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Synthesis and Study of Nitro-Substituted Polybenzimidazoles. II

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ABSTRACT

Poly[2,2'-(m-nitro-o-phenylene)-5,5'-bibenzimidazole] (m-NO_2-PBI), its p-nitroisomer (p-NO_2-PBI), their N-methyl derivatives, and the nitration product of poly[2,2'-(o-phenylene)-5,5'-bibenzimidazole] are prepared and characterized by IR spectral study and by thermal study based on DTA. Properties of the first two polymers have been compared with those of their model compounds 2,2'-di(o- (or m) nitrophenyl)-5,5'-bibenzimidazole and (m- (or p) nitro-o-phenylene)bibenzimidazole. The properties of the N-methylation products are compared with those of the parent polymers.

INTRODUCTION

Polybenzimidazoles (PBIs) from 3,3'-diaminobenzidine (DAB) and dibasic acids, both aliphatic and aromatic, have been reported in literature [1, 2]; some of these are known for their high thermal stability [3, 4]. A review of the literature in connection with such polymers reveals that substituted PBIs are prepared using tetraamino derivatives of diphenyl ether [5], diphenylmethane [6],

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diphenyl sulfone [7], and N-methyl and N-phenyl derivatives of DAB [8]. Fluorinated aliphatic dibasic acids have been employed to prepare the corresponding fluorinated PBIs [8]. There are no reports about substituted PBIs from bz-substituted phthalic acid and DAB. Hence it was thought interesting to undertake the work described in the present paper dealing with the synthesis and characterization of bz-nitrosubstituted PBIs. Poly[2,2'-(m-nitro (I) and p-nitro (II)-o-phenylene)-5,5'-bibenzimidazole]s were prepared by condensing DAB with 3-nitro- and 4-nitrophthalic acids, respectively. Such polymers have been prepared by interfacial polycondensation of DAB-tetrahydrochloride with 3-nitro- and 4-nitrophthaloyl chloride, respectively. A nitro derivative (III) has been prepared by nitration of the poly[2,2'-(o-phenylene)-5,5'-bibenzimidazole] sample, designated as PBI(melt) [9]. IR spectral properties and thermal behavior of these polymers are studied. These properties are compared mutually and also with those of their appropriate model compounds like 2,2'-di(o- (IV) or m- (V) nitrophenyl)-5,5'bibenzimidazole and (m- (VI) or p- (VII) nitro-o-phenylene)-bibenzimidazole.

EXPERIMENTAL

Polycondensation of 3-Nitrophthalic Acid with DAB: Formation of Poly[2,2'-(m-nitro-o-phenylene)-5,5'-bibenzimidazole] (m-NO_2-PBI) (II)

3-Nitrophthalic acid (2.11 g, 0.01 mol), 3,3'-diaminobenzidine (2.14 g, 0.01 mol), and freshly distilled phenol (5 g) were mixed and heated under nitrogen at 220°. After the reaction temperature was attained, the reaction started within 15 min and a dark brown melt was formed which became a viscous solid. The temperature was then raised to 250° and kept there for 45 min. It was then finally heated at 275° for 1 h under nitrogen. The reaction mixture was cooled. The residue was powdered and mixed with xylene (20 mL). The xylene was then distilled to remove water as an azeotropic mixture. This process was carried out twice, using fresh xylene each time. Finally the product was repowdered and repeatedly treated with boiling alcohol. The product was a reddish-brown powder, insoluble in all solvents including formic acid, except for concentrated sulfuric acid from which it could be recovered on dilution with water. The IR spectrum of the original sample and of the sample obtained from sulfuric acid solution on dilution with water were superposable.

Polycondensation of DAB and 4-Nitrophthalic Acid: Formation of Poly[2,2'-(p-nitro-o-phenylene)-5,5'-bibenzimidazole] (p-NO_2-PBI, melt) (II)

The reaction was carried out and the product was purified as described above. The polymer was a reddish-brown powder. It was insoluble in all solvents including formic acid but soluble in concentrated sulfuric acid. It did not melt up to 360°C.

Interfacial Polycondensation of DAB and 3-Nitrophthaloyl Chloride: Formation of Poly[2,2'-(p-nitro-o-phenylene)-5,5'-bibenzimidazole (p-NO_2-PBI, interface) (Ia)

Tetrahydrochloride of 3,3'-diaminobenzidine (3,6 g, 0.01 mol) was dissolved in water containing sodium carbonate (2.16 g, 0.02 mol). 3-Nitrophthaloyl chloride (2.5 g, 0.01 mol) dissolved in benzene (10 mL) was added dropwise to this solution with vigorous stirring. After the addition was completed, stirring of the reaction mixture was continued for 1 h. The polymer was filtered, washed, and stirred in with water (100 mL) containing sodium carbonate (5 g) for 1.5 h. The polymer was filtered and exhaustively treated with alcohol. It was a reddish-brown powder. It was insoluble in all solvents except concentrated sulfuric acid. It did not melt up to 340°.

p-NO_2PBI (interface) (IIa) was prepared similarly from 4-nitrophthaloyl chloride.

Condensation of DAB and Phenyl-o-nitrobenzoate: Formation of 2,2'-Di-(o-nitrophenyl)-5,5'-bibenzimidazole (IV)

A mixture of DAB (1.07 g, 0.005 mol) and phenyl-o-nitrobenzoate (2.43 g, 0.01 mol) was heated at 220° under N_2 for 2 h, cooled and treated with 5% sodium hydroxide solution, filtered, and washed thoroughly with water. It was then treated with boiling alcohol. The product was soluble in DMF, DMSO, and acetic acid. Yield 1.5 g. It did not melt up to 350°.

2,2'-Di-(m-nitrophenyl)-5,5'-bibenzimidazole(V) was prepared from DAB (1.07 g, 0.01 mol) and phenyl-m-nitrobenzoate (2.43 g, 0.01 mol). The cooled reaction mixture was treated with 5% aqueous NaOH, filtered, and washed with water following the method described above. It was soluble in DMF, DMSO, and acetic acid. Yield 1.7 g. It did not melt up to 350°C.

Condensation of o-Phenylenediamine with 3-Nitrophthalic Acid: Formation of (m-Nitro-o-phenylene)-bibenzimidazole (VI)

A mixture of o-phenylenediamine (2.16 g, 0.02 mol) and 3-nitrophthalic acid (2.11 g, 0.01 mol) was heated at 230° under N_2, cooled, and scraped out. The powdered product was treated with bicarbonate solution to remove free acid. It was then treated with boiling water until it was completely free from amine. It was crystallized from dimethylformamide-water mixture as a yellow powder. Yield 1.8 g. It did not melt up to 350°.

(p-Nitro-o-phenylene)bibenzimidazole (VII) was prepared according to the process described above from o-phenylenediamine and 4-nitrophthalic acid. It was crystallized from DMF-water mixture (1:1) as a dark yellow powder. Yield 1.0 g. It did not melt up to 350°.

POLYMER REACTIONS

N-Methylation of m-NO_2-PBI

Dimethylsulfate (1 mL) was added to a suspension of finely powdered m-NO_2-PBI sample (0.25 g) in aqueous alkali (10%, 20 mL). The mixture was stirred at 80° for 24 h. The solid was filtered and washed thoroughly with water and dried. The product was treated twice with boiling ethanol (10 mL) and then with acetone. The product was dark brown in color and was insoluble in common organic solvents. It did not melt up to 350°. The sample is labeled N-Me-m-NO_2-PBI.

N-Methylation of p-NO_2-PBI

The reaction was carried out on p-NO_2-PBI sample and the product was purified as described above. It was a dark brown powder and did not melt up to 350°. The sample is designated N-Me-p-NO_2-PBI.

Nitration of Poly[2,2'-(o-phenylene)-5,5'-bibenzimidazole] (III)

Finely powdered poly[2,2'-(o-phenylene)-5,5'-bibenzimidazole] sample PBI (melt) [9] (0.35 g) was stirred in a mixture of fuming nitric acid (3.8 mL) and concentrated sulfuric acid (3.2 mL). The well-stirred reaction mixture was heated on a water bath at 60° for an hour. It was cooled and poured on crushed ice (20 g). The solid was filtered and washed with water and dried. It was yellow in color. It did not dissolve in common organic solvents. Its elemental analysis distinctly showed the presence of one NO_2 group per repeat unit.

MEASUREMENTS

See Table 1 for the elemental analysis of the polybenzimidazoles.

IR spectra of all the PBI samples and the model compounds were taken in KBr. The polymer samples were heated in vacuum at 80° for this purpose.

TABLE 1. Elemental Analysis of Polybenzimidazoles

		Required			Found		
Polymer samples	Formula	C%	H%	N%	C%	H%	N%
m-NO_2-PBI (melt) I	$C_{20}H_{11}N_5O_2$[a]	67.9	3.1	19.8	62.7[b]	3.1	18.8[b]
m-NO_2-PBI (inter) Ia	$C_{20}H_{11}N_5O_2$	67.9	3.1	19.8	62.9	3.0	19.1
p-NO_2-PBI (melt) II	$C_{20}H_{11}N_5O_2$	67.9	3.1	19.8	62.5	3.0	18.8
p-NO_2-PBI (inter) IIa	$C_{20}H_{11}N_5O_2$	67.9	3.1	19.8	63.0	2.9	19.2
N.Me of I	$C_{21}H_{13}N_5O_2$	68.7	3.5	19.1	65.3	3.0	18.4
N.Me of II	$C_{21}H_{13}N_5O_2$	68.7	3.5	19.1	65.9	3.1	18.6
Nitration product of PBI (melt) III	$C_{20}H_{11}N_5O_2$	67.9	3.1	19.8	63.1	3.1	18.7
(m-Nitro-o-phenylene) bibenzimidazole(IV)	$C_{20}H_{13}N_5O_2$	67.6	3.6	19.7	62.9	2.8	18.6
(p-Nitro-o-phenylene) bibenzimidazole(V)	$C_{20}H_{13}N_5O_2$	67.6	3.6	19.7	62.8	3.0	18.7
2,2'-Di(o-nitrophenyl)-5,5'-bibenzimidazole (VI)	$C_{26}H_{16}N_6O_4$	65.5	3.3	17.6	61.3	3.1	16.8
2,2'-Di(m-nitrophenyl)-5,5'-bibenzimidazole (VII)	$C_{26}H_{16}N_6O_4$	65.5	3.3	17.6	62.3	2.9	16.9

[a] Formula of repeat unit.

[b] If correction for the weight of residue of the combustion boat were applied, C% improved to 66.0% and N% improved to 19.2%.

TABLE 2. DTA and Kinetic Parameters of Polybenzimidazoles

Polymer sample	Exotherm starts at $t_1 \pm 5°C$	Peak temperature, $t_2 \pm 5°C$	Termination at $t_3 \pm 5°$	Energy of activation (kcal/mol)	Order of reaction (n)
I	340	440	510	18.2	1.1
Ia	350	440	530	18.6	1.2
II	340	460	530	19.1	1.0
IIa	355	460	550	19.0	1.1
N-Me-I	355	435	470	21.0	1.0
N-Me-II	355	440	475	21.0	1.0
III	365	500	580	20.0	0.9
IV	340	500	560	14.2	0.9
V	340	500	560	14.4	1.1
VI	330	445	520	15.0	1.0
VII	340	450	530	15.0	0.9

DTA of the polymer samples and model compounds was carried out in air using a Linseis DT Analyzer at a heating rate of 7°/min up to 600°. TGA of polymer samples I and II was carried out using a Du Pont 900 Thermal Analyzer in air at a heating rate of 7°/min. The results are presented in Table 2.

Viscosity Measurements

Viscosity of NO_2.PBI samples was measured in 0.5% solution of polymer sample in concentrated sulfuric acid. For this purpose each polymer sample was heated in vacuum at 80°C until its DSC thermogram did not show an endotherm around 100 to 120°, unlike the parent sample. In the absence of this treatment the polymer solution in concentrated sulfuric acid showed a lower viscosity than that shown by the pure solvent. Strongly absorbed water in the polymer sample changed the nature of the pure concentrated H_2SO_4. The specific viscosities of 0.5% solutions of polymer samples I, Ia, II, IIa, and III ranged from 0.025 to 0.027 dL/g.

RESULTS AND DISCUSSION

Examination of the data of elemental analysis reveals that the observed percentage values of C, H, and N are somewhat lower than the expected values as calculated on the basis of the structure of the repeat unit of the polymer. This happens in the case of polymers of high thermal stability. The observed values of C, H, and N of the nitration product of PBI (melt) (IV) suggests that at least one NO_2 group is introduced per repeat unit of the polymer.

All the m-NO_2-PBI and p-NO_2-PBI samples and the two N-Me derivatives of these polymers and the model compounds IV to VII are deep brown in color and are infusible up to 350°. The polymer samples are insoluble in common organic solvents including formic acid. The model compounds are, however, highly soluble in some solvents mentioned in the Experimental section. The nitration product of PBI is yellow in color and is insoluble in all solvents including formic acid. It is interesting to note that unsubstituted PBI samples are soluble in formic acid [1, 9]. It seems that strong intermolecular interaction between NO_2 groups and NH of the benzimidazole part of the polymer chain is responsible for this difference in solubility.

The IR spectra of m-NO_2-PBI samples I and Ia prepared by two different techniques are identical; this is also true of the spectra of p-NO_2-PBI samples II and IIa. Spectra of all these polymer samples and of polymer sample III, except those of N-Me-m-NO_2-PBI and N-Me-p-NO_2-PBI, comprise a broad band extending from 3400 to 2800 cm^{-1}. A band that broad is absent in the spectra of the N.Me derivatives of m-NO_2- and p-NO_2-PBI samples. The PBI (melt) polymer sample comprises a sharp band around 1690 cm^{-1} in its IR spectrum [9]. Such a sharp band is observed around 1733 cm^{-1} in the spectra of both m-NO_2- and p-NO_2-PBI samples, and at 1700 cm^{-1} in the spectrum of the nitration product of PBI (melt). Bands characteristic of the benzimidazole ring [10], and which have been observed in the spectrum of PBI (melt) [11] near 1620, 1660, 1500, 1460, 1420, and 1278 cm^{-1}, are also observed in the spectra of m-NO_2- and p-NO_2-PBI. Bands at corresponding positions are also observed in the spectra of II and of the nitration product of PBI (melt). A pair of bands indicative of the presence of the NO_2 group appear at 1535 and 1354 cm^{-1} in the spectrum of m-NO_2-PBI and at 1529 and 1354 cm^{-1} in the spectrum of p-NO_2.PBI. The former band around 1530 cm^{-1}, due to asymmetric stretching, is strong enough to mask partially some of the C=C bands in the region. In the spectrum of the nitration product of PBI (melt) the bands characteristic of the NO_2 group appear at 1524 and 1342 cm^{-1}. Comparison of the region from 1600 to 1400 cm^{-1} and also the region from 1130 to 760 cm^{-1} in the spectra of nitration product with those of the corresponding region in the spectra of m-NO_2-PBI and of p-NO_2-PBI reveals that there is a characteristic difference. This suggests that the nitration product of the PBI (melt) sample is a result of nitration of either of the benzene residues labeled A of the benzimidazole part of the repeat unit of the polymer chain and not the result of nitration of the benzene ring of type B. This is supported by the higher reactivity of the A-type ring than that of the B-type ring. Comparison of the spectra of m-NO_2-PBI with those of its model compounds IV and VI reveals many similar spectral characteristics. Such a similarity is observed in the spectra of p-NO_2-PBI and those of model compounds V and VII.

Examination of the results of differential thermal analysis of the polymer samples reveals that thermal degradation apparently involves one step. Analysis of these data by the Reich method revealed that the exothermic changes are first-order processes overall and have an energy of activation ranging from 19 to 21 kcal/mol depending upon the nature of the polymer. It has been reported earlier by the present authors that the DT thermogram of polybenzimidazole prepared under melt conditions commences around 460° and terminates around 620° [9]. The results reported in Table 2 reveal that both the m-NO_2- and p-NO_2-PBI polymer samples and their N-methyl derivatives are comparatively less stable than the unsubstituted PBI (melt) polymer sample. The N-methylation products of m-NO_2- and p-NO_2-PBI are less stable than their parent polymer samples. The nitration product of PBI (melt) is distinctly more stable than m-NO_2- and p-NO_2-PBI polymer samples. Among the m-NO_2- and p-NO_2-PBI samples, the latter appears to be slightly more stable on the basis of the results of DTA. However, comparison of data based on TG analysis of the polymer samples reveals that the p-NO_2-PBI sample is distinctly more stable than the m-NO_2-PBI sample. TG analysis of these two samples carried out in air at a heating rate of 7°/min revealed that m-NO_2-PBI (melt) polymer sample lost 12 and 70% and p-NO_2-PBI polymer sample lost 9 and 58% of their weights when heated up to 350 and 500°C, respectively. Comparison of the DTA data of m-NO_2-PBI and its model compounds IV and V reveals that there is an apparent similarity in thermal behavior. However, the energy of activation of degradation of model compounds IV and VI is around 13 to 14 kcal/mol while the energy of activation of degradation of m-NO_2-PBI is in the range from 19 to 21 kcal/mol. Such a trend is also revealed on comparison of the thermal behavior of p-NO_2-PBI and its model compounds V and VII.

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