Polybenzimidazoles: Thermally Stable Materials

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ABSTRACT

Polybenzimidazoles were prepared in poly(phosphoric acid)
from isophthalic acid (I), terephthalic acid (T), and 3,3'-di-
aminobenzidine tetrahydrochloride dihydrate (DAB). Homo-
polymers of I, T, and various IT copolymers have been pre-
pared. The polymers were characterized by viscosity, IR
spectra, and nitrogen estimation. The effect of copolymer
composition on UV and visible spectra, solubility in various
solvents, and density was also investigated. The relative
thermal stability of the polymers was evaluated by TGA and
DTA.

INTRODUCTION

Aromatic polybenzimidazoles have been investigated in the past to
achieve better thermal and oxidative stability, retention of stiffness
and toughness at elevated temperatures. Polymers having p- or
m-phenylene groups in the backbone have been reported in the liter-
ature [1-3]. These polymers were found to be very rigid and almost
insoluble in most of the organic solvents [4] and their processing is

difficult. Work on poly-1,3,4-oxadiazoles [5, 6] has indicated that random copolymer having p-phenylene and m-phenylene groups along with 1,3,4-oxadiazole groups in the backbone yield fibers of good mechanical and thermal properties. Polybenzimidazoles from isophthalic acid, m-phenylenediacetic acid, and tetraamine have been reported by Levy [3, 7]. The melt condensation of 3,3'-diamino-benzidine and phenyl esters of isophthalic and terephthalic acids to yield the benzimidazole copolymers has been reported earlier [8, 9]. However the inherent viscosity of these polymers was below 0.1 [9]. The thermal behavior and other properties depend significantly on $[\eta]$.

In the present paper we report the work carried out on some random copolymers having p- and m-phenylene groups and benzimid-azoles groups in the backbone. Structures of the type A may be expected in the polymer backbone, as a result of polymerization of DAB, I, and T in PPA.

A
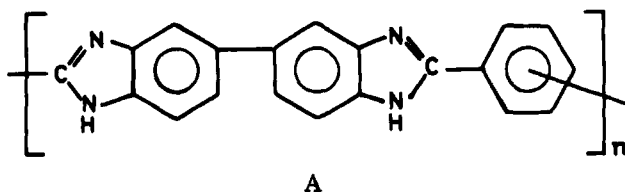
The relative proportion of m- or p-phenylene groups in the poly-mer backbone will depend on the initial molar feed of I and T.

The polymers were characterized by intrinsic viscosity, IR spectra, and nitrogen estimation. The effect of copolymer composi-tion on polymer properties such as solubility, density, UV and visible spectra, fluorescent spectra, and thermal stability in air was also investigated.

EXPERIMENTAL

All solution polymerization reactions in PPA were carried out as described earlier [10]. Homopolymer of isophthalic acid was pre-pared by taking equimolar quantities of DAB and acid and carrying out the reaction in inert atmosphere in PPA, which acted as a solvent as well as a dehydrating agent. Copolymers were prepared by using DAB and different molar ratios of I and T. An Ubbelohde suspension

TABLE 1. Preparation of Polybenzimidazoles: Conditions for Condensation Polymerization

No.	Sample	Amount of starting material (g)			
		I	T	DAB	PPA
1	I_0	0.850	0.00	2	50
2	I_1T_1	0.425	0.425	2	50
3	I_2T_1	0.554	0.277	2	50
4	I_1T_2	0.277	0.554	2	50

TABLE 2. Characterization of Polybenzimidazoles

No.	Sample	N (%)		Intrinsic viscosity $[\eta] \times 10^{-2}$ (cm^3/g)	K'	K''
		Calcd	Found			
1	I_0	18.18	17.60	0.37	0.68	-0.51
2	I_1T_1	18.18	16.70	0.51	0.22	-0.59
3	I_2T_1	18.18	16.73	0.48	0.21	-0.40
4	I_1T_2	18.18	16.80	1.66	0.22	-0.30

level viscometer was used for the determination of $[\eta]$ at 30°C in 98% sulfuric acid (Analar). The polymer concentration was varied between 0.4 and 0.1 g/dl.

The density of the polymers at 30°C was determined by the suspension method in aqueous zinc chloride solution [11].

IR spectra of films cast from dimethyl sulfoxide solutions was recorded on a MK3 Spectromaster. The UV–visible range spectra of these polymers was recorded in 98% H_2SO_4 (AR) by use of a SP-700 spectrophotometer. The fluorescent spectra of the samples were recorded by a Unicam spectrofluorimeter in the 370–620 nm wavelength region. The spectra were recorded in concentrated H_2SO_4 and the polymer concentration was between 0.002 mg/dl and 0.001 mg/dl.

A Stanton HT-D thermogravimetric balance was used for thermal

analysis. Polymer samples of 20 ± 2 mg were taken for each experi-
ment and were heated at a constant rate of 6°C/min.

The solubility measurements were carried out in a thermostatic
air cabin at 25 ± 2°C. A 0.005-g portion of polymer was placed in
5 ml of the desired solvent (DMSO, DMF, DMAC, anhydrous HCOOH,
glacial acetic acid, and m-cresol). The hydrolytic stability of the
polymers was studied by treating the samples with 20% NaOH or 20%
H_2SO_4 at 50°C for 24 hr. The polymers were then characterized by
intrinsic viscosity and UV-visible range spectra after repeated
washing with water.

The DTA of the samples was carried out by using a Stanton Redcroft
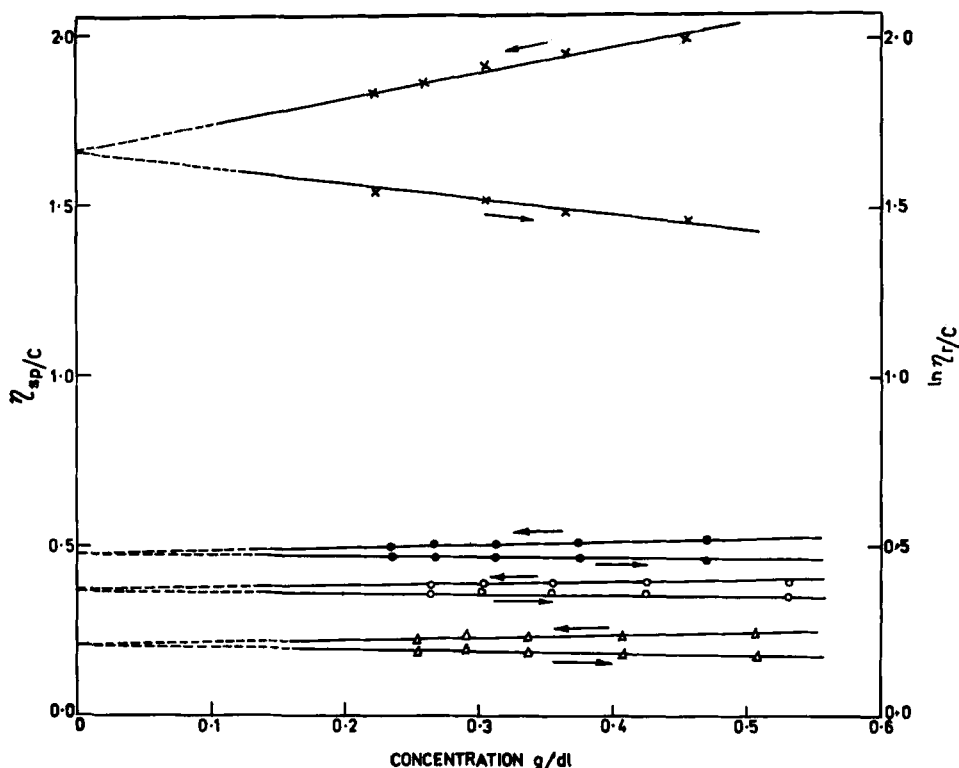

FIG. 1. Intrinsic viscosity evaluation of the polymers: (○) I_0;
(●) $I_2 T_1$; (×) $I_1 T_2$; (△) $I_1 T_1$. (Scale has been shifted along y-axis
for sample $I_1 T_1$ by 0.3 to avoid superimposition of lines.)

TABLE 3. IR Bands of Polymbenzimidazoles

| | Wave number (cm^{-1}) | | | |
I_0	I_1T_1	I_2T_1	I_1T_2	Assignment[a]
1660(sh)	1620	1670(m)	1630	C=C, -C=N
1575	-	1570	-	Conjugation between benzene and imidazole rings
1510	-	-	-	
1400	1445	-	1448	Characteristic of substituted benzimidazole in plane vibration
1250	1235	1220	1295	C-N stretching
1180(b)	1130(w)	1160	-	Characteristic of benzimidazole
1125				
1080(b)	1015	1070	1090(b)	Characteristic of 2-substitution
965	950	950	-	Benzene ring vibration
935	900	900	910	Heterocyclic ring vibration
850	850	845	855	Two adjacent hydrogens in six-membered ring (C-H out-of-plane bending)
810	800	800	805	Three adjacent hydrogens in six-membered ring (C-H out-of-plane bending)
750	775	730	760	Heterocyclic ring vibration
-	700	-	700	2-Substituted benzimidazole
640	660	650	670(sh)	
590	600	-	610	
505	520(b)	-	520(b)	3,4-Disubstituted biphenyl C-H out-of-plane

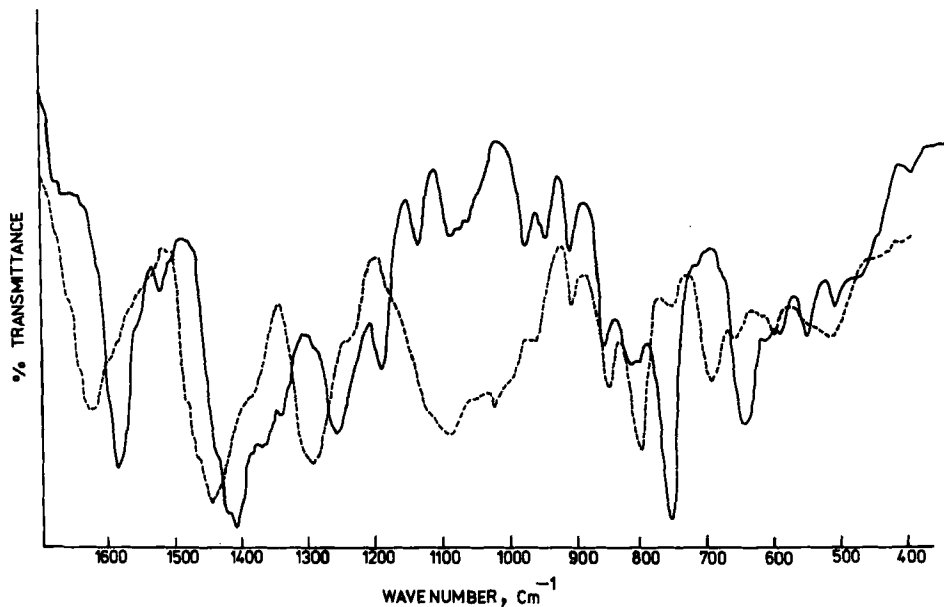[a]Data of Feairheller and Eaton [16].

FIG. 2. IR spectra of polybenzimidazole film: (—) I_0; (--) I_1T_2.

differential thermal analyzer. A 4-5 mg sample of each sample was heated in an inert atmosphere at a constant rate of 6°C/min.

RESULTS AND DISCUSSION

Table 1 gives the condition for preparing the polybenzimidazoles. The copolymers of I and T having different proportion of m-phenylene and p-phenylene residues in the polymer backbone were prepared by changing the molar ratios of I and T in the initial feed from 1:0 (I_0), 1:1 (I_1T_1), 2:1 (I_2T_1), and 1:2 (I_1T_2).

The calculated and observed values of percentage nitrogen are given in Table 2. The experimental value was slightly less than the theoretical values. The intrinsic viscosity of the polybenzimidazoles was determined at 30°C (Fig. 1). The intrinsic viscosity of the copolymers increased with increasing p-phenylene groups in the backbone (Table 2). The K' and K" values of the equations of Huggins [12] and
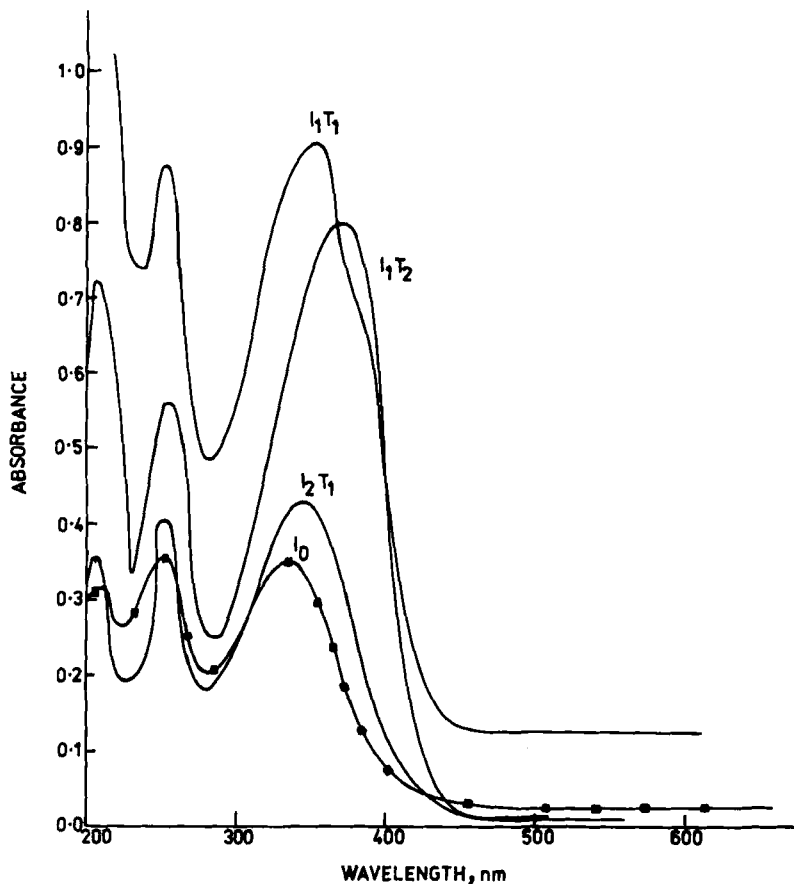
FIG. 3. UV and visible range spectra of polybenzimidazoles.

Kraemer [13] were also evaluated from η_{sp}/c versus c and by ln η_r/c versus c plots, and the values are given in Table 2.

The structure of these polymers was confirmed by IR spectroscopy. The absorption bands characteristic of benzimidazole ring were present in the spectra (Table 3 and Fig. 2).

The UV and visible range spectra of all polymers in concentrated sulfuric acid are given in Fig. 3. There is a bathochromic shift in the λ_{max} as the concentration of p-phenylene groups in the copolymer

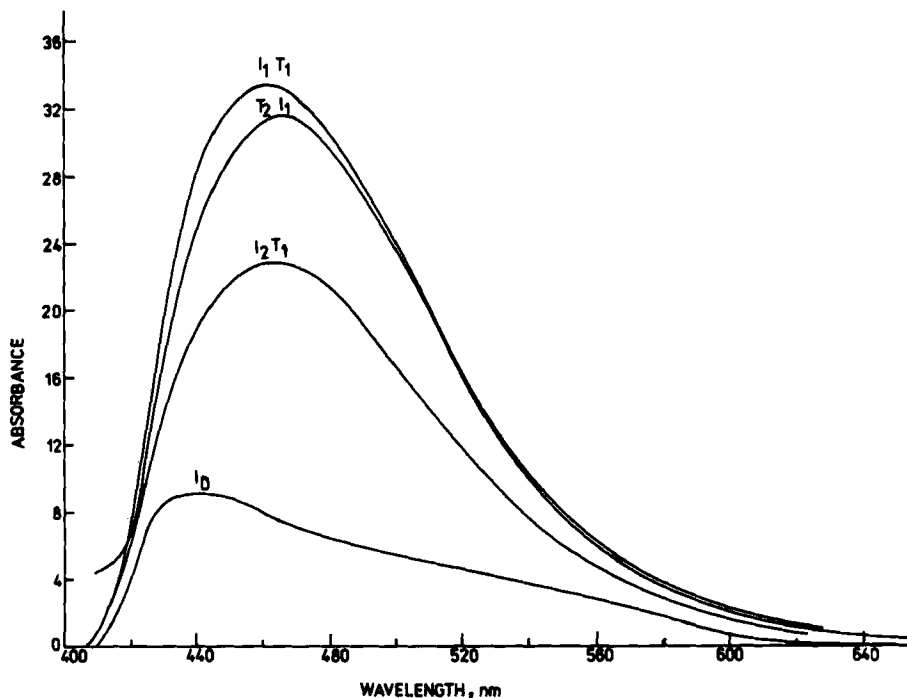FIG. 4. Fluorescent spectra of polybenzimidazoles.

is increased. Thus for I_0, I_2T_1, and I_1T_2 the λ_{max} is 335, 340, and 370 nm, respectively (Table 4). The p-phenylene compounds for which dipolar excited states are possible are expected to have a higher value of λ_{max} than the m-phenylene compounds where analogous structures are not possible [14]. From the fluorescent spectra (Fig. 4) the values for λ_{max} were determined (Table 4).

The density of I_0 is greater than those of copolymers I_1T_1 and I_2T_1. However a further increase in p-phenylene groups (I_1T_2) resulted in an increase in the density. Obviously the packing of molecules would be better if symmetrical p-phenylene groups were present (Table 4).

The qualitative solubility behavior of homopolymers and copolymers in various solvents is given in Table 5. The solubility of the

TABLE 4. Some Properties of Polybenzimidazoles

No.	Sample	λ_{max} (nm)	E^a	$\lambda_{fl, max}$	Density (g/cm^3)
1	I_0	210	1176.90	435	1.311
		254	1346.66		
		335	1312.71		
2	$I_1 T_1$	254	1722.77	460	1.190
		355	1794.06		
3	$I_2 T_1$	206	512.69	470	1.283
		254	579.40		
		340	607.84		
4	$I_1 T_2$	206	1573.43	465	1.332
		254	1232.52		
		370	1756.99		

[a] E calculated by dividing the optical density by concentration (g/100 cm^3).

copolymers decreased with increasing p-phenylene groups in the backbone.

The primary thermograms obtained by heating the samples in air at a constant rate of 6°C/min are given in Fig. 5. Most of the samples are stable up to 500°C. From these thermograms the temperature at various percentage weight losses were calculated (Table 6). It is obvious from Table 6 that the introduction of p-phenylene groups in the backbone increases the thermal stability of the benzimidazole. The 10% decomposition temperature (DT) of $I_1 T_1$ is highest. However the 50% DT of $I_1 T_2$ is maximum, and that of I_0 is the lowest. Thus $I_1 T_2$ started decomposing at a lower temperature but it attained stability after about 30% loss. In case of $I_1 T_1$ and $I_1 T_2$, even at 900°C approximately 30% of the residual weight was present.

The integral procedural decomposition tempterature (IPDT) was calculated according to the method of Doyle [15] (Table 6). The IPDT values were calculated in the temperature range of 100 to 700°C. On the basis of IPDT values, one can write the following

TABLE 5. Solubility of Polymers

No.	Sample	Solubility[a]						
		H_2SO_4 (conc.)	DMSO	DMAC	DMF	Anhydr. HCOOH	m-Cresol	Glacial CH_3COOH
1	I_0	+++	++	++	++	+++	-	-
2	I_1T_1	+++	++	++	++	+++	++	-
3	I_2T_1	+++	++	-	++	+++	-	-
4	I_1T_2	+++	++	-	++	+++	++	-

[a]Solubility: (+++) soluble at ambient temperature; (++) partially soluble or swelling; (-) no swelling, no dissolution.
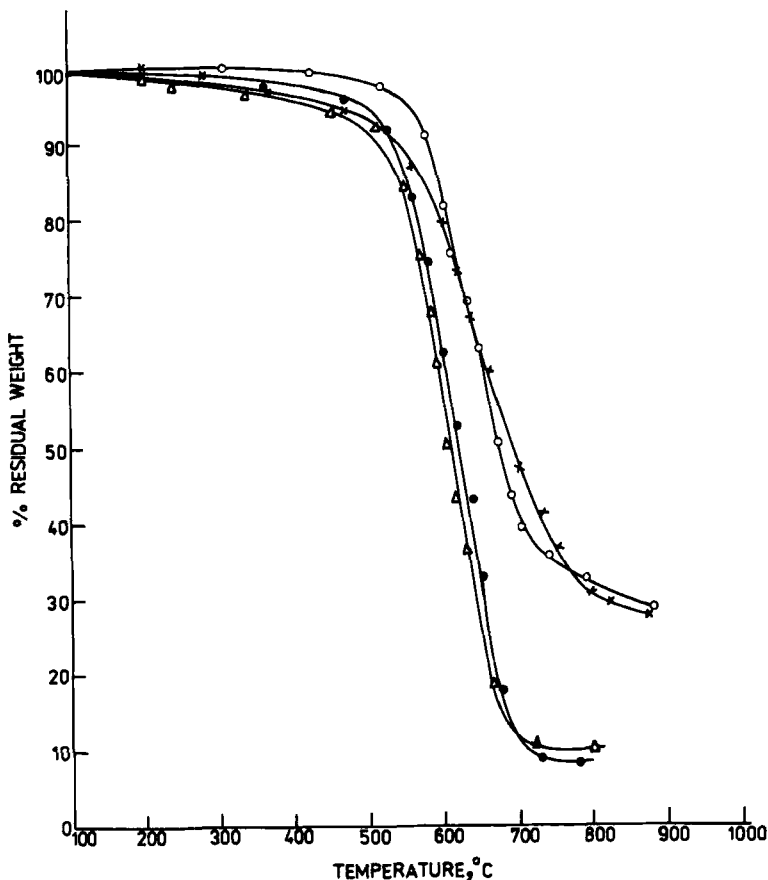
FIG. 5. Primary thermograms of polybenzimidazoles: ($\triangle$) I_0; ($\circ$) $I_1 T_1$; ($\bullet$) $I_2 T_1$, ($\times$) $I_1 T_2$.

stability order: $I_1 T_1 > I_1 T_2 > I_2 T_1 > I_0$. The IPDT values for PBI having p-phenylene groups (T_0) has been reported [4] as 616. Thus I_0 is less stable than T_0 polymers. The IPDT sums up the entire shape of the thermogram, and since $I_1 T_2$ sample started decomposing at a lower temperature, the IPDT values were lower. The IPDT values in the temperature range 100-900°C were found to be 617, 720, 630, and 708 for I_0, $I_1 T_1$, $I_2 T_1$, and $I_1 T_2$ respectively.
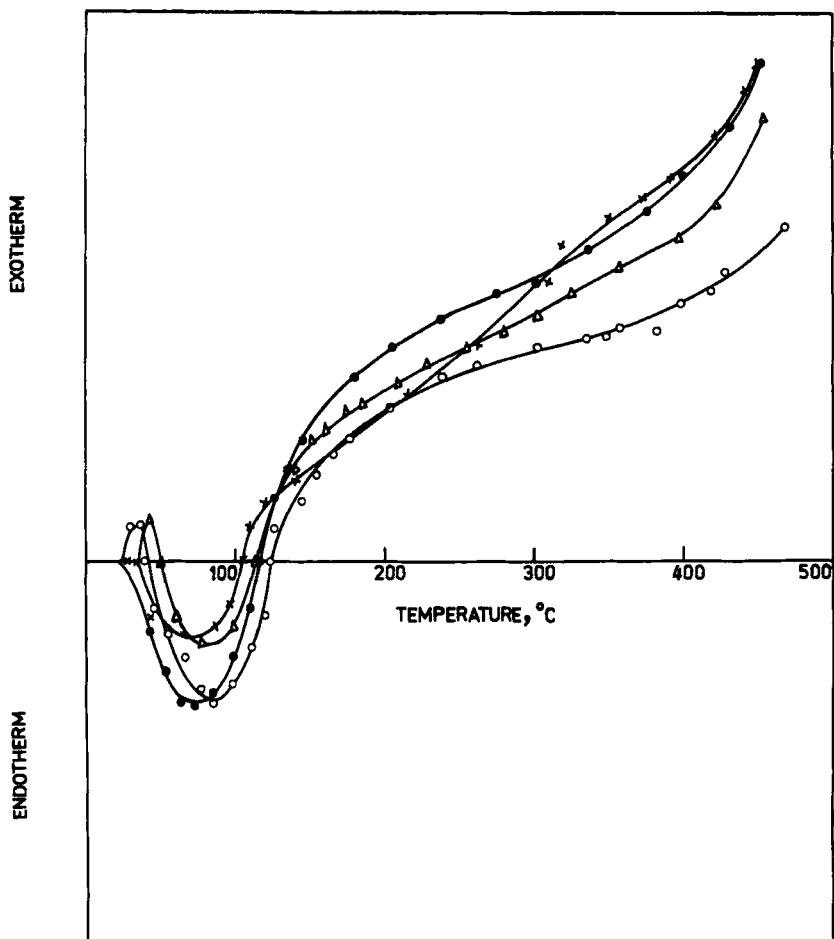
FIG. 6. Differential thermograms of polybenzimidazoles: (○) I_0; (△) $I_1 T_1$; (●) $I_2 T_1$; (×) $I_1 T_2$.

TABLE 6. Thermal Properties of Polymers

| No. | Sample | Decomposition temperature at various % weight losses (°C) | | | | | IPDT (°C) |
		10% DT	20% DT	30% DT	40% DT	50% DT	
1	I_0	530	560	585	595	605	593.00
2	$I_1 T_1$	580	605	625	650	670	652.00
3	$I_2 T_1$	535	560	595	610	625	610.00
4	$I_1 T_2$	530	600	630	660	695	614.20

Thus the difference between $I_1 T_2$ and $I_1 T_1$ is reduced to only 12°C. It is a bit difficult to assign the reason for the early decomposition in $I_1 T_2$.

The differential thermometry curves of polymers show endothermic peaks around 80-90°C and exothermic peaks above 400°C (Fig. 6). As there is no weight loss around 100°C in TGA, the endothermic behavior in DTA may be due to some phase transition.

The hydrolytic stability of the polymers was studied by treating the samples with concentrated acid and alkali. No marked change in intrinsic viscosity and UV spectra was obtained. This indicates that the polymers are resistant to acid and alkali.

As a result of these investigations it may be concluded that polybenzimidazoles having p-phenylene and m-phenylene groups in the backbone have good thermal and chemical stability. They are more soluble than polymers having only p-phenylene groups and more thermally stable than the polymers having m-phenylene groups.

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