DTA and Viscometric Study of Poly [2,2'.(o-phenylene)-5-5'-bibenzimidazole]. 1

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ABSTRACT

Three samples of poly[2,2'-(o-phenylene]-5,5'-bibenzimidazole] (PBI) were prepared by condensation of 3,3'-diaminobenzidine (DAB) with, respectively, phthalic anhydride in p-cresol under N_2, with phthaloyl chloride in a xylene-water system containing carbonate, and with phthalimide in polyphosphoric acid. Solutions of these PBI samples in formic acid exhibited an anomalous dependence of the reduced viscosity on concentration. This polyelectrolyte behavior of the polymer solution was analyzed by application of empirical relations. The intrinsic viscosity of the PBI samples was measured in formic acid containing 1% (w/v) KBr. A solution of the N-methyl derivative of a PBI (melt) sample showed normal behavior in a viscometric study. The results of DTA of three PBI samples, one N-methyl PBI (melt) sample, and three model compounds are compared and analyzed with a view to estimating the energy of activation and the order of degradation reaction.

INTRODUCTION

The syntheses of poly[2,2'-(o-phenylene)-5,5'-dibenzimidazoles] based on condensation of 3,3'-diaminobenzidine (DAB) with, respectively, phthalic acid [1], phthalic anhydride [1], diphenyl phthalate

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[1], phthalonitrile [2], and phthaloyl chloride [3] have been reported. In the reported interfacial polycondensation [3], phthaloyl chloride is condensed with DAB endcapped with 2,3,4,5-tetraphenyl-2,5-endoxo-tetrahydrobenzoic acid in a DMF-water mixture. The final step in the reported polycondensation of DAB with phthalic anhydride in phenol under nitrogen atmosphere involved heating the reaction mixture at 400°C in vacuum to remove the last traces of water and thereby to increase the molecular weight [1]. In the methods described in the present communication, less vigorous reaction conditions have been employed with a view to obtaining polymer samples of comparatively lower molecular weight and hence of higher solubility. The polymer samples described in the present communication were prepared by methods different from those reported in the literature [1-3]. In one method, DAB was condensed with phthalic anhydride in the presence of p-cresol under nitrogen and in the final stage the reaction mixture was refluxed with xylene, and xylene was removed by distillation. This polymer sample is designated as PBI (melt). The other two methods comprised condensation of DAB with phthaloyl chloride in a xylene-water mixture containing carbonate and phthalimide in the presence of polyphosphoric acid (PPA). These samples have been designated as PBI (interface) and PBI (PPA), respectively.

A review of literature reveals that most of the properties of PBI from DAB and phthalic acid or its anhydride or acid chloride have been reported [1-4]. However, there are no reports about the systematic study of differential thermal analysis of these polymer samples and a viscometric study in solution. Hence it was thought interesting to undertake the DTA and viscometric study of the three polymer samples and the N-methyl derivative of the PBI (melt) sample. These properties of the PBI samples are compared with each other and also with those of the model compounds 2,2'-diphenyl-5,5'-bibenzimidazole (DPB), 2,2'-(o-phenylene)-bibenzimidazole (PBB), and 2-phenylbenzimidazole (PB). The structure of part of the polymer chain is shown to bring out the inherent model structures mentioned above:
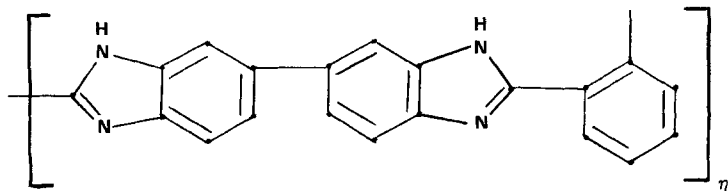
EXPERIMENTAL

Materials

Diaminobenzidine (DAB) was prepared by the reported method [1]. Phthalic anhydride, phthaloyl chloride, and phthalimide were prepared and purified by reported methods. The formic acid used was 98% pure. p-Cresol, xylene, K_2CO_3, and dimethylsulfate were obtained as laboratory grade reagents.

Polymer Synthesis

Polycondensation of DAB with Phthalic Anhydride. Formation of Polymer Sample, PBI (melt). A mixture of phthalic anhydride (1.48 g, 0.01 mol), DAB (2.14 g, 0.01 mol), and p-cresol (5 g) was heated under nitrogen to 220°C. The reaction mixture was in the form of a brown melt when the temperature reached 220°C. Within about 20 min thereafter it became highly viscous and began to solidify. The temperature was then raised up to 250°C and heating was continued for 90 min, allowing the temperature to rise to 280°C. The reaction mixture was cooled to 150°C. Xylene (10 mL) was carefully added to the mixture. The reaction mixture was refluxed with xylene. Xylene was removed by distillation. Mixing and refluxing with xylene was repeated twice. The reaction mixture was cooled and powdered. The powdered material was refluxed with ethanol (20 mL) and filtered. This treatment was repeated thrice. The polymer sample (2 g) was a gray-colored solid. It did not melt up to 350°C. It is insoluble in all solvents except formic acid and concentrated sulfuric acid.

Analysis: Calculated for $(C_{20}H_{12}N_4)_n$: C, 77.92%; H, 3.9%; N, 18.18%. Found: C, 73.8%; H, 3.7%; N, 17.8%.

Polycondensation of DAB with Phthaloyl Chloride. Formation of Polymer Sample PBI (interface). A solution of tetrahydrochloride of DAB (3.6 g, 0.01 mol) in water (50 mL) was mixed with vigorous stirring with a solution of phthaloyl chloride (2.03 g, 0.01 mol) in xylene (50 mL). Solid potassium carbonate (2.8 g, 0.02 mol) was added to the vigorously stirred mixture. Vigorous stirring was continued for half an hour at room temperature (30° C). The solid product was filtered and washed with ethanol and dried. The dried mass was powdered and repeatedly refluxed with boiling ethanol (25 mL) and filtered. The process was repeated thrice. Yield, 2.2 g. The polymer sample did not melt up to 350°C. It is soluble only in formic acid and concentrated sulfuric acid.

Analysis: Calculated for $(C_{20}H_{12}N_4)_n$: C, 77.92%; H, 3.9%; N, 18.18%. Found: C, 74.3%; H, 3.4%; N, 17.6%.

Polycondensation of DAB Hydrochloride with Phthalimide in Polyphosphoric Acid (PPA). Formation of Polymer Sample PBI (PPA). To a solution of tetrahydrochloride of DAB (1.8 g, 0.005 mol) in polyphosphoric acid (30 g) at 140°C, finely powdered phthalimide (0.73 g, 0.005 mol) was added under a thin stream of N_2. The temperature was raised to 220°C and heating was continued under a thin stream of N_2 for 12 h at 220°C. The reaction mixture was cooled and diluted with water (300 mL), and solid was filtered and washed with a large excess of 10% carbonate solution. The solid was then repeatedly refluxed with ethanol and filtered. The polymer was a gray-colored solid insoluble in all solvents except formic acid and concentrated sulfuric acid. It did not melt up to 350°C. Yield, 1.0 g.

Analysis: Calculated for $(C_{20}H_{12}N_4)_n$: C, 77.92%; H, 3.9%; N, 18.18%. Found: C, 75.1%; H, 3.3%; N, 17.9%.

Synthesis of Model Compounds

2,2'-Diphenyl-5,5'-bibenzimidazole (DPB) and o-phenylenebibenzimidazole (PBB) were prepared by reported methods [1, 5]. They are soluble in acetic acid and dimethylformamide (DMF). 2-Phenylbenzimidazole (PB) was prepared by a reported method [6]. It is soluble in common solvents.

N-Methylation of Polymer Sample PBI (melt)

Finely powdered PBI (melt) (0.2 g) was suspended and stirred in 5% aqueous sodium hydroxide (30 mL) for an hour. Dimethylsulfate (1 mL) was added to the mixture with stirring. The mixture was heated at 80°C with stirring for an hour. The solid was filtered, washed, and dried. Its color was nearly the same as that of the parent polymer. It did not melt up to 350°C. It dissolved only in concentrated sulfuric acid and formic acid.

Analysis. Calculated for $(C_{21}H_{14}N_4)_n$: C, 78.2%; H, 4.3%; N, 17.3%. Found: C, 76.1%; H, 3.9%; N, 16.3%.

IR Spectroscopy

The IR spectra of the three PBI samples, the N-MePBI (melt), and the two model compounds (DPB and PBB) were scanned in KBr. The IR spectra of the three PBI samples are found to be identical. The spectra of polymer samples PBI (melt), PBI (PPA), and the two model compounds are shown in Fig. 1.

Viscosity Measurements

The viscosity of the three polymer samples, the N-MePBI (melt) derivative, and the three model compounds were measured in 98% formic acid and/or for formic acid containing KBr by using an Ubbelohde suspended level-type viscometer. Other details of the experiments are shown in Tables 1-4.
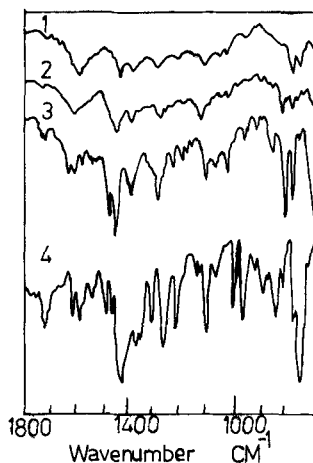
FIG. 1. IR spectra of (1) PBI (melt) sample, (2) PBI (PPA) sample, (3) Model compound DPB, and (4) Model compound PBB.

Differential Thermal Analysis

The DTA of the three polymer samples, the N-MePBI (melt) derivative, and the three model compounds was carried out in air using a Linseis DT-analyzer at a heating rate of 7°C/min up to 600°C. All experiments were carried out under almost identical conditions by keeping all the variables constant as far as possible. The details of the thermograms comprising only one exotherm are presented in Table 6.

RESULTS AND DISCUSSION

All the polymer samples are found to be soluble only in formic acid and concentrated sulfuric acid. Even the N-methyl derivative of PBI (melt) is found to exhibit an almost similar solubility behavior. The two model compounds (DPB and PBB) having very high melting points are soluble in acetic acid and DMF. The IR spectra of all three polymer samples are similar in all aspects. Comparison of the IR spectrum of each of the three polymer samples with the IR spectra of the two model compounds revealed that the spectrum of each polymer sample differed from that of the model compound PBB in several aspects and resembled the spectrum of the model DPB in several aspects (vide Fig. 1).

TABLE 1. Values of Reduced Viscosity (η_{red}) at Different Concentrations of PBI Samples. Solvent: Formic Acid (98%)

Concentration of polymer sample (g/dL)	η_{red} (dL/g) of polymer samples					
	PBI (melt)		PBI (interface)		PBI (PPA)	
	30°C	40°C	30°C	40°C	30°C	40°C
1.0	0.622	0.520	0.334	0.277	0.825	0.786
0.7144	0.703	0.575	0.424	0.352	0.930	0.852
0.5556	0.774	0.620	0.499	0.419	1.064	0.945

Analysis of Results of Viscosity Measurements

The values of reduced viscosity of solutions of the three polymer samples in formic acid are presented in Table 1. Comparison of these values of solutions of equal concentrations reveals that a trend, $\eta_{(red)}[\text{PBI(PPA)}] > \eta_{(red)}[\text{PBI (melt)}] > \eta_{(red)}[\text{PBI (interface)}]$, is observed at two temperatures. This is also the trend in the average molecular weights of the three polymer samples. Examination of the values of the reduced viscosity of solutions of each of three samples reveals that this viscosity parameter increases with a decrease in concentration. The results are shown graphically in Fig. 2. This is contrary to expectation. This polyelectrolyte behavior is attributed to protonation of the NH grouping of the repeating units of PBI molecules in formic acid solution. With an increase in dilution, more and more of the protonated centers become free and become solvated to a greater and greater extent. This results in an increase in the size of the polymer molecules in solution and brings about an increase in reduced viscosity with dilution of the solution. This reasoning is indirectly supported by the observation that a solution of N-methyl derivative of PBI (melt) in formic acid shows normal behavior in a viscometric study. Its reduced viscosity decreases with a decrease in concentration. In the N-MePBI (melt) the solvation of the protonated center is highly limited due to the steric effect. Values of the reduced viscosity of solutions of the N-MePBI (melt) sample are shown in Table 2. Values of the intrinsic viscosity of N-MePBI (melt) shown in the same table are estimated by extrapolating the linear plot of reduced viscosity vs concentration to zero concentration.

The viscosity of the two model compounds (DPB, PBB) and also of 2-phenylbenzimidazole (PB) was studied in solutions in formic acid concentrations ranging from 0.5 to 1.0 g/dL. Examination of the data of reduced viscosity at different concentrations, as presented in
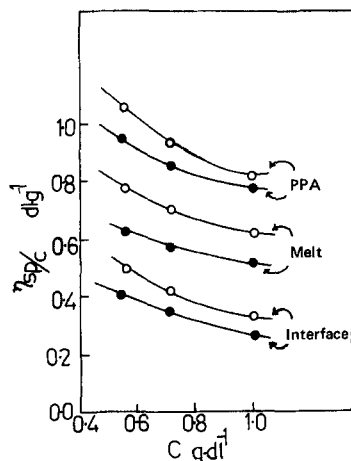
FIG. 2. Plots of reduced viscosity (η_{red}) vs concentration (C) of PBI polymer samples at 30°C (o) and 40°C (•) (solvent: formic acid).

TABLE 2. Reduced viscosity (η_{red}) at Different Concentrations and Intrinsic Viscosity $[\eta]$ of N-Methylated PBI (melt) Sample. Solvent: Formic Acid (98%)

Temperature (°C)	η_{red} (dL/g)			$[\eta]$ (dL/g)
	0.7144	0.5556	0.4545	
30	0.58	0.572	0.557	0.50
40	0.519	0.502	0.489	0.433

Table 3, reveals that the reduced viscosity of PBB decreases with a decrease in concentration. However, in the case of the other model compound, DPB, whose IR spectrum bears a good resemblance to that of the PBI polymer samples, the variation of reduced viscosity with concentration is abnormal. It is also observed that the reduced viscosity of 2-phenylbenzimidazole (PB) in formic acid solution increases with a decrease in concentration. In this respect the behavior of PBI polymer samples is similar to that of the model compounds DPB and 2-phenylbenzimidazole (PB). The viscosity behavior of these two compounds in formic acid containing 1% (w/v) KBr becomes normal, as expected. The results are shown in Table 3.

TABLE 3. Reduced (η_{red}) and Intrinsic $[\eta]$ Viscosities of Model
Compounds in Formic Acid in the Presence and the Absence of
Electrolyte at 35°C

Concentration of model compound (g/dL)	Concentration of KBr (g/dL)	η_{red} (dL/g) of model compounds		
		DPB	PBB	PB
1.000	0.00	0.0752	0.056	0.284
0.5556	0.00	0.088	0.041	0.334
		-	$[\eta] = 0.22$	-
1.000	1.00	0.075	-	0.029
0.5556	1.00	0.0637	-	0.027
		$[\eta] = 0.049$	-	$[\eta] = 0.025$

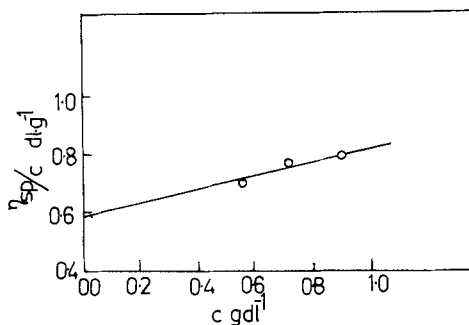

FIG. 3. Plot of reduced viscosity (η_{red}) vs concentration (C) of
PBI (PPA) sample at 30°C. [Solvent: formic acid containing 1% (w/v)
KBr.]

The polyelectrolyte behavior of the solutions of the three polymer
samples in formic acid was suppressed by adding KBr to the solution.
The viscosity of each polymer sample was measured in formic acid
containing 1% (w/v) KBr at two temperatures. Plots of reduced vis-
cosity against concentration were made and extrapolated to zero con-
centration to evaluate the intrinsic viscosity. The plot based on the
data of PBI (PPA) is shown in Fig. 3, and intrinsic viscosity values
are shown in Table 4.

TABLE 4. Intrinsic Viscosity $[\eta]$ of Polymer Samples in Formic Acid (98%). Concentration Range of Polymer: 0.5 to 1.0 g/100 mL

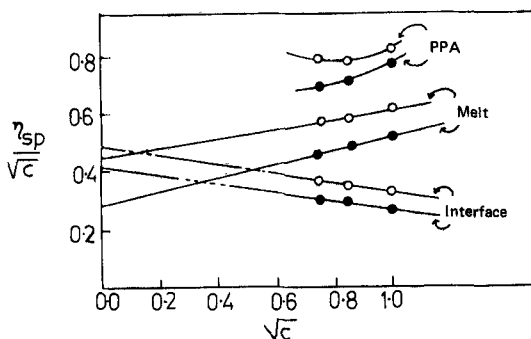| KBr (g/dL) | $[\eta]$ (dL/g) of polymer samples | | | | | |
| | PBI (melt) | | PBI (interface) | | PBI (PPA) | |
	30°C	40°C	30°C	40°C	30°C	40°C
1.0	0.390	0.350	0.285	0.235	0.590	0.472
2.0	0.280	0.250	0.270	0.140	0.425	0.350

FIG. 4. Application of empirical Relation (1).

Jones and Dole [7], Fuoss and Cathers [8], and Stivala and his co-workers [9, 10] have proposed empirical relations to correlate the appropriate viscosity function with concentration for solutions of polymers exhibiting polyelectrolyte behavior. The present authors selected three empirical relations for correlating the data presented in Table 1. In order to examine the applicability of Relation (1), proposed by Jones and Dole [7], plots of $\eta_{sp}/\sqrt{c}$ vs $\sqrt{c}$ were made. These plots are shown in Fig. 4.

$$\eta_{sp}/\sqrt{c} = A + B\sqrt{c} \tag{1}$$

Examination of these plots reveals that plots based on the data of the polymer sample PBI (PPA) are curvilinear, and those based on the data of the polymer sample PBI (interface) are linear with a negative slope. Only the plots based on the data of polymer PBI (melt) are linear with a positive slope.
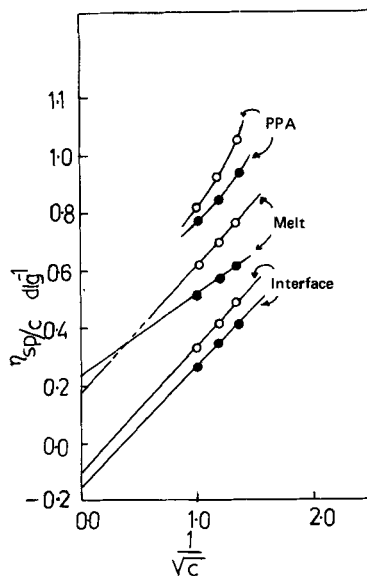
It has been reported that

FIG. 5. Application of empirical Relation (2).

$$\eta_{sp}/c = Z = \frac{A}{1 + B\sqrt{c}} \tag{2}$$

represents experimental data in a much better manner than Correlation (1) and other similar correlations [8]. In order to examine the applicability of Relation (2), plots of $1/Z$ against $\sqrt{c}$ were made. These plots are shown in Fig. 5. They are linear with a positive slope (B/A). From these plots, values of the constants A, B/A, and B were estimated. These are shown in Table 5.

Stivala and co-workers showed that

$$\eta_{sp}/c = [\eta]_\alpha + \frac{k[\eta]_\alpha}{\sqrt{c}} \tag{3}$$

could correlate experimental data about solutions of polymer, showing polyelectrolyte behavior in solvents like methanol or other protic solvents. This relation is applied to the present sets of data by making plots of η_{sp}/c vs $1/\sqrt{c}$. Such plots are shown in Fig. 6, and values of $[\eta]_\alpha$ and k are shown in Table 5. Examination of these data reveals that plots based on the data of PBI (melt) and PBI (interface) are

TABLE 5. Values of Coefficients of Empirical Relations

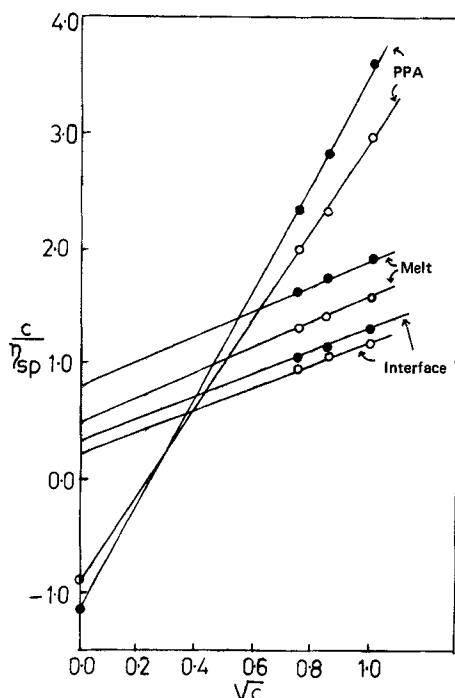| Temperature (°C)	Polymer sample	Equation (2)			Equation (3)	
		A	B/A	B	$[\eta]_\alpha$	k
30	PBI (melt)	2.222	1.149	2.554	0.185	2.762
	PBI (interface)	-1.136	3.837	-4.382	-0.155	-2.846
	PBI (PPA)	5.555	1.03	5.722	-a	-a
40	PBI (melt)	1.162	1.043	1.212	0.24	1.282
	PBI (interface)	-0.8547	4.75	-4.061	-0.155	-3.388
	PBI (PPA)	2.5	0.9033	2.258	-a	-a

aPlots are curvilinear.

FIG. 6. Application of empirical Relation (3).

linear and the plot based on the data of PBI (PPA) is curvilinear.
The analysis of data about polyelectrolyte behavior in terms of
empirical relations reveals that out of the three empirical relations,
Eq. (2) represents the experimental data in a much better manner than
do empirical Relations (1) and (3).

DTA STUDY

   The results of the DTA of polymer samples and model compounds
are shown in Table 6. Two independent experiments were carried out
for each sample, using different amounts of the polymer samples in a
1:2 ratio. The DTA exotherms were analyzed by application of the
Reich method [11] to estimate the order and energy of activation of
the degradation reactions. These data are also presented in Table 6.
Examination of these data reveals that among the three polymer
samples the PBI (melt) is apparently more stable thermally than the
other two polymer samples, PBI (interface) and PBI (PPA). N-MePBI
(melt) is less stable than the parent polymer. These data also reveal

TABLE 6. Results of DTA Analysis of PBI Samples and Model Compounds

Sample	Peak starting temperature (°C)	Peak temperature (°C)	Peak end temperature (°C)	Energy of activation[a] (kcal/mol) ± 5	Order of reaction[a] ± 0.2
PBI (PPA)	440	505	560	34.0	1.2
PBI (melt)	460	545	620	36.0	1.1
PBI (interface)	440	495	550	34.0	1.2
N-Me PBI (melt)	390	450	500	30.0	0.9
PB	450	500	540	27.0	0.9
DPB	430	500	540	26.0	0.9
PBB	410	500	540	25.0	1.2

[a]By Reich method [11].

that the degradation reaction of all the samples, including the model compounds, can be considered as first-order degradation reactions. The energy of activation for the degradation of the three polymer samples is around 35 kcal/mol; that for the degradation reaction of N-MePBI (melt) is around 30 kcal/mol. Comparison of the results of the DTA of the two model compounds (DPB and PBB) and of 2-phenylbenzimidazole (PB) with those of the polymer samples reveals a striking overall similarity with the only difference being that the energy of activation of the degradation of each of the three model compounds is lower than that of a similar reaction of any one of the polymers.

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