(3) The thermal degradation has been found to be determined by different mechanisms, depending on the process of preparation and the method of treatment.

Translated by V. ALFORD

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SYNTHESIS AND INVESTIGATION OF THE PROPERTIES OF SOME HOMOGENEOUS AND MIXED POLYBENZIMIDAZOLES*

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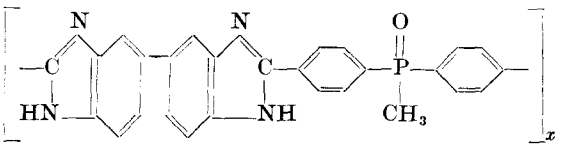
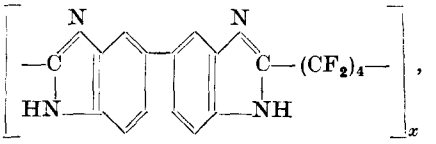
POLYBENZIMIDAZOLES PBIA) are new organic polymers which are distinguished by a thermal stability which is unusually high for this type. This type of polymer is synthesized by the polycondensation of tetra-amines and dicarboxylic acids [1] or their esters [2, 3]. We have already [4] studied the mechanism of the formation of polybenzimidazoles on the example of poly-2,2′-(octamethylene)-5,5′-dibenzimidazole.

The present work deals with an attempt to prepare certain new types of homogeneous PBIA, particularly those containing phosphorus:



and fluorine:



and also certain mixed PBIA.

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Table 1 shows some of the properties of synthesized homogeneous PBIA, and the Figure *a* shows their thermomechanical properties.

It can be seen from the Table that, with the exception of those containing fluorine, all the PBIA obtained are heat resistant polymers which begin to

TABLE 1. CERTAIN PROPERTIES OF HOMOGENEOUS POLYBENZIMIDAZOLES PREPARED FROM 3,3'-DIAMINOBENZIDINE AND THE DIPHENYL ESTERS OF DICARBOXYLIC ACIDS

Diphenyl ester	Temperature, °C		Reduced viscosity‡
	softening*	degeneration point†	
bis-(*p*-carboxyphenyl)methyl-phosphine oxide	480	520	0·20
Perfluoroadipic acid	—	240	—
Terephthalic acid††	510	510	—
Isophthalic acid††	520	520	—
Sebacic acid	280	400	10·0

* From thermomechanical curves.
† Results of thermogravimetric analysis.
‡ 0·5% solution in formic acid at 20°.
†† Insoluble in HCOOH.

degenerate at around 400–520°. All the PBIA were synthesized by melt polycondensation of 3,3'-diaminobenzidine (DAB) with the diphenyl ester of the corresponding dicarboxylic acid. The polycondensation of DAB with diphenylperfluoroadipate above 210° was accompanied by degeneration of the product of condensation to acid products. In this case the degeneration is probably accompanied by the liberation of HF. Analysis shows that a rise in the reaction temperature has a considerable effect on the elementary composition of the condensation products, causing a marked reduction in the fluorene content. For instance, the product of polycondensation of DAB with diphenylperfluoroadipate prepared at 210° contains 48·71% carbon, 2·71% hydrogen, 32·82% fluorene and 13·31% nitrogen, while if this reaction is conducted at 250° the products of the condensation are 54·40% carbon, 3·05% hydrogen, 24·80% fluorene and 15·23% nitrogen.

Theor., %: a) for the polyamide $C_{16}H_{12}N_4F_8O_2$—C 43·25; H 2·72; F 34·21; N 12·61; b) for polybenzimidazole $C_{16}H_8N_4F_8$—C 47·07; H 1·98; F 37·23; N 13·72.

The products of the condensation are infusible and insoluble.

When homogeneous PBIA were prepared from the same aromatic compounds (DAB, terephthalic and isophthalic acids) these polymers were found to have much lower solubility in organic solvents than that indicated by Vogel and Marvel [2]. An investigation of the effect of the conditions of polycondensation on the viscosity of solutions of the product PBIA in formic acid (see Table 2)

showed that independent of the conditions of polycondensation the solubility of the polymers remained low and the viscosity of PBIA solutions could be determined with only a 0·2% solution of the polymer in formic acid. At reaction temperatures of 300° or above insoluble polymers are formed. The formation

TABLE 2. INFLUENCE OF CONDITIONS OF POLYCONDENSATION ON THE REDUCED VISCOSITY OF POLYBENZIMIDAZOLE PREPARED FROM THE DIPHENYL ESTER OF ISOPHTHALIC ACID AND 3,3′-DIAMINOBENZIDINE*

Polycondensation conditions			Reduced viscosity of 0·5% solution formic acid	Polycondensation conditions			Reduced viscosity of 0·5% solution formic acid
Temperature, °C	Time, hours	Vacuum, mm Hg		Temperature, °C	Time, hours	Vacuum, mm Hg	
270	0·5	1	0·40	300	3·0	1	Insoluble
270	1·0	1	0·44	320	0·5	1	,,
270	2·0	1	0·47	320	0·5	3×10^{-2}	,,
270	4·0	1	0·50	260–280	3·5	4×10^{-2}	,,
270	8·0	1	0·80				

* Polycondensation was conducted in two stages [4]. In the first the starting materials were heated in a nitrogen flow at 220–260° for half an hour, and then in a vacuum (1 mm) at 260° for half an hour. After grinding the product polymer ($\eta_{red}=0{\cdot}20$) further polycondensation was conducted.

of an insoluble polymer when the temperature rises could be due either to the cross linking of the macromolecules as a result of side reactions, or to a sudden increase in the molecular weight of the product polymer. A similar effect, the formation of an insoluble infusible polymer, is something we have also observed in the synthesis of poly-2,2′-(octamethylene)-5,5′-dibenzymidazole at elevated temperatures [4].

We emphasize that the phosphorus-containing PBIA has much better solubility than the homogeneous PBIA given above. It dissolves quite easily in formic or sulphuric acid.

Besides the PBIA enumerated above we also prepared a number of mixed PBIA on DAB base with mixtures of diphenyl esters of dicarboxylic acids: a) terephthalic-isophthalic; b) sebacic and isopthalic, and c) sebacic and terephthalic taken in different ratios. Some of the properties of the mixed PBIA obtained are shown in Table 3 from which we can see that those prepared from aromatic components (DAB and the diphenyl esters of terephthalic and isophthalic acids) are infusible and have very limited solubility, due to which it was not even possible to determine the viscosity of solutions of these polymers. Looking at the figures in Table 4, we can see that the solubility of these mixed PBIA varies as a function of the composition of the mixture of the original components. As the concentration of the terephthalic acid residues in the poly-

mers rises, their solubility also rises a little. But the improvement on that of the original polymers is onyl slight. The solubility of the polymers was below 0·2% in the solvents studied (see Table 4). They were insoluble at room temperature in highly polar solvents such as cresol, acetic acid, benzyl alcohol, dimethylformamide.

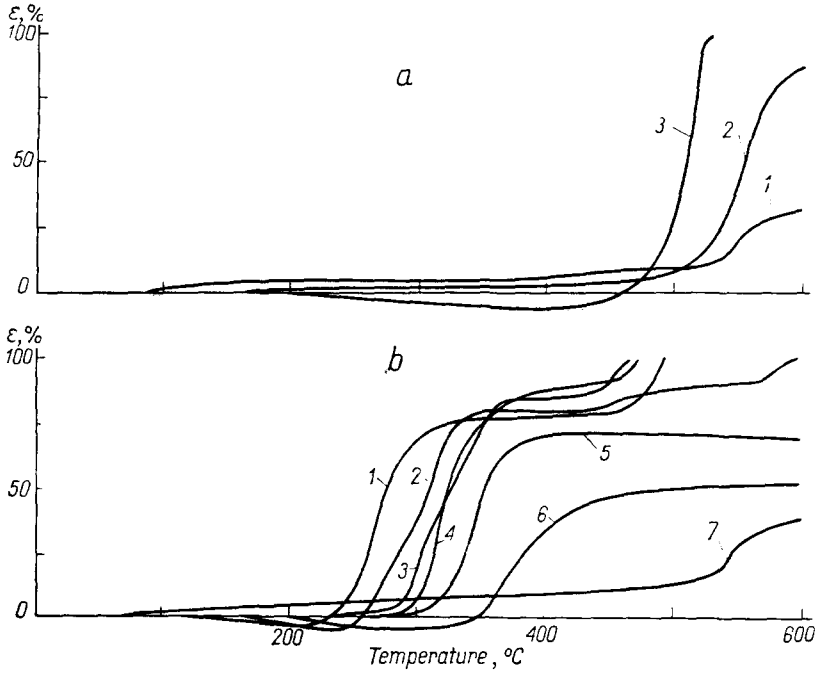
TABLE 3. SOME PROPERTIES OF MIXED POLYBENZIMIDAZOLES

Molar ratio of diphenyl esters of dicarboxylic acids	Softening temperature*, °C	Reduced viscosity of 0·5% solution in formic acid
Terephthalic : isophthalic	does not fuse	
1·0 :0	,,	—
0·8 : 0·2	,,	—
0·6 : 0·4	,,	—
0·5 : 0·5	,,	—
0·4 : 0·6	,,	—
0·2 : 0·8	,,	—
0 : 1·0	,,	—
Sebacic : isophthalic		
1·0 : 0	235	8·00
0·8 : 0·2	270	2·70
0·6 : 0·4	300	3·06
0·5 : 0·5	320	1·98
0·4 : 0·6	340	1·56
0·2 : 0·8	365	0·98
0 : 1·0	—	—
Sebacic : terephthalic		
0·8 : 0·2	225	2·88
0·5 : 0:5	—	1·58
0·2 : 0·8	—	—

* Determined from thermomechanical curves.

Mixed PBIA containing aliphatic besides aromatic units, are distinguished by different properties (solubility, melting point, thermal stability) from those which are prepared only from aromatic compounds (see Table 3 and Fig. *b*). Figure *b* gives the thermomechanical properties of mixed PBIA prepared from DAB and the diphenyl esters of isophthalic and sebacic acids. Table 4 gives the results obtained in a qualitative analysis of the solubility of mixed PBIA prepared from DAB and diphenyl esters of the dicarboxylic acids. These mixed polymers dissolve in quite a number of solvents, and their solubility increases somewhat with the content of the aliphatic component (sebacic acid radicals).

All the PBIA synthesized are heat resistant polymers which do not begin to disintegrate until 400–500°, depending on their structure. More detailed study of their heat resistance will be given in the next article.



Thermomechanical properties of: *a*—polybenzimidazoles prepared from 3,3′-diaminobenzidine and the diphenyl esters of isophthalic (*1*), and terephthalic acids (*2*) and bis-(*p*-carboxyphenyl)methylphosphine oxide (*3*); *b*—mixed polybenzimidazoles prepared from 3,3′-diaminobenzidine and the diphenyl esters of sebacic and terephthalic acids. The molar ratio diphenyl ester of sebacic : diphenyl ester of isophthalic acid: *1*—1·0 : 0·0; *2*—0·8 : 0·2; *3*—0·6 : 0·4; *4*—0·5 : 0·5; *5*—0·4 : 0·6; *6*—0·2 : 0·8; *7*—0·0 : 1·0.

EXPERIMENTAL

3,3′-diaminobenzidine was prepared by the method described in [4], m.p. 179–180° (179–180° [2]).

Diphenyl esters of terephthalic and isophthalic acids were prepared by melting phenol with the acid dichlorides of the corresponding acids. The melting point of the diphenylisophthalate was 136° (137–138° [5]), of terephthalate 190–191° (190–191° [5]).

Diphenyl ester of perfluoroadipic acid. 2 g perfluoroadipic chloride and 1·2 g phenol were put into a flask with a counterflow cooler. The mixture was heated for 3 hr at the boiling point of the chloride (132°). The reaction product was washed in decalene and then recrystallized, part of the product becoming resinous. The yield was 55% of the theoretical, m.p. 63–64°.

$C_{18}H_{10}F_8O_4$. Exp., %: C 48·95; 48·86; H 2·42; 2·40; F 34·36; 34·58.
Theor. %: C 48·88; H 2·28; F 34·37.

Polycondensation. A general description of the procedure for polycondensation has been given in [2, 4]. The conditions of the synthesis for these PBIA are given in Table 2.

TABLE 4. SOLUBILITY OF MIXED POLYBENZIMIDAZOLES PREPARED FROM 3,3′-DIAMINOBENZIDINE AND DIPHENYL ESTERS OF CERTAIN DICARBOXYLIC ACIDS*

Molar ratio of diphenyl esters of the following acids	Solvents											
	sulphuric acid		formic acid		cresol		benzyl alcohol		dimethyl-formamide		dimethyl-sulphoxide	
	at room temperature	during heating	at room temperature	during heating	at room temperature	during heating	at room temperature	during heating	at room temperature	during heating	at room temperature	during heating
Isophthalic : terephthalic												
1 : 0	−	−	−	+	−	−	−	+	−	−	+	+
0·8 : 0·2	−	−	+	+	−	−	−	+	−	−	+	+
0·6 : 0·4	−	+	+	+	−	−	−	+	−	−	+	+
0·5 : 0·5	−	+	+	+	−	−	−	+	−	−	+	+
0·4 : 0·6	−	+	+	+	−	−	−	+	−	−	+	+
0·2 : 0·8	−	+	−	+	−	−	−	+	−	−	+	+
0 : 1	+	+	−	+	−	−	−	+	−	−	+	+
Sebacic : isophthalic												
1 : 0	+	+	+	+	−	+	−	+	−	+	+	+
0·8 : 0·2	+	+	+	+	−	+	−	+	−	+	+	+
0·6 : 0·4	+	+	+	+	−	+	−	−	−	+	+	+
0·5 : 0·5	+	+	+	+	−	−	−	+	−	+	+	+
0·4 : 0·6	+	+	+	+	−	−	−	+	−	−	+	+
0·2 : 0·8	+	+	+	+	−	−	−	+	−	−	+	+
Sebacic : terephthalic												
0·8 : 0·2	+	+	+	+	−	+	+	+	−	+	−	+
0·5 : 0·5	+	+	+	+	−	−	−	−	−	+	−	+
0·2 : 0·8	+	+	+	+	−	−	−	−	−	−	−	+

* + soluble; − insoluble.

CONCLUSIONS

(1) Phosphorus containing polybenzimidazole was synthesized from 3,3′-diaminobenzidine and the diphenyl ester of bis-(*p*-carboxyphenyl)methylphosphine oxide, and its composition has been studied.

(2) Mixed polybenzimidazoles have been synthesized from 3,3′-diaminobenzidine and the diphenyl esters of terephthalic, isophthalic and sebacic acids and their properties have been studied.

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POLYMERIZATION IN HIGHLY VISCOUS MEDIA AND THREE-DIMENSIONAL POLYMERIZATION—VIII. DETERMINATION OF THE INITIATION RATE CONSTANTS OF RADICAL POLYMERIZATION IN ONLY PARTIALLY SET DIMETHACRYLATE BUTYLENE GLYCOL IN THE PRESENCE OF SOME PEROXIDE AND AZO INITIATORS*

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WE HAVE already reported the findings [1, 2] which indicate the influence exerted by a sharp change in the physical properties of a polymerization system upon the rate constant k_g and k_b, of the elementary stages of growth and chain breaking respectively, in the setting of polyster acrylates (PEA). The gelling at low degrees of conversion ($\Gamma<1\%$), together with the approach of the system to the glassy state at $\Gamma=80$ to 50%, cause changes in k_b and k_g which lead to the effect of spontaneous acceleration or slowing down of the process of PEA polymerization. The present report gives the results obtained by measuring the initiation rate constant k_i and k_d the decomposition rate constant in the thermal degradation of benzoyl peroxide (BP), dicyclohexylperoxidicarbonate (DPD) and azobisisobutyronitrile (ABN) in dimethacrylatebutyleneglycol (MB) up to 40–70% set. The method of measurement and the treatment of the experimental results has already been described in [3].

RESULTS AND DISCUSSION

In previous experiments we estalished that, with in the accuracy of the experimental procedure, the k_i values obtained were independent of the initial concentration of the initiator $[I_0]$ in the range 1–4 wt. %, and also of the degree

* Vysokomol. soyed. **6**: No. 7, 1256–1260, 1964.