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Polybenzimidazoles. III. Synthesis and Study of Poly[2,2'-(R-substituted-o-phenylene)-5,5'-bibenzimidazole]

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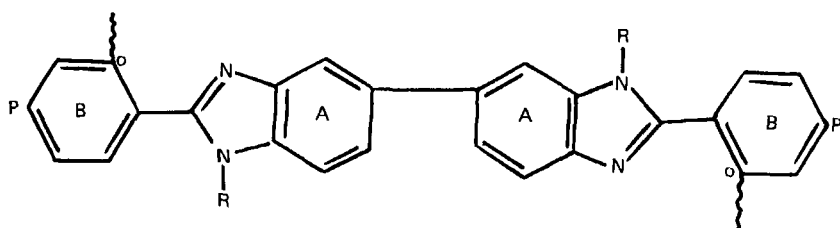
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ABSTRACT

Poly[2,2'-(R-substituted-o-phenylene)-5,5'-bibenzimidazole]s [R = m-NH₂(I), m-NHAc (II), p-Cl (III), and the N-methylation products of II and III and the chlorination product of poly[2,2'-(o-phenylene)-5,5'-bibenzimidazole] (IV)] are prepared and characterized by their IR spectral study and thermal analysis. Model compounds, 2,2'-di(R'-phenyl)-5,5'-bibenzimidazoles [R' = O-NH₂ (Im), o-NHAc (IIIm), and m-chloro (IIIIm)] are prepared for comparison of their properties with those of the polymer samples I, II, and III, respectively.

INTRODUCTION

Perusal of the literature in connection with the polybenzimidazoles (PBIs) from 3,3'-diaminobenzidine (DAB) and phthalic acid reveals that there are reports about the synthesis of PBIs with X being nil [1, 2] or O, SO₂, or CH₂ [3-5] and R = H and of N-substituted (R = Me, Ph) derivatives of poly[2,2'-(o-phenylene)-5,5'-bibenzimidazole] [6]. The literature reveals that there are no reports about such PBIs with substitution in Ring A or B. The present



communication deals with the synthesis of poly[2,2'-(*m*-NH₂ (I), *m*-NHAc (II), and *p*-Cl (III) -(*o*-phenylene)-5,5'-bibenzimidazole]s. *N*-Methylation products of II and III were prepared. Chlorination of the PBI sample, which is poly[2,2'-(*o*-phenylene)-5,5'-bibenzimidazole] [10], is carried out to afford a chlorination product (IV). IR spectral characteristics and the results of DTA of these polymer samples are reported. Selected model compounds of Polymers I, II, and III viz., 2,2'-di(*o*-amino (Im), *o*-NHAc (II_m), and *m*-chloro (III_m) phenyl)-5-5'-bibenzimidazoles, respectively, were prepared for comparative study.

EXPERIMENTAL

The monomers 3-aminophthalic acid [7], 3-*N*-acetamidophthalic acid [7], 4-chlorophthalic acid [8], DAB [2], and isatoic anhydride [9] were prepared by the reported methods.

Polycondensation of 3-Aminophthalic Acid with DAB: Synthesis of Poly[2,2'-(*m*-amino-*o*-phenylene)-5,5'-bibenzimidazole]: (*m*-NH₂-PBI) I

3-Aminophthalic acid (1.81 g, 0.01 mol), 3,3'-diamino benzidine (2.14 g, 0.01 mol) and freshly distilled phenol (5 g) were mixed and heated under nitrogen at 220°C. The reaction mixture turned into a dark brown thick melt which became a viscous solid on further heating. The reaction temperature was raised to 260°C and kept there for 45 min. The reaction mixture was then finally heated at 280°C for 90 min under nitrogen. The residue was treated with boiling water and then with boiling ethanol. The polymer was a dark brown powder. Yield, 1.3 g. It was insoluble in all organic solvents including formic acid and was soluble only in concentrated sulfuric acid.

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

The reaction was carried out and the product was purified as described above. The polymer was a brown powder. It was insoluble in all solvents including formic acid but soluble in concentrated sulfuric acid. Yield, 1.49 g from 2.149 g of DAB. It did not melt up to 300°C.

Polycondensation of 4-Chlorophthalic Acid and DAB: Formation of Poly[2,2'-(p-chloro-o-phenylene)-5,5'-bibenzimidazole]: (p-Cl-PBI) III

The reaction was carried out by heating a mixture of 4-chlorophthalic acid (2.0 g, 0.01 mol), 3,3'-diaminobenzidine (2.14 g, 0.01 mol) and phenol (5 g) under nitrogen at 230°C. The reaction mixture, which turned into a brown viscous solid during 30 min, was subsequently heated to 255°C for 1 h and at 285°C for 1.5 h. The cooled reaction mixture was treated with boiling ethanol (20 mL) thrice. The brown-colored polymer did not melt up to 300°C. Yield, 1.5 g. It was soluble only in concentrated sulfuric acid.

Synthesis of Model Compounds

2,2'-Di(o-aminophenyl)-5,5'-bibenzimidazole (Im)

3,3'-Diaminobenzidine (2.14 g, 0.01 mol) and isatoic anhydride (prepared from anthranilic acid) (1.63 g, 0.01 mol) were mixed and heated under nitrogen at 240°C for 2 h. The reaction temperature was increased to 270°C and kept there for 1/2 h. The solid was finely powdered and exhaustively treated with ethanol. Yield, 1.0 g. It was crystallized from a DMF:water mixture in brown powder. It did not melt up to 340°C.

The N-acetamino derivative (IIIm) of this model compound (Im) was prepared by treating Im with excess acetyl chloride in a DMF:water mixture. It did not melt up to 340°C.

Both model compounds Im and IIIm are soluble in DMF, DMSO, and formic acid.

2,2'-Di(m-chlorophenyl)-5,5'-bibenzimidazole (IIIIm)

Phenyl-m-chlorobenzoate (2.32 g, 0.01 mol) and 3,3'-diaminobenzidine (1.07 g, 0.005 mol) were mixed and heated under nitrogen at 200°C for 2 h. The product was scrapped and treated as described above. The yellowish brown powder did not melt up to 340°C. It was soluble in DMF, DMSO, formic acid, and acetic acid.

Polymer Reactions

N-Methylation of m-NHAc-PBI

To a suspension of finely powdered polymer sample II (0.25 g), in aqueous alkali (5% w/v, 20 mL), dimethylsulfate was added. The reaction mixture was stirred at 60°C for 24 h. The solid was filtered and washed with water thoroughly. The dried residue did not melt up to 340°C. The sample was labeled as N-Me-m-NHAc-PBI.

N-Methylation of p-Cl-PBI

To a suspension of polymer sample III (0.25 g) in aqueous alkali (10% w/v, 20 mL), dimethylsulfate (1 mL) was added. The reaction mixture was heated on a water bath with constant stirring for 4 h. The solid was filtered and washed with water. It was soluble only in concentrated sulfuric acid. The sample was designated as N-Me-p-Cl-PBI.

Chlorination of Poly[2,2'-(o-phenylene)-5,5'-bibenzimidazole

A suspension of "PBI" sample [10] (0.1 g) in concentrated hydrochloric acid (25 mL) was left overnight with stirring. To this suspension, powdered potassium chlorate (1.5 g) was added over a period of 2 h with constant stirring at 20-25°C. The stirring was continued further for 1 h. The reaction mixture was filtered. The solid was washed thoroughly with water. It was a light brown colored powder. It did not melt up to 350°C. Its chlorine analysis revealed that on an average a mole of chlorine atoms is introduced per mole of repeat unit.

MEASUREMENTS

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

The DTA of the polymer samples and their model compounds was carried out in air using a Linseis DT analyzer at a heating rate of 7°/min up to 600°C. The results are presented in Table 1. Kinetic parameters were evaluated following the Reich method [11].

RESULTS AND DISCUSSION

All the polymer samples listed in Table 2 are dark brown colored solids. They are infusible up to 350°C. The polymer samples are insoluble in all common organic solvents including formic acid. The

TABLE 1. DTA and Kinetic Parameters of Substituted PBIs

Sample	Peak starts at $t_1 \pm 5^\circ\text{C}$	Peak maxima at $t_2 \pm 5^\circ\text{C}$	Peak ends at $t_3 \pm 5^\circ\text{C}$	Energy of activation E^\ddagger (kcal/mol)	Order of reaction n
m-NH ₂ -PBI (I)	365	465	570	21.2	1.10
m-NHAc-PBI (II)	360	470	575	21.0	0.90
N-Me-m-NHAc-PBI	330	460	545	20.5	0.80
2,2'-Di(m-aminophenylene)-5,5'-bibenzimidazole (Im)	250	550	570	18.0	0.80
p-Cl-PBI (III)	440	555	635	35.3	0.84
Chlorinated "PBI" (IV)	440	535	595	36.8	1.20
N-Me-p-Cl-PBI	410	525	600	33.8	1.00
2,2'-Di(m-chlorophenyl)-5,5'-bibenzimidazole (III _m)	430	545	590	31.8	0.96
"PBI" sample [10]	460	545	620	36.0	1.10

TABLE 2. Elemental Analysis of Substituted PBIs

Sample	Formula	Elemental analysis									
		Required					Found				
		C%	H%	N%	Cl%	C%	H%	N%	Cl%		
m-NH ₂ -PBI (I)	C ₂₆ H ₁₈ N ₆	75.3	4.3	20.2	-	71.8	3.0	19.1	-		
m-NHAc-PBI (II)	C ₃₀ H ₂₂ N ₆ O ₂	72.0	4.4	16.8	-	69.2	3.1	15.9	-		
N-Me-m-NHAc-PBI	C ₃₁ H ₂₄ N ₆ O ₂	70.3	4.6	16.3	-	68.6	3.4	15.7	-		
2,2'-Di(o-aminophenyl)- 5,5'-bibenzimidazole (Im)	C ₂₆ H ₂₀ N ₆	75.0	4.8	20.1	-	72.4	3.4	19.1	-		
N-Acetyl derivative of Im (IIIm)	C ₃₀ H ₂₄ N ₆ O ₂	72.0	4.8	16.8	-	70.0	3.5	15.1	-		
p-Cl-PBI (III)	C ₂₆ H ₁₄ N ₄ Cl ₂	68.8	3.0	-	15.6	66.3	2.6	-	15.2		
n-Me-p-Cl-PBI	C ₂₇ H ₁₆ N ₄ Cl ₂	69.3	3.4	-	15.2	67.2	2.9	-	14.8		
Chlorinated "PBI" sample	C ₂₆ H ₁₄ N ₄ Cl ₂	68.8	3.0	-	15.6	66.8	3.0	-	15.1		
2,2'-Di(m-chlorophenyl)- 5,5'-bibenzimidazole (IIIm)	C ₂₆ H ₁₆ N ₄ Cl ₂	68.5	3.5	-	15.5	66.2	3.0	-	15.2		

model compounds are, however, highly soluble in some solvents as mentioned in the experimental part. The N-methylation products are dark brown in color and insoluble in all organic solvents. The chlorination product of the "PBI" sample [10] was light brown in color and soluble only in concentrated sulfuric acid.

Examination of the data of elemental analysis reveals that the observed values of C, H, and N% are somewhat lower than the expected values calculated on the basis of the repeat unit of polymer. This is also the experience of other workers who have worked with thermally stable polymers [12, 13].

A comparison of the spectrum of the polymer sample and its model compound revealed that most of the characteristic bands in the IR spectrum of the model compound were found at corresponding positions in the spectrum of the polymer sample for which the said compound stood as a model compound. For example, typical benzimidazole bands [14] observed in the IR spectrum of poly[2,2'-(*o*-phenylene)-5,5'-bibenzimidazole] [15] are also observed in the spectra of all the polymer samples reported in the present communication and of their model compounds at 1695, 1600, 1560, 1530, 1485, and 1450 cm^{-1} .

The DT thermogram of *m*-NH₂-PBI (I) reveals that the polymer sample remains unchanged up to about 365°C and the rate of degradation increases slowly beyond this temperature up to about 570°C; at this temperature the degradation was nearly complete. Analysis of the results of DTA of this polymer sample by the Reich method revealed that the order of degradation reaction is around one and the energy of activation is around 21 kcal/mol. Comparison of the DT thermogram of Polymer I and its model compound (Im) showed that, like Polymer I, the model compound exhibits only one exotherm originating at a slightly lower temperature (250°C) and terminating around 570°C. The order of degradation and energy of activation of this compound (Im) are 0.8 and 18.0 kcal/mol, respectively.

Comparison of the results of the DTA of *m*-NHAc-PBI and *m*-NH₂-PBI reveals that both these polymers exhibit similar thermal behaviors. *m*-NHAc-PBI and its model compound II_m exhibit thermal behaviors of degradation similar to model compound II (~16 kcal/mol) as compared to 21 kcal/mol for such a reaction of polymer *m*-NHAc-PBI. The N-methylation product of *m*-NHAc-PBI is less stable than that of *m*-NH₂-PBI and *m*-NHAc-PBI.

Examination of the DT thermogram of *p*-Cl-PBI revealed that its degradation commenced at 440°C and the rate of degradation increased gradually above this temperature and was a maximum at 555°C. Beyond 555°C the rate of degradation decreased rapidly; the degradation appeared to be completed at 635°C. The energy of activation and the order of degradation reaction were found to be around 35 kcal/mol and 0.8, respectively. Comparison of DT thermograms of *p*-Cl-PBI and its model compound III_m reveals an apparent similarity in their thermal behavior.

As chlorination of phthalic acid affords 4-chlorophthalic acid as

the main product [9], it was expected that chlorination of the "PBI" sample would afford III. The IR spectra of the chlorination products IV and III are distinctly different. This indicated that the two samples have different structures. Besides, of the two types of phenyl rings A and B in the repeat unit of the "PBI" sample, phenyl ring A is more reactive for electrophilic substitution than phenyl ring B. Hence it is considered that chlorination has most probably occurred on any one of the phenyl rings A of the repeat unit. Comparison of the results of DTA of chlorination product (IV) with those of its parent polymer and polymer sample III reveals that the chlorination product is the least stable of the three. Comparison of results of DTA of polymer samples I to III and of the "PBI" sample [10] reveals that polymer samples I and II are less stable and the polymer sample III is more stable than the "PBI" sample with no substituents.

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