR and ^{1}H-NMR spectroscopies, X-ray diffraction, solution viscosity, solubility and solubility parameters, and differential thermal analysis. Most of the polymers possess amorphous structure and fairly high decomposition temperatures (450–485°C). These polymers having solubility parameters in the range δ 11.44–11.85, as determined by the group contribution technique, are soluble at room temperatures in aprotic polar solvents. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides have reached universal acceptance as high-performance polymers because of their outstanding thermal stability. The utilization of these polymers, however, is restricted by their poor processing characteristics. Polyester–imides have been reported as alternative materials to polyimides due to the combination of good solubility and thermal properties.

The first reports on the synthesis of polyester–imides appeared in the late 1960s.[1,2] Subsequently, a number of workers[3–8] have shown a great deal of interest in the development of this class of polymers, especially to substitute polyimides as high-temperature polymers. Some reports have appeared in which polyester-imides were obtained from imide-containing functional monomers, viz., bis-N-hydroxy imides,[9,10] diimide acids and their esters,[11–13]

and N-(4-hydroxyphenyl)trimellitimide.[14,15] This paper describes the synthesis of ordered polyester-imides, having regular enchainment of ester and imide groups and possessing good solubility characteristics and thermal properties, by the reaction between imide-containing dicarboxylic acids and ethylene glycol.

EXPERIMENTAL

Materials

Trimellitic anhydride (Fluka) was purified by recrystallization from acetic anhydride. 4,4'-Diaminodiphenyl ether (Fluka) and 4,4'-diaminodiphenyl methane (Fluka) were purified by vacuum drying at 50–60°C. 4,4'-Diaminodiphenyl sulfone (Fluka) was recrystallized from aqueous ethanol followed by vacuum drying. 4,4'-Diaminodiphenyldisulfide (Aldrich) was used as received. Ethylene glycol (BDH) was purified by first refluxing over anhydrous sodium sulfate and then distilling under vacuum. p-Aminobenzoic acid (Loba) and glycine (Loba) were used as received.

The solvents used in the synthesis, viz., *N*-methyl-2-pyrrolidone, dimethyl formamide, and toluene, were dried over P_2O_5, distilled at low pressure, and stored over 4 Å molecular sieves. Other solvents/chemicals used for solubility tests were of laboratory-grade reagents and were used without further purification.

Monomer Synthesis

Monoimidodicarboxylic Acids

N- (Carboxymethyl) trimellitimide (MIDA-1). Trimellitic anhydride (19.2 g, 0.1 mol) and glycine (7.5 g, 0.1 mol) were placed in a 250 mL round-bottom flask equipped with a mercury-seal stirrer, a thermometer, a nitrogen inlet tube, and a Dean and Stark trap with a water-cooled condenser. Toluene, 60 mL, were added to the flask and the reaction carried out under reflux until there was no further elimination of water. The toluene was distilled off and the product precipitated out by pouring the contents of the flask into 500 mL of distilled water. It was purified by washing repeatedly with methanol and dried under vacuum at 60°C: yield 75%; mp 249°C.

N - (*p* - Carboxyphenyl)trimellitimide (MIDA-2). To a 250 mL round-bottom flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet tube were added 90 mL of dimethyl formamide, 24.6 g (0.18 mol) *p*-aminobenzoic acid, and 34.5 g (0.18 mol) trimellitic anhydride. The reaction mass was heated under stirring and the temperature raised to 132–134°C in 2.5 h. The reaction mixture was then poured over four times its volume of distilled water. The precipitated product was filtered, washed with distilled water, and dried under vacuum at 110°C: yield 74%; mp 290°C.

Diimidodicarboxylic Acids

N,N'- (4,4'-Diphenylsulfone)bistrimellitimide (DIDA-1). Trimellitic anhydride (15.3 g, 0.08 mol) was dissolved in 50 mL of *N*-methyl-2-pyrrolidone at 50°C in a 250 mL round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a thermometer. After cooling the solution to room temperature, 4,4'-diaminodiphenyl sulfone (9.9 g, 0.04 mol) was added to the flask and left for 5 h at room temperature under stirring. The temperature was then slowly raised to 180°C and maintained there for 4 h to complete the reaction. The product was isolated by pouring the reaction mixture into

500 mL of distilled water, filtered, and repeatedly washed with distilled water. The product was dried under vacuum at 60°C: yield 78%; mp 390°C.

A similar procedure was followed in the synthesis of *N,N'*- (4,4'-diphenylether) bistrimellitimide (DIDA-2): yield 72%, mp 390°C; N,N'(4,4'-diphenylmethane)bistrimellitimide (DIDA-3): yield 70%, mp 380°C; and N,N'-(4,4'-diphenylsulfide)bistrimellitimide (DIDA-4): yield 65%, mp 390°C.

All the monomers were purified by recrystallization from boiling acetic anhydride. The structures of the functional monomers are given in Tables I and VI.

Polymer Synthesis

Polyester–imides were synthesized by transesterification reaction between imidodicarboxylic acids and excess of ethylene glycol using *N*-methyl-2-pyrrolidone as solvent. A typical reaction of the formation of polyester–imide from *N*-(carboxymethyl)trimellitimide and ethylene glycol is schematically shown in Figure 1.

The procedure adopted for polyester–imide synthesis is as follows: Imidodicarboxylic acid (0.1 mol) was reacted with ethylene glycol (0.5 mol) using calcium acetate as catalyst (0.05%) and *N*-methyl-2-pyrrolidone as solvent. The calculated amounts of the reactants were placed into a 250 mL round-bottom flask fitted with a mercury-seal stirrer, a thermometer, a water condenser, and a nitrogen inlet tube. The temperature was raised slowly under stirring to 175 ± 5°C and maintained there for 4 h. The temperature was further raised to 260°C at the rate of 15°C/h and maintained there for 2 h, and, finally, vacuum was applied to remove the residual solvent and unreacted ethylene glycol.
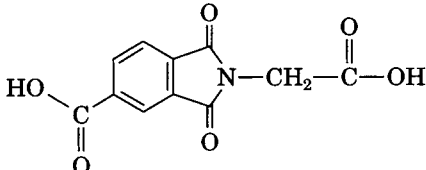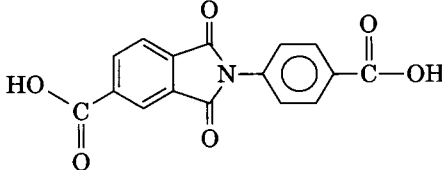
The structures of polyester–imides derived from monoimido- and diimidodicarboxylic acids and ethylene glycol are shown in Tables II and III, respectively.

CHARACTERIZATION

Spectral Analysis

IR spectra were recorded using KBr pellets on a Perkin-Elmer Model 882 infrared spectrophotometer. ^{1}H-NMR spectra were obtained in DMSO-d_6 by using 80 MHz NMR spectrometer.

Table I   Monoimidodicarboxylic Acids: Monomer Structures and Elemental Analysis

Monomer		Elemental Analysis (%)		
Code	Structure	C	H	N
MIDA-1	N-(carboxymethyl)trimellitimide	Calcd 53.01 Found 53.36	2.81 2.87	5.62 5.31
MIDA-2	N-(p-carboxyphenyl)trimellitimide	Calcd 61.73 Found 60.98	2.89 2.51	4.50 4.55

Melting Points

Melting points of the functional monomers were determined by differential thermal analysis (DTA), using a Leeds and Northup thermal analyzer.

Elemental Analysis

Elemental analysis of the monomers was carried out using an elemental analyzer Model CHN-600 of Leco Corporation, U.S.A.

Viscosity

Inherent viscosity (dL/g) of the polymer was measured at 30°C using 0.5% (g/mL) solution of the polymer with an Ubbelohde viscometer.
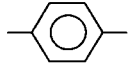
Solubility

A 10% solution (wt/vol) was taken as criterion for the solubility of a polymer. Polyesterimide, 0.5 g, was placed in 5 mL of each of the solvents and al-

Table II   Properties of Polyesterimides Based on Monoimidodicarboxylic Acids

$$HO—CH_2—CH_2—O \left[C \cdots N—X—C—O—CH_2—CH_2—O \right]_n H$$

Polymer		Inherent Viscosity[a] (dL/g)	Density (g/cc)	Decomposition Temperature in Air[b] (°C)
Code	X			
PEI-M$_1$	—CH$_2$—	0.2854	1.348	360
PEI-M$_2$	—⟨○⟩—	0.2921	1.360	450

[a] 0.5% solution in N-methyl-2-pyrrolidone.
[b] By differential thermal analysis.

Figure 1   Schematic of polyester–imide synthesis.

lowed to stand for 48 h in closed test tubes and then observed to judge solvent effects.

Solubility Parameters

The solubility parameter (δ) was calculated from Small's group contribution method,[16] using the following relationship:

$$\delta - \rho \left| \frac{\Sigma\, G}{M} \right|$$

where $\Sigma\, G$ is the sum of Small's group contribution (i.e., molar attraction volume); M, the formula weight of the polymer repeat unit; and ρ, the density of the polymer. The molar attraction values reported by Hoy[17,18] have been used to calculate the solubility parameter. The calculations are shown in Tables IV and V.

Density

The density of the polymer was determined by a pycnometer in toluene at 30°C.

Differential Thermal Analysis (DTA)

Thermal decomposition temperature of the polymer was determined by DTA, using a Leed and Northup thermal analyzer at a heating rate of 12.5°C/min in air with α-Al_2O_3 material in Robert-Gruinshaw-type ceramic holder. The Pt—Pt 10% Rh was used as the differential thermocouple.

X-ray Analysis

The crystallinity of the polymer was determined with a Philips X-ray diffractometer (Model No. PW-100) using Ni-filtered CuKα radiation (1.5418 Å).

RESULTS AND DISCUSSION

Imidodicarboxylic Acid Monomers

The structures of monoimidodicarboxylic acids and diimidodicarboxylic acids along with the data of elemental analysis are given in Tables I and VI, respectively. The percentage composition of the ele-

Table III Properties of Polyester-Imides Based on Diimidodicarboxylic Acids
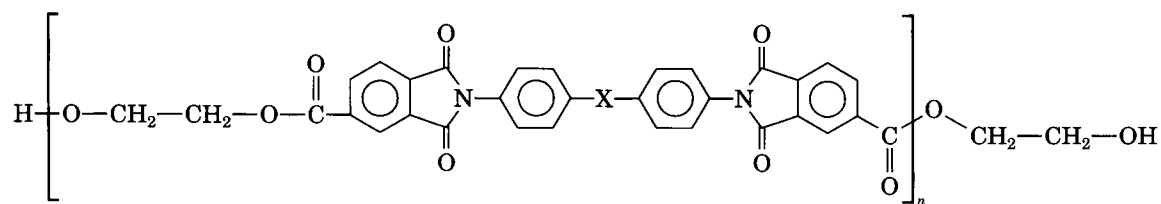
H–[O—CH₂—CH₂—O—C(=O)—(phthalimide)—N—(C₆H₄)—X—(C₆H₄)—N—(phthalimide)—C(=O)—O—CH₂—CH₂—OH]ₙ

Polymer		Inherent Viscosity[a] (dL/g)	Density (g/cc)	Decomposition Temperature in Air[b] (°C)
Code	X			
PEI-D$_1$	—SO$_2$—	0.319	1.398	485
PEI-D$_2$	—O—	0.349	1.392	450
PEI-D$_3$	—CH$_2$—	0.334	1.380	450
PEI-D$_4$	—S$_2$—	0.325	1.404	470

[a] 0.5% solution in N-methyl-2-pyrrolidone.
[b] By differential thermal analysis.

Table IV Calculations of Solubility Parameters of the Polyester–Imides Based on Monoimidodicarboxylic Acids

—[C(=O)—(phthalimide)—N—X—C(=O)—O—CH₂—CH₂—O]ₙ—

Repeat unit in polymer

		Polymer			
		$X = $ —CH$_2$, (PEI-M$_1$)		$x = $ —ϕ—, (PEI-M$_2$)	
Functional Group	G Value (cal-cm^3)$^{1/2}$	No. Functional Groups/Substitutions in Polymer Repeat Unit	Total G Value for Polymer	No. Functional Groups/Substitutions in Polymer Repeat Unit	Total G Value for Polymer
—CH$_2$—	131.50	3	394.50	2	263.00
—CH=(arom.)	117.12	3	351.36	7	819.84
>C=(arom.)	98.12	3	294.36	5	490.60
>C=O	262.96	2	525.92	2	525.92
>N—	61.08	1	61.08	1	61.08
—COO—	326.58	2	653.16	2	653.16
Five-membered ring	20.99	1	20.99	1	20.99
Six-membered ring	−23.44	1	−23.44	2	−46.88
Para substitution	40.33	1	40.33	2	80.66
Ortho substitution	9.62	1	9.62	1	9.62
Meta substitution	6.60	1	6.60	1	6.60
ΣG			2334.48		2884.66
Solubility parameter $\delta = |\rho[(\Sigma G)/M]|$			11.44		11.55

Table V   Calculation of Solubility Parameters of Polyester–Imides Based on Diimidodicarboxylic Acids

Repeat unit in polymer

Functional Group	G Value $(cal\text{-}cm^3)^{1/2}$	No. Functional Groups/Substitutions in Polymer Repeat Unit	Total G Value of Polymer x			
			—SO$_2$— (PEI-D$_1$)	—O— (PEI-D$_2$)	—CH$_2$— (PEI-D$_3$)	—S$_2$— (PEI-D$_4$)
—CH$_2$—	131.50	2	263.00	263.00	263.00	263.00
—CH=(arom.)	117.12	14	1639.68	1639.68	1639.68	1639.68
>C=(arom.)	98.12	10	981.20	981.20	981.20	981.20
>C=O	262.96	4	1051.84	1051.84	1051.84	1051.84
>N—	61.08	2	122.16	122.16	122.16	122.16
—COO—	326.58	2	653.16	653.16	653.16	653.16
Five-membered ring	20.99	2	41.98	41.98	41.98	41.98
Six-membered ring	−23.44	4	−93.76	−93.76	−93.76	−93.76
Para substitution	40.33	2	80.66	80.66	80.66	80.66
Ortho substitution	9.62	2	19.24	19.24	19.24	19.24
Meta substitution	6.60	2	13.20	13.20	13.20	13.20
—CH$_2$—	131.50	1			131.50	
—O—	114.98	1		114.98		
—S—	209.42	2				418.84
—SO$_2$—	439.38	1	439.48			
ΣG			5211.84	4887.34	4903.36	5191.20
Solubility parameter $\delta = |\rho[(\Sigma G)/M]|$			11.71	11.85	11.84	11.73

ments determined experimentally match very well with those calculated for the proposed structures. The functional monomer, N-(carboxymethyl)trimellitimide, is reported by us for the first time.

The diimidodicarboxylic acid monomers (DIDA series) possess very high melting points as compared with the monoimidodicarboxylic acids (MIDA). This can be attributed to the structural symmetry of the DIDA acids, which is absent in the monoimidodicarboxylic acids.

The IR absorption frequencies summarized in Table VII fully characterize the structures of the imidocarboxylic acids. The strong absorption bands in the regions 1785–1775 (imide I, symmetric carbonyl stretching), 1720–1715 (asymmetric imide

carbonyl stretching), 1390–1365 (imide II, imide ring vibration, axial), 1115–1110 (imide III, imide ring vibration, transverse), and 720–715 cm^{-1} (imide IV, imide ring vibration, out-of-plane) establish the presence of imide rings in the structures of the monomers synthesized. In addition to these, the IR spectra of the diimidodicarboxylic acids (DIDA series) show the absorption bands that are related to the various linkages in the diamine units of the monomers. The bands appearing at 1300 and 1152 cm^{-1} are assigned to the symmetric and asymmetric stretchings of —SO$_2$— group in the spectrum of N, N' - (4, 4' - diphenylsulfone) bistrimellitimide (DIDA-1). Similarly, the absorption peaks of —O—; —CH$_2$—; and —C—S— and —S—S vibrations are found at 1225; 2700–2800; and 605

Table VI   Diimidodicarboxylic Acids: Monomer Structures and Elemental Analysis

Code	Structure	Elemental Analysis (%) C	H	N	S
DIDA-1	*N*,*N*′,(4,4′-diphenylsulfone)bistrimellitimide	Calcd 60.40 Found 60.92	2.68 2.73	4.69 3.63	5.36 4.98
DIDA-2	*N*,*N*′,(4,4′-diphenylether)bistrimellitimide	Calcd 65.69 Found 65.51	2.92 2.98	5.11 5.02	— —
DIDA-3	*N*,*N*′,(4,4′-diphenylmethane)bistrimellitimide	Calcd 67.42 Found 67.31	3.37 3.28	5.24 5.17	— —
DIDA-4	*N*,*N*′,(4,4′-diphenylsulfide)bistrimellitimide	Calcd 60.40 Found 60.81	2.68 2.43	4.69 4.52	10.70 9.98

Table VII   IR Spectral Data of Imidodicarboxylic Acid Monomers (Absorption in cm^{-1})

Monomer	Imide C=O Symmetric (Imide I)	Asymmetric	Imide Ring Vibration Axial (Imide-II)	Transverse (Imide-III)	Out-of-Plane (Imide-IV)	Carboxyl C=O	O—H, C—O	Aromatic Ring	Other Absorptions
MIDA-1	1785	1720	1385	1110	720	1690	3500–3100, 1260	1625, 1600, 1590	—
MIDA-2	1780	1715	1365	1115	720	1680	3500–3100, 1220	1600, 1580	—
DIDA-1	1775	1720	1380	1115	720	1690 1220	3600–3100, 1220	1620, 1590	1300, 1152 (—SO$_2$—)
DIDA-2	1780	1715	1390	1110	715	1690	3600–3100, 1225	1600, 1580, 1500	1225 (φ—O—φ)
DIDA-3	1780	1720	1370	1110	720	1680	3500–3100, 1220	1600	2900–2800 (—CH$_2$—)
DIDA-4	1785	1710	1380	1100	720	1690	3500–3100, 1220	1590, 1510	500 (S—S), 605 (—C—S—S—)

and 500 cm^{-1}, respectively, in the IR spectra of N,N'-(4,4'-diphenylether)bistrimellitimide (DIDA-2), N,N'-(4,4'-diphenylmethane)bistrimellitimide (DIDA-3), and N,N'-(4,4'-diphenylsulfide)bistrimellitimide, respectively.

The values of chemical shifts of various protons in the ^{1}H-NMR spectra of the imidodicarboxylic acid monomers are compiled in Table VIII. The integrated ratios of the different protons are fully in conformity with the structures of these monomers as shown in Tables I and VI. It can be seen in Table VIII that the aromatic protons ("a," "b," and "c") of the trimellitimide units are found in the lower field when compared to those ("d" and "e") of the diamine units of the diimidodicarboxylic acids. The proton "a," which is *ortho* to both carboxyl and imide carbonyls, appeared as a singlet at δ 8.43–8.56; proton "b," *ortho* to carboxyl and *meta* to imide carbonyl, as doublet at δ 8.31–8.46; and proton "c," *meta* to carboxyl and *ortho* to imide, at δ 8.04–8.41. The aromatic protons "d" and "e" of the diamine units are found as doublets at δ 7.56–8.20 and 7.31–8.09, respectively. The spectrum of N-(carboxymethyl)-trimellitimide shows a singlet at δ 4.43 due to methylene protons "f," sandwiched by imide ring and carboxyl group. The peak that appeared as a single at δ 2.1 in the spectrum of N,N'-(4,4'-diphenylmethane)bistrimellitimide is assigned to the methylene protons "i" of the monomers.

Polyester–imides

The IR spectrum of polyester–imide, PEI–D, is reproduced in Figure 2 as an example of the polyester–imides reported in this paper. The IR spectrum of polymers shows the presence of all the characteristic imide bands, namely, 1780, 1725, 1380, 1115, and 725 cm^{-1}. The absorption band due to ester carbonyl (C=O) is completely obscured by the band due to asymmetric stretching of imide carbonyl in the region around 1725 cm^{-1}. The peak due to C—O—C absorption of the ester group is observed in the spectra of all polyester–imides in the region around 1240 cm^{-1}. The polyester–imides obtained from DIDA-1, DIDA-2, DIDA-3, and DIDA-4 monomers could very easily be distinguished from each other by the absorption peaks at 1152, 1225, 2900–2800, and 500–600 cm^{-1} due to —SO$_2$—, —O—, —CH$_2$—, and —C—S—S— vibrations, respectively.

The crystalline nature of the polymer was studied by X-ray diffraction (Fig. 3). Except for the polymer PEI-D$_4$, which is derived from N,N'(4,4'-diphenylsulfide)bistrimellitimide and ethylene glycol, all other polyester–imides showed amorphous struc-
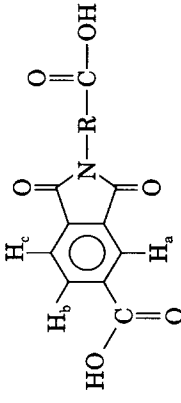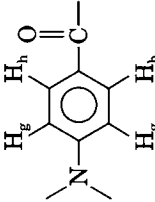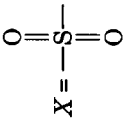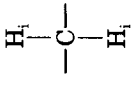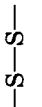
tures. The PEI-D$_4$ polymer showed some degree of crystallinity. The partial crystallinity of this polymer also accounts for its highest density among the polymers (PEI-D series) obtained from the diimidodicarboxylic acid monomers. The polyester–imides derived from diimidodicarboxylic acids exhibited higher densities than did those derived from monoimidodicarboxylic acids (Tables II and III). This could be due to the structural symmetry of the DIDA acids, which results in the formation of polyester–imides with a segmental symmetry.

The values of inherent viscosities of PEI-D polymers are much higher than those of PEI-M polymers (Tables II and III). This could be attributed probably to the higher molecular weights of PEI-D polymers as a consequence of higher monomer molecular weights than those used in PEI-M polymers, assuming that the degree of polymerization remains the same in both series. Among the PEI-D series, the order of viscosity of the polymers is found to be in the order PEI-D$_2$ > PEI-D$_3$ > PEI-D$_4$ > PEI-D$_1$. The lower values of inherent viscosities (Tables II and III) indicate that the polymers obtained do not possess very high molecular weight. Other workers[7,19] have also reported lower values for different polyesterimides.

The results of the solubility test given in Table IX reveal that the polyester–imides reported here are easily soluble in the solvents whose solubility parameters are in the range of δ 11.1–13.0. These include m-cresol, N,N-dimethyl acetamide, N,N-dimethyl formamide, dimethyl sulfoxide, formic acid, and N-methyl-2-pyrrolidone. All these polymers are soluble in concentrated sulfuric acid. The solubility parameters (δ) calculated from the group contribution method as detailed in Tables IV and V were found to be 11.44, 11.55, 11.71, 11.85, 11.84, and 11.73 for the polyester–imides PEI-M$_1$, PEI-M$_2$, PEI-D$_1$, PEI-D$_2$, PEI-D$_3$, and PEI-D$_4$, respectively. Thus, the solubility parameters of the polyester–imides reported here are found to be in the same range as those of solvents mentioned above in which these polymers are soluble at ambient temperature.

The values of the decomposition temperatures of polyester–imides derived from diimidodicarboxylic acids (PEI-D series), determined by differential thermal analysis, are found to be in the range 450–485°C (Table III). These values are fairly high and indicate good thermal stability of the polyester–imides. This could be attributed to the presence of aromatic/heterocyclic units, contributed by the diimidodicarboxylic acid functional monomers, in the backbone of the polymers. The PEI-D$_2$ and PEI-D$_3$ polymers, which are derived from diimidodicarboxylic acids containing ether and methylene linkages,

Table VIII   ¹H-NMR Spectral Data of Imidodicarboxylic Acid Monomers

Monoimidodicarboxylic acid (MIDA)

Diimidodicarboxylic acid (DIDA)

Monomer		Proton Chemical Shifts (δ ppm)								
Code	R/X	H_a	H_b	H_c	H_d	H_e	H_f, H	H_g	H_h	H_i
MIDA-1	R = C(H_f)_2	8.43 (S, 1H)	8.34 (d, 1H)	8.12 (d, 1H)			4.43 (S, 2H)			—
MIDA-2		8.43 (S, 1H)	8.31 (d, 1H)	8.04 (d, 1H)	—	—	—	7.24 (d, 2H)	8.69 (d, 2H)	
DIDA-1	X = SO_2	8.47 (S, 2H)	8.33 (d, 2H)	8.12 (d, 2H)	7.83 (d, 4H)	7.74 (d, 4H)	—	—	—	—
DIDA-2	O	8.53 (S, 2H)	8.37 (d, 2H)	8.08 (d, 2H)	7.56 (d, 4H)	7.31 (d, 4H)	—	—	—	—
DIDA-3	C(H_i)_2	8.56 (S, 2H)	8.46 (d, 2H)	8.41 (d, 2H)	8.20 (d, 4H)	8.09 (d, 4H)				2.10 (S, 2H)
DIDA-4	S—S	8.56 (S, 2H)	8.44 (d, 2H)	8.15 (d, 2H)	7.84 (d, 4H)	7.59 (d, 4H)			—	—

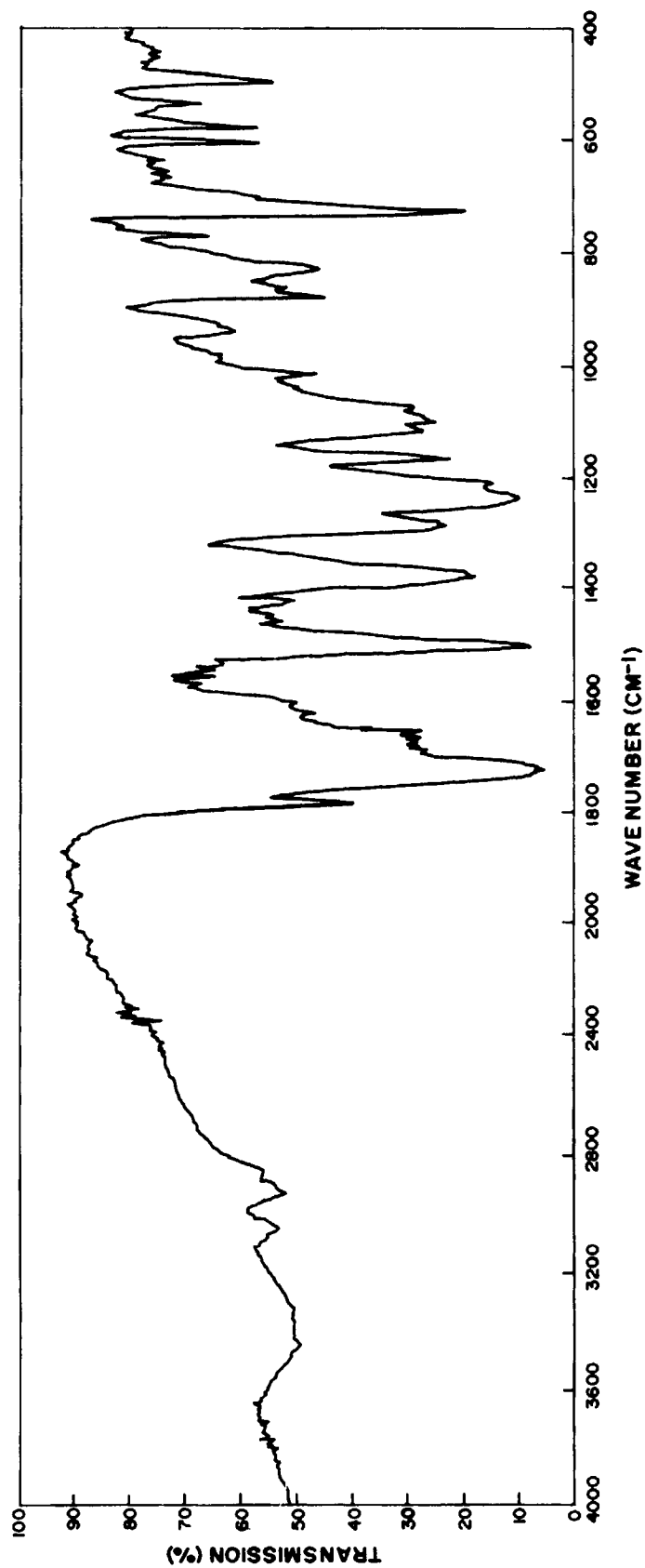The carboxyl protons appeared beyond 11 δ ppm.

Figure 2   Infrared spectrum of polyester–imide (PEI-D$_2$).
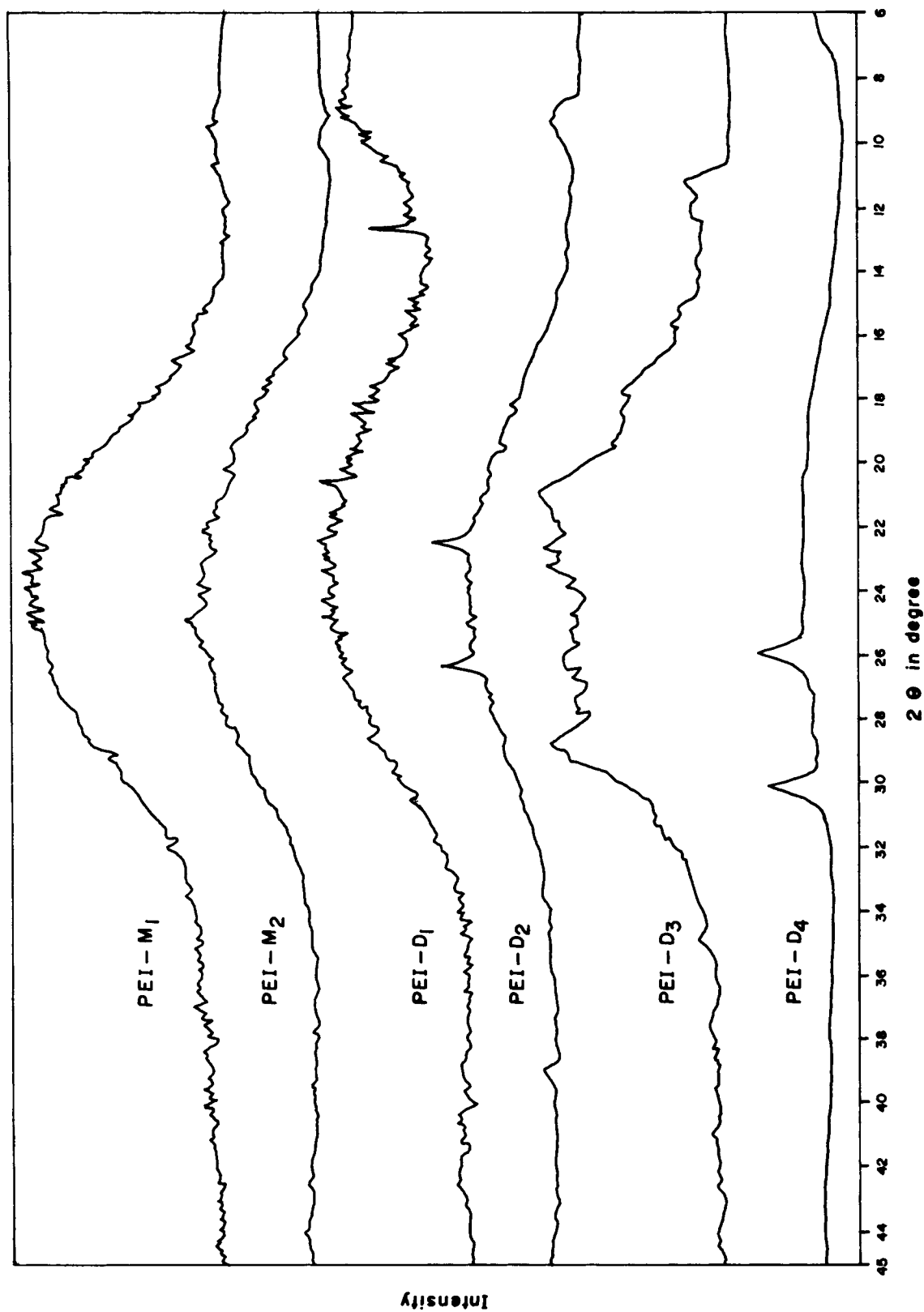
Figure 3 X-ray diffractograms of polyester–imides.

Table IX Solubility of Polyester–Imides[a]

Solvent[b]	Polymer					
	PEI-M$_1$	PEI-M$_2$	PEI-D$_1$	PEI-D$_2$	PEI-D$_3$	PEI-D$_4$
1. Benzene (9.6)	−	−	−	−	−	−
2. Chloroform (9.3)	++	−	−	−	−	−
3. m-Cresol (11.1)	++	+	++	++	++	++
4. Cyclohexanone (9.6)	++	+	+	+	+	+
5. Diacetone alcohol (9.7)	−	−	−	−	−	−
6. N,N-Dimethyl acetamide (11.1)	++	++	++	++	++	++
7. N,N-Dimethyl formamide (12.1)	++	+	++	++	++	++
8. Dimethyl sulfoxide (13.0)	++	+	++	+	+	++
9. 1,4-Dioxane (10.0)	−	−	−	−	−	−
10. Formic acid (12.2)	++	++	++	+	++	++
11. Methyl ethyl ketone (9.3)	−	−	−	−	−	−
12. N-Methyl-2-pyrrolidone (11.2)	++	++	++	++	++	++
13. Methylene chloride (9.9)	−	−	−	−	−	−
14. Sulfuric acid	++	++	++	++	++	++
15. Toluene (8.9)	−	−	−	−	−	−
16. Xylene (8.8)	−	−	−	−	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble on heating; ±, swelling at room temperature; −, insoluble.

[b] Figures shown in parentheses are solubility parameters of solvents.

exhibit slightly lower decomposition temperatures, compared to the PEI-D$_1$ and PEI-D$_4$ polymers containing sulfone and disulfide linkages in the polymer backbone. Among the PEI-M polyester-imides, the PEI-M$_2$ polymer possesses higher decomposition temperature (450°C) than that of PEI-M resin (360°C) (Table II). This is due to the higher content of aromatic segments in the backbone of the PEI-M$_2$ polyester–imide than in that of the PEI-M$_1$ polymer.

CONCLUSIONS

The polyester–imides with alternate imide–ester–ester or imide–imide–ester–ester linkages with —SO$_2$—, —O—, —CH$_2$—, or —S—S— bridges in between prepared by the transesterification reaction between imidodicarboxylic acids and ethylene glycol have been demonstrated to possess excellent solubility characteristics with fairly high decomposition temperatures (450–480°C). These polymers, therefore, might be used as novel processable thermally stable polymers with moderate thermooxidative stability.

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