CONCLUSIONS

(1) Polybenzimidazoles have been prepared from 3,3′,4,4′-tetra-aminodiphenylmethane and the diphenyl esters of adipic, sebacic, isophthalic and terephthalic acids, and the properties of the polymers have been studied.

(2) It is shown that the introduction of a methylene group between the benzimidazole rings leads to some increase in the solubility of the polybenzimidazoles. The heat resistance of the polymers is practically unchanged.

Translated by E. O. PHILLIPS

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THE PREPARATION OF SOME POLYBENZIMIDAZOLES CONTAINING PHOSPHORUS, BORON AND OXYGEN ATOMS IN THE CHAIN*†

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THE polybenzimidazoles described by us previously [1–3] are the products of polycondensation of tetramines with dicarboxylic acid esters, not containing hetero-atoms.

The purpose of the present work was to prepare some polybenzimidazoles containing hetero-atoms in the main chain (phosphorus, boron and oxygen), in order to examine the effect of these on the properties of the polymers.

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The starting materials were 3,3′-diaminobenzidine, 3,3′,4,4′-tetra-aminodiphenylmethane, the diphenyl esters of 4,4′-dicarboxydiphenyl oxide and bis-(*p*-carboxyphenyl)methylphosphine oxide, and the tetrabutyl ester of 1,4-phenylenediboronic acid. The constants of these materials are given in the experimental part.

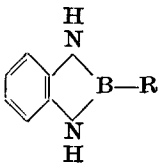
The polymers were prepared by the method of reference [2], by heating a mixture of the reactants for half an hour at 220–260° and then for 5 hours with a steady increase in temperature from 260° to 320–350°, at a residual pressure of 10^{-3} mm. In the case of tetrabutyl 1,4-phenyleneboronate the temperature was increased to 420°.

For the polymers obtained the viscosity of a 0·5% solution in concentrated formic acid was measured, the X-ray diffraction patterns were recorded, and the softening point under a layer of paraffin, the solubility in various solvents and the heat resistance were determined. The results are given in Table 1.

The polymers are yellow-brown powders. The elementary composition of the products is close to that of the polybenzimidazole unit. The small discrepancy is evidently explained by the presence of some amino-amide units, as we have found previously in the case of polybenzimidazoles not containing hetero-atoms [1–3].

X-ray analysis showed that poly-2,2′-(*p*-diphenylene oxide)-5,5′-dibenzimidazole and the polybenzoborimidazolines are crystalline substances. The polymers obtained from 3,3′-4,4′-tetra-aminodiphenylmethane and the diphenyl esters of 4,4′-dicarboxydiphenyl oxide and bis-(*p*-carboxyphenyl)-methylphosphine oxide are amorphous.

It is seen from Table 1 that all the above polymers are very heat resistant materials, not decomposing up to 490–500°. The polymer obtained by reaction between 3,3′,4,4′-tetra-aminodiphenylmethane and the tetrabutyl ester of 1,4-phenylenediboronic acid does not decompose even at 500°. It is well known that the cyclic system containing a boron atom



forms easily and has an ultraviolet spectrum similar to that of benzimidazole [4–6]. On these grounds Letsinger and Hamilton suggested that this system possesses a system of π-electrons and can be represented by the resonance form [6]:

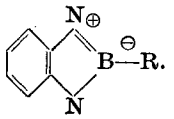
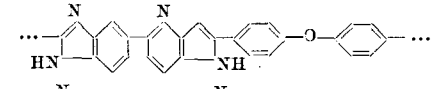
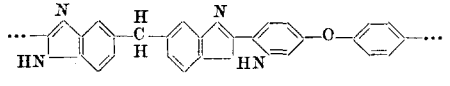
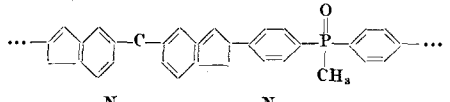
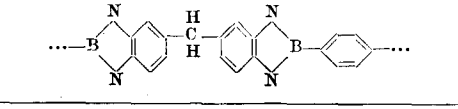


TABLE 1. SOME PROPERTIES OF THE POLYBENZIMIDAZOLES

No	Structural unit of polymer	Reduced viscosity, 0·5% solution in HCOOH	Temperature, °C		Elementy composition, %							
					C		H		E§			
			softening*	onset of decomposition‡	calculated	found	calculated	found	calculated	found	calculated	found
1		1·14	460–470*	500	78·11	76·60 76·42	4·02	4·07 4·27	13·96	12·70 12·60	—	—
2		1·58	350–370*	500	78·20	76·84 76·62	4·38	4·41 4·53	13·52	12·96 12·83	—	—
3		1·00	380–400†	490	72·95	69·45 69·45	4·62	4·95 4·99	12·18	11·26 11·14	6·72	6·64 6·80
4		0·16	500†	500	70·90	69·11 69·35	5·01	5·16 5·17	17·40	17·80 17·72	6·72	6·39 6·30

* From thermomechanical curves.
† In an apparatus for determination of tack temperature.
‡ Thermogravimetric results.
§ E=O, B or P respectively.

The aromatic character of this system also explains the high heat resistance of polymers containing repeating benzimidazole units. For example this polybenzimidazoline loses only ~7% in weight when it is heated in a current of nitrogen to 550°. It should be noted that this polymer has a low reduced viscosity, measured at 0·5% concentration in formic acid.

The polybenzimidazole from 3,3',4,4'-tetra-aminodiphenylmethane and the diphenyl ester of 4,4'-dicarboxydiphenyl oxide has the highest molecular weight (η_{red}=1·58).

TABLE 2. SOLUBILITY OF POLYMERS IN VARIOUS SOLVENTS

No.*	Sulphuric acid	Formic acid	Tricresol	Dimethylformamide	Dimethylsulphoxide	Acetic acid	Benzyl alcohol	Relative solubility
1	3	3	1	2	3	1	0	13
2	3	3	2	3	3	1	0	15
3	3	3	1	2	3	1	0	13
4	3	2	1	3	3	1	0	13

* Serial numbers as in Table 1.

Explanation of scale: 0—insoluble in boiling solvent; 1—dissolves partially in boiling solvent, precipitates in the cold; 2—soluble in boiling solvent; 3—soluble at room temperature.

Data on the solubility of the polymers are presented in Table 2. The polybenzimidazoles containing oxygen atoms in the main chain are soluble in the cold in sulphuric acid, formic acid and dimethylsulphoxide, and on heating in dimethylformamide and tricresol. The corresponding polymer without oxygen in the main chain was prepared by Vogel and Marvel [3] from 3,3'-diaminobenzidine and the diphenyl ester of 4,4'-dicarboxydiphenyl. This polymer is soluble only in sulphuric acid, and is only partially soluble in formic acid. The polybenzimidazole from 3,3',4,4'-tetra-aminodiphenylmethane and the diphenyl ester of 4,4-dicarboxydiphenyl oxide has better solubility than the polymer of almost the same structure without the CH_2 group between the benzimidazole nuclei.

The polymer from 3,3',4,4'-tetra-aminodiphenylmethane and the diphenyl ester of bis-(*p*-carboxyphenyl)methylphosphine oxide is more soluble than the polymer obtained by us previously [7] from 3,3'-diaminobenzidine, which does not contain the methylene group between the benzimidazole nuclei. An interesting and valuable property of the phosphorus-containing polymer is its nonflammability. When the polymer is placed in the flame of a burner it smoulders and chars but on removal from the flame it extinguishes immediately. The self-extinguishing property of this polymer is associated with the phosphoryl group present in its structure (P content 6·80%). A similar effect is found in phosphorus-containing polyamides (P content 6–12%) [8].

Thus it is seen that the introduction of ether oxygen and phosphoryl groups does not reduce the heat resistance of the polymers, but increases their solubility to some extent.

Polybenzoborimidazole is also a highly heat resistant polymer.

More detailed results of the study of the heat resistance of these polymers will be given in a later communication.

EXPERIMENTAL

The diphenyl ester of 4,4′-dicarboxydiphenyl oxide was prepared by fusing phenol with the dichloranhydride of 4,4′-dicarboxydiphenyl oxide; m.p. 186–188°

Found, %: C 75·48; 75·39; H 4·33; 4·53

$C_{26}H_{18}O_5$. Calculated, %: C 76·04; H 4·40

The tetrabutyl ester of 1,4-phenylenediboronic acid was prepared by the method of Nielson and McEwen [9]; b.p. 212°/2 mm, n_D^{25} 1·4670 (according to reference [9], b.p. 152–162/0·1 mm, n_D^{25} 1·4680).

The diphenyl ester of bis-(p-carboxyphenyl)methyl phosphine oxide was obtained from the corresponding acid chloride [10] and sodium phenate. The melting point of the ester after recrystallization (from methanol and then from toluene) was 244–246°.

Found, %: C 70·73, 70·74; H 4·75, 4·60; P 6·72, 6·75.

$C_{27}H_{21}O_5P$. Calculated, % C 71·05; H 4·64; P·6·79

For the characteristics of the tetramines see references [2] and [3].

CONCLUSIONS

(1) Polybenzimidazoles containing oxygen and phosphorus atoms in the main chain have been synthesized and studied.

(2) A polybenzoborimidazoline has been prepared from 3,3′,4,4′-tetra-amino-diphenylmethane and the tetrabutyl ester of 1,4-phenylenediboronic acid.

(3) It is shown that all the polymers obtained in this work are very heat-resistant substances and they possess better solubility than similar polybenz-imidazoles that do not contain hetero-atoms.

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