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POLYAZOLES

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I. INTRODUCTION

Modern technology has an urgent need of thermostable polymeric materials. Apart from retaining their strength at high temperatures, the polymers must meet such requirements as resistance to hydrolysis, organic solvents, and mineral acids, good dielectric properties, etc. This results from the development of such new branches of technology as rocket construction, high-speed aviation, electronics, and instrumentation, and also from the more severe demands made on polymers which are widely used in electrical and mechanical engineering, paints and varnishes, and many other branches of industry.

The demands made on the thermal stability of polymers depend on how long the polymer will be located in a high-temperature zone. For example, modern aircraft require materials which have the limiting operating temperatures indicated below [1]. Still higher demands are made on materials for spacecraft.

Length of operation, h	30 000	1000	1	5 min
Temperature, °C	177	260	540	830

During recent years broad investigations have been conducted, both abroad and in the Soviet Union, on the synthesis of heat-resistant polymers, among which the most interesting are those containing heterocycles in the main chain of the macromolecule.

Polybenzimidazoles and polypyromellitimides have already found application. It is probable that in the immediate future use will also be made of polyquinoxalines [2], polymethylquinazolones [3], polyimidazolopyrrones (pyrrones) [4,5], and polymers containing 1,3,5-triazine [6,7] and other rings.

At the present time the class of heterocyclic polymers which has been studied most thoroughly comprises the polyazoles. However, this class of polymers has not been adequately represented in the numerous reviews devoted to heat-resistant polymers [8-14]. We have tried to fill this gap, and reflect the overall progress made in synthesising polyazoles containing azole rings in the main chain and in studying their properties.

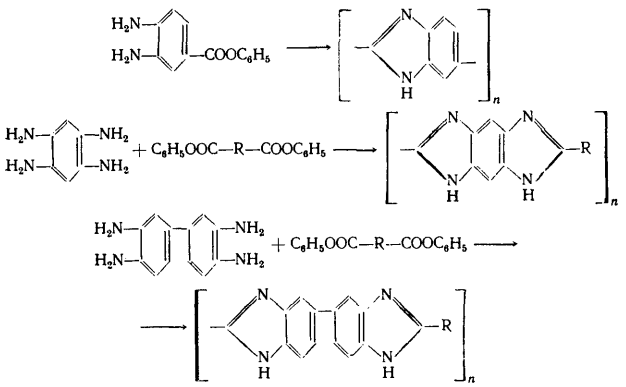
Imdividual representatives of the polyazoles—e.g. polyaminotriazoles and polythiazoles—were obtained long ago. Extraordinary interest in polyazoles as promising heat-resistant materials arose after 1959, when Brinker and Robinson, and later Marvel and his coworkers, published papers on the synthesis of polybenzimidazoles.

II. POLYBENZAZOLES

Polybenzazoles were first described by Brinker, Robinson, and Cameron [15,16], who obtained polybenzimidazoles based on biphenyl-3,3′,4,4′-tetra-amine and aliphatic dicarboxylic acids, and polybenzoxazoles based on *o*-hydroxyaminophenylalkanoic acids. The polybenzimidazoles obtained proved to be more stable than polyamides to the action of light and water. From this moment an intensive study began of the properties of polybenzazoles, in the first instance of polybenzimidazoles.

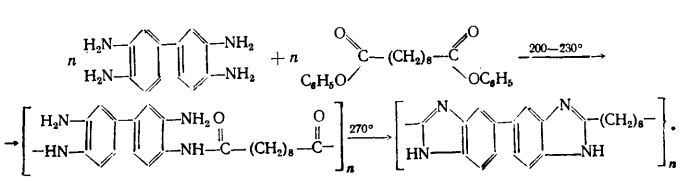
1. Methods of Preparing Polybenzazoles

Polybenzazoles have been obtained in various ways. Vogel and Marvel [17] found that aromatic polybenzimidazoles of high molecular weight can be prepared by the polycondensation of tetra-amines with diphenyl esters of dicarboxylic acids:

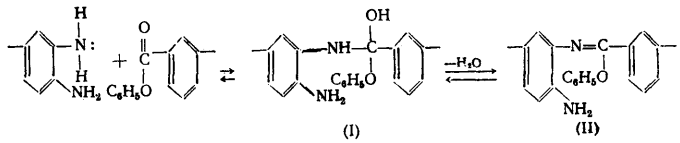


The general method developed for most of the polymers described consists in heating the reactants in the complete absence of oxygen, initially at 220–280°C, and then with the temperature raised to 400°C at 0.1 mmHg. The mass does not melt at this temperature, and the method consists essentially in solid-phase polycondensation. To obtain better results Marvel [8] proposes conducting the reaction in a rotating stainless-steel vessel, a few steel balls being placed in the mass of the polymer with the aims of stirring and improving heat transfer.

Korshak, Izyneev, and their coworkers [18-21] suggested, on the basis of elementary analysis and potentiometric titration of the reaction products, that the process in this case occurs in two stages, a polyaminoamide being formed in the first stage:

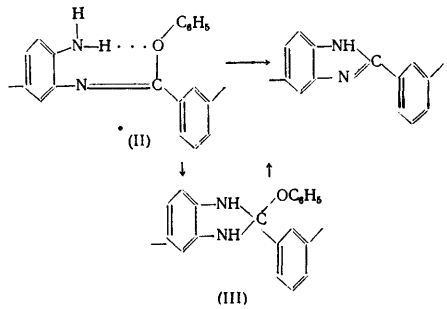


Wrasidlo and Levine [22] concluded from a detailed study of the formation of polybenzimidazoles that the reaction begins with nucleophilic attack by the amine on a carbonyl carbon atom in the diphenyl ester, an intermediate product of aldol type (I) being formed, which after dehydration gives a new intermediate product having the structure of a Schiff's base (II):



The intermediate product (II) can exhibit stereoisomerism, so that the *syn*-form can undergo intramolecular hydrogen bonding. According to these workers the formation of such hydrogen bonds promotes the intramolecular elimination of phenol and prevents the appearance of cross-linked and branched products.

The intermediate product (II) can probably exist in equilibrium with the benzimidazoline structure (III). The final process in the condensation is the elimination of phenol and formation of the polybenzimidazole:



Polybenzoxazoles of various structures have also been obtained by this process [23,24].

The overall mechanism of the formation of polybenzazoles is quite complicated. In the early stages, involving mainly the formation of polyamide units, the reaction is obviously reversible, and obeys the laws characteristic of equilibrium polycondensation. This applies in particular to the effect of excess of the reactants (Fig. 1) and to additions of monofunctional compounds. The chain termination which is usual for equilibrium polycondensation then occurs [25,26]. In the first stage, acidolysis and aminolysis of the polymer chains can obviously take place.

In the later stages, when the macromolecules contain mainly benzazole rings, the process loses its reversible character, since azole rings are exceptionally stable, as Korshak et al. [27] showed, and such polymers do not undergo degradative or exchange reactions.

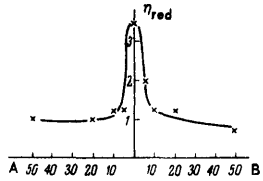
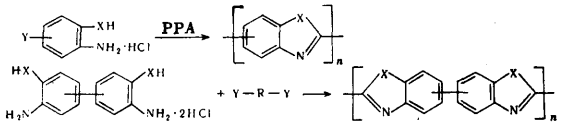
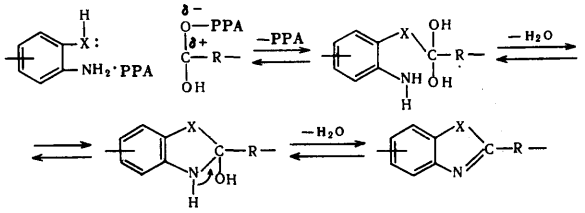


Fig. 1. Variation in reduced viscosity in formic-acid solution of poly-2,2′-octamethylene-5,5′-bibenzimidazolyl with excess (mole %) of the initial reactants:
A) biphenyl-3,3′,4,4′-tetra-amine;
B) diphenyl sebacate.

Iwakura and his coworkers[28-30] worked out a method for obtaining polybenzazoles in polyphosphoric acid (PPA). Polybenzimidazoles, polybenzoxazoles, and polybenzothiazoles of various structures were obtained according to the general scheme



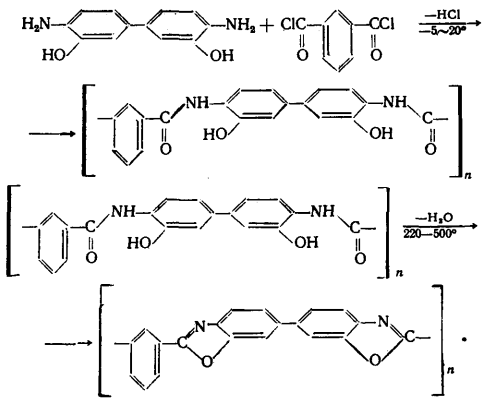
where X = NH.HCl, O, S and Y = COOH, $COOCH_3$, $CONH_2$, CN. An advantage of this method is the use of the more stable hydrochlorides instead of a tetra-amine, or an *oo'*-dihydroxy- or *oo'*-dimercapto-diamine. According to these workers[29] the benzazole polymers are formed by the reaction mechanism



where X = NH, O, S. The polyphosphoric acid enhances the reactivity of the electrophilic carbon atom in the carbonyl group, and acts as an efficient dehydrating agent.

Vogel and Marvel[17] showed that the method of interfacial polycondensation is not very suitable for the synthesis of polybenzimidazoles of high molecular weight: the polybenzimidazoles obtained had a reduced viscosity of only 0.09–0.22 dl g^{-1}.

A method which has been successfully applied to the synthesis of polybenzazoles consists in low-temperature polycondensation in a solvent followed by cyclisation of the resulting polymers at a high temperature. Kubota and Nakanishi[31], using this method, were the first to obtain completely aromatic polybenzoxazoles. In the first stage of the reaction a hydroxylated polyamide was obtained in dimethylacetamide solution, and its cyclisation yielded a polybenzoxazole:



Maksimov et al.[32] applied this method to the synthesis of polybenzothiazoles. A difficulty in this case was that the instability of the benzidinedithiol made necessary its use in the form of its hydrochloride, which was less active than the base under conditions of low-temperature polycondensation. The variation in the molecular weight during synthesis of the polymercaptopolyamide is illustrated in Fig. 2. The degree of polymerisation remains practically unchanged on cyclisation.

2. Polybenzimidazoles

Table 1 lists the properties of the polybenzimidazoles which have been described in the literature. It is seen that the properties of polybenzazoles depend fundamentally both on the structure of the original amine and on that of the acid component.

Vogel and Marvel[17] synthesised fully aromatic polybenzimidazoles from biphenyl-3,3',4,4'-tetra-amine and diphenyl esters of aromatic dicarboxylic acids. They showed that the phenyl esters gave with the tetra-amine polymers of higher molecular weight than when the acids or their methyl esters were used, since in the latter two cases polycondensation was accompanied by methylation of the amino-groups or decarboxylation as side-processes. The poly-2,2'-(*p*-phenylene)-5,5'-bibenzimidazolyl and poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazolyl which these workers obtained were highly thermostable, beginning to decompose in air only at temperatures above 500°C.

Plummer and Marvel[37] obtained polybenzimidazoles based on biphenyl-3,3',4,4'-tetra-amine and isomeric naphthalenedicarboxylic acids. The products were not so thermostable as the above polymers. These same workers showed that the condensation of diphenyl ferrocene-1,1'-dicarboxylate and of diphenyl imidazole-4,5-dicarboxylate with biphenyl-3,3',4,4'-tetra-amine yields polybenzimidazoles of fairly low reduced viscosity. The former of these polymers exhibited high thermal stability, while the latter was considerably less stable.

Dark brown or black polymers are obtained by the condensation of diphenyl fumarate or of a mixture of maleic anhydride and phenol with biphenyl-3,3',4,4'-tetra-amine. These polybenzimidazoles are to a considerable extent decomposed at 300°C.

Korshak, Izyneev, and their coworkers[18,19] obtained a poly-2,2'-octamethylene-5,5'-bibenzimidazolyl having a reduced viscosity in formic acid of 14 dl g^{-1}. Use of a vacuum of 0.01–0.001 mmHg in the second stage of the polycondensation contributed to the production of a polymer of high molecular weight and good mechanical properties.

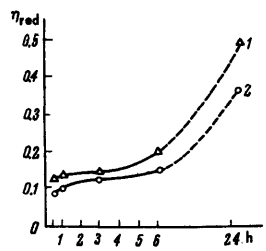


Fig. 2. Dependence of reduced viscosity of poly-3,3'-dimercaptobiphenyl-4,4'-yleneisophthalamide in H_2SO_4 on duration of reaction:
1) in the absence of pyridine; 2) in the presence of pyridine.

TABLE 1. Polybenzimidazoles.

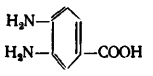
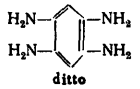
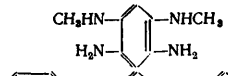
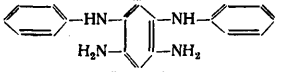
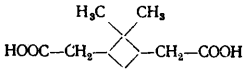
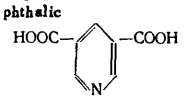
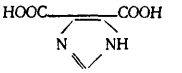
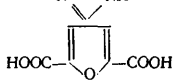
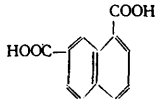
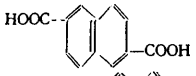
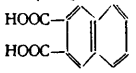
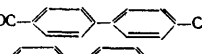
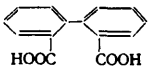
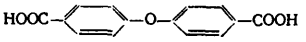
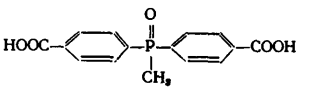
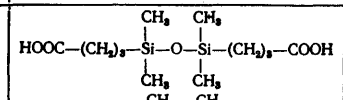
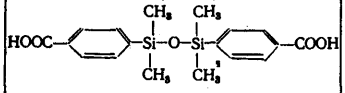
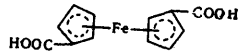
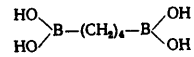
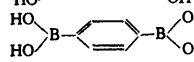
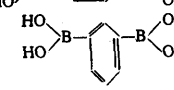
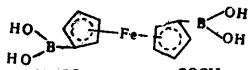
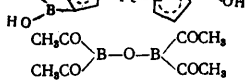
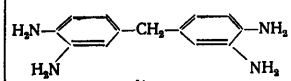
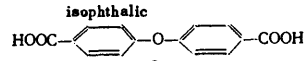
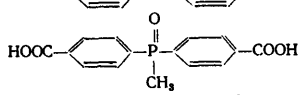
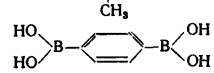
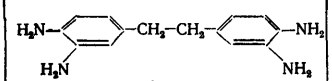
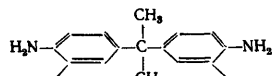
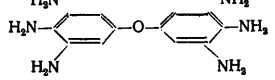
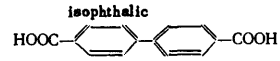
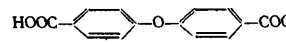
Polymer No.	Formula or name of initial components: bis-o-diamine	Formula or name of initial components: acid	Reduced viscosity in HCOOH, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	Structure*	Solubility** in: HCOOH	Solubility** in: DMF	Ref.
1	—		1.27; 1.95 (H_2SO_4)	>450	450	cr.	+	—	17, 30
2		adipic	2.51	490 decomp.	—	cr.	+	—	17
3	ditto	terephthalic	0.08 (H_2SO_4)	—	—	cr.	+	—	17
4	»	isophthalic	1.10	—	—	cr.	+	—	17
5		isophthalic	0.214 (H_2SO_4)	—	300	—			33
6		isophthalic	0.81	>500	500	—	+		34
7		oxalic	0.3 ***	—	300—400	—			35
8	ditto	malonic	0.3 ***	—	300—400	—			35
9	»	succinic	2.71	470 decomp.	300—400	—	+		34, 35
10	»	glutaric	1.19	420	300—400	—	+		34, 35
11	»	adipic	3.19	450 decomp.	300—400	am.	+	×	17, 35, 36
12	»	azelaic	0.94 (H_2SO_4)	—		am.			36
13	»	sebacic	1.4.9	470 decomp.	300—400	am.	+	+	15, 16.5, 17, 36
14	»	undecanedioic	0.73 (H_2SO_4)	—	—	am.			36
15	»	$HOOC-(CH_2)_{20}-COOH$	—	—	—	—	—		36
16	»	$HOOC-CH=CH-COOH$	0.07 (DMS)	250 decomp.	200	—	+		37
17	»		1.38	400 decomp.	—	—	+		17
18	»	terephthalic	1.00	—	500	cr.	+	—	17, 28
19	»	isophthalic	3.34	—	500	am.	+	×	17, 28
20	»	phthalic	5.01	—	500	—	+		34
21	»		1.48	—	—	cr.	+	×	17
22	»		0.16	550 decomp.	550	—	+		37
23	»		0.74	480 decomp.	—	cr.	+	+	17
24	»		2.70	—	—	am.	+	—	17
25	»		1.26 (H_2SO_4)	>550 decomp.	500—550	—	—	—	37
26	»		1.10	550 decomp.	350—450	—	+		37
27			0.61	400 decomp.	150—350	—			37
28	ditto		0.86 (H_2SO_4)	—	—	cr.	×	—	17
29	»		2.99	430	300—350	am.	+	+	17
30	»		1.14	460—470	—	cr.	+	×	38, 39
31	»		—	520	—	—	+	×	40

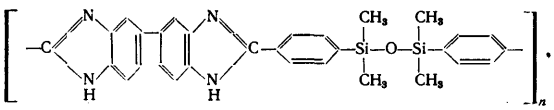
TABLE 1 (cont'd).

Polymer No.	Formula or name of initial components: bis-o-diamine	Formula or name of initial components: acid	Reduced viscosity in HCOOH, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	* Structure	Solubility** in: HCOOH	Solubility** in: DMF	Ref.
32	»		0.12 (C_2H_5OH)	215	—	am.	+	+	41
33	»		0.49 (DMS)	420—450	—	—	+	+	41
34	»		0.20	—	150—250	—			37
35	»	HOOC—$(CF_2)_3$—COOH	0.20 (DMS)	300 decomp.	220—230 (in argon)	—	+		37
36	»	HOOC—$(CF_2)_4$—COOH	—	—	240	—			40
37	»	HOOC—$(CF_2)_6$—COOH	0.17 (H_2SO_4)	300 decomp.	250	—	+		37
38	»		—	350—370	—	—	+		42
39	»		0.35 (DMS)	—	500—600	cr.			42, 43
40	»		0.15 (DMS)	>550	450—500	—		+	43
41	»		0.14 (DMA)	—	350—550	—		+	43
42	»		0.26***	does not melt	400—500	—			44
43		adipic	8.16	290—300; 200 glass point	460	lcr.	+	+	45
44	ditto	sebacic	4.62	260—270; 200 glass point	460	am.	+	—	45
45	»	terephthalic	1.06	400—410	500	am.	+	—	45
46	»	isophthalic	1.82	380—390	490	am.	+	—	45
47	»		1.58	350—370	500	am.	+	+	38
48	»		1.00	380—400	490	am.	+	+	38
49	»		0.16	500	500	cr.	+	+	38
50		malonic	0.63 (*m*-cresol)	—	—	am.			15
51	ditto	adipic	—	—	—	—			15
52		adipic	—	—	—	—			
53		sebacic	2.5	240—245	300—350	—	+	+	46
54	ditto	isophthalic	1.26	390	500	—	+	+	39, 46
55	»		0.7 (DMS)	—	—	—	+		39
56	»		0.5 (DMS)	—	—	—	+		39

* Abbreviations: cr. = crystalline; lcr. = low degree of crystallinity; am. = amorphous polymer.
** Symbols: + = soluble; × = partly soluble; – = insoluble; DMF = dimethylformamide.
*** Intrinsic viscosity.
**** DMA = dimethylacetamide; DMS = dimethyl sulphoxide.

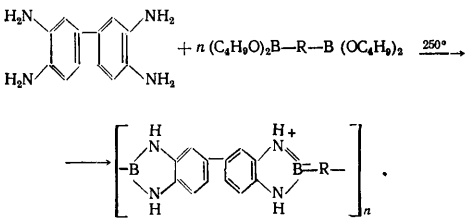
Plummer and Marvel[37] synthesised polybenzimidazoles based on biphenyl-3,3',4,4'-tetra-amine and perfluoropolymethylenedicarboxylic acids, in the hope that they would be more thermostable than polymers based on ordinary aliphatic acids. However, the fluorinated polybenzimidazoles already begin to decompose at 200–250°C. Other workers[47,48] have also referred to the low thermal stability of polyperfluoromethylenebenzimidazoles.

Mulvaney and Marvel[41] described the properties of a polybenzimidazole having the structure

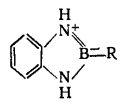


This polymer is less thermostable, possesses a higher solubility, and melts at a far lower temperature than aromatic polybenzimidazoles. The polymer begins to melt at 420–450°C, but even after being heated to 450°C it retains its solubility in dimethyl sulphoxide, dimethylformamide, and formic acid.

Mulvaney, Bloomfield, and Marvel[43], as well as Bamford and Fordham[42], obtained polybenzoborimidazolines from biphenyl-3,3′,4,4′-tetra-amine and the appropriate diboronic esters:



A cyclic molecule containing a boron atom

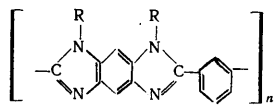


possesses a system of π-electrons, and its ultraviolet spectrum is similar to that of benzimidazole[49-51]. In view of their aromatic character these polymers are quite thermostable, the loss in weight in nitrogen at 450–500°C being ~10% for the polymer based on benzene-*p*-diboronic acid.

Polybenzazoles containing respectively oxygen and phosphorus in the main chain have been prepared and investigated. Polybenzimidazoles containing these elements have been described by Frunze et al.[38] and also by Foster and Marvel[39]. The introduction of oxygen improves the solubility and should probably improve the mechanical characteristics of polybenzazoles. Thus from biphenyl-3,3′,4,4′-tetra-amine and diphenyl oxy-*pp*′-dibenzoate a polymer has been obtained possessing a crystalline structure and soluble in sulphuric acid, formic acid, and dimethyl sulphoxide in the cold, and in dimethylformamide and tricresol on heating. The polymer obtained from diphenylmethane-3,3′,4,4′-tetra-amine and the same ester is soluble in dimethylformamide in the cold. A polybenzimidazole containing phosphorus, which has the interesting and important property of non-flammability, has been obtained by the interaction of diphenylmethanetetra-amine and diphenyl methyloxodiphenylphosphorane-*pp*′-dicarboxylate. When the polymer is introduced into the burner flame, it slowly smoulders and chars, but on withdrawal from the flame it is immediately extinguished. The self-quenching of this polymer is due to the presence of the phosphoryl group (phosphorus content 6.8%). An analogous phenomenon has been observed with phosphorus-containing polyamides[52].

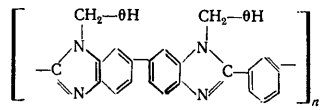
In all the preceding cases the properties—mainly the solubility—of the polybenzimidazoles were varied by a suitable choice of acid components having various structures. However, it is evident from the data which are cited that a considerable improvement in solubility was accompanied by a sharp fall in thermal stability. More recent work has shown that the properties of polybenzimidazoles can be modified, while adequate thermal stability is maintained, also by varying the structure of the initial amine, e.g. by introducing various substituents into the molecule of a fully aromatic tetra-amine, or by obtaining mixed polymers.

Marvel and his coworkers[33,34] prepared *N*-substituted polybenzimidazoles of general formula



where R = C_6H_5, CH_3. The phenylated polymer showed practically the same thermal stability as the analogous unsubstituted polybenzimidazole. The methylated polymer began to decompose in air at 300°C.

An *N*-substituted polybenzimidazole has recently been synthesised[53] having the structure

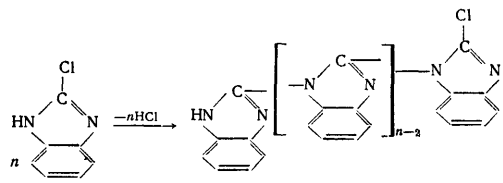


where θ represents



by reaction between the sodium salt of polybenzimidazole and 1-bromomethylcarborane. Polycarboranylmethylbenzimidazole loses only 25% of its weight when heated in air to 900°C.

By heating 2-chlorobenzimidazole at its melting point, Harrison and Ralph[54] obtained an insoluble high-melting polymer, which did not decompose up to 400°C:



Frunze et al.[45] have synthesised several polybenzimidazoles based on diphenylmethanetetra-amine and dicarboxylic acids. These polymers are yellow to brownish vitreous products, which soften between 260° and 400°C and possess a mainly amorphous structure. The ultraviolet spectra of these polybenzimidazoles[55] have absorption maxima close to those of model compounds, but exhibit some bathochromic and hypsochromic shifts, which were referred to also by Vogel and Marvel[17] when discussing fully aromatic polybenzimidazoles. The polybenzimidazoles based on diphenylmethanetetra-amine possess somewhat better solubility than the corresponding polymers based on benzidinediamine, while having approximately the same thermal stability.

Polybenzimidazoles have been described based on a tetra-amine containing an ether link between phenyl groups[39,46]. Korshak et al.[56] suggested preparing polybenzazoles containing various substituents on the central carbon atom of

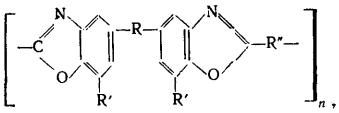
the initial amine. The resulting polymers were distinguished by better solubility.

Mixed polybenzimidazoles containing residues of two different dicarboxylic acids have been synthesised by Korshak and his coworkers[40,57]. The thermal stability of the mixed polybenzimidazoles is somewhat below that of the homopolymers, as is evident from Fig. 3, which shows the variation in the decomposition temperature with the composition of the initial mixture. Mixed polybenzimidazoles containing units of an aliphatic dicarboxylic acid decompose at lower temperatures (in the range 400–520°C) than do polybenzimidazoles synthesised solely from aromatic components. Thus the decomposition point of polybenzimidazoles obtained from biphenyl-3,3′,4,4′-tetra-amine and diphenyl isophthalate and terephthalate lies in the range 460–520°C.

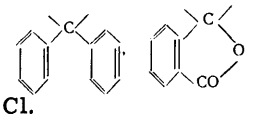
3. Polybenzoxazoles and Polybenzothiazoles

Great interest has recently been evinced in polybenzoxazoles and polybenzothiazoles (Table 2), analogues of polybenzimidazoles, since it has been supposed that they will show greater resistance than polybenzimidazoles to oxidative thermal degradation.

Several communications appeared almost simultaneously on the synthesis of polybenzoxazoles based on 4,4′-diaminobiphenyl-3,3′-diol[23,31,58]. It was noted that polybenzoxazoles are inferior to polybenzimidazoles in solubility. In order to improve the solubility of the former, Korshak et al.[24,60,61] synthesised polymers containing various substituents in the benzene ring of the benzoxazole, of general formula



where R = $C(CH_3)_2$, $C(CH_3)(C_6H_5)$, $C(C_6H_5)_2$,



and R′ = H, CH_3, Cl.

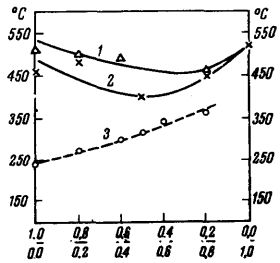


Fig. 3. Variation, with molar composition of mixed polybenzimidazoles based on biphenyl-3,3′,4,4′-tetra-amine, in:
1) decomposition temperature of polymers from sebacic and isophthalic acids;
2) decomposition temperature of polymers from terephthalic and isophthalic acids;
3) softening point of polymers from sebacic and isophthalic acids.

The resulting polymers, while possessing high thermal stability (loss in weight begins at 400–500°C when R″ represents an aromatic group), dissolve in a wide range of organic solvents—chloroform, tetrachloroethane, tricresol, benzyl alcohol, pyridine, dimethylformamide, etc.—except in the case of polymers containing halogen in the side-chain and with the central carbon atom forming part of a phthalidylidene group. Polymers in which R″ represents an aromatic radical pass into an infusible and insoluble state when heated to 450°C. Unfortunately, the authors do not discuss the effect of molecular weight on the solubility of the polybenzoxazoles obtained.

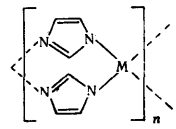
Polybenzothiazoles were first synthesised in 1962 by Kipriyanov and Mushkalo[63]. However, these workers merely obtained an oligomeric condensation product of 4-amino-3-mercaptobenzoic acid. Hergenrother et al.[62] suggested that polybenzothiazoles should be synthesised in two stages: in the first stage a precondensate of low molecular weight is formed in boiling diethylaniline solution, and this passes on further condensation in the solid phase into a polybenzothiazole of high molecular weight. Imai et al.[29,30] synthesised several new polybenzothiazoles and isomeric polybenzoxazoles by their method of polycondensation in polyphosphoric acid.

All the authors note the great stability to heat and thermal oxidation of the polybenzothiazoles, which, however, are soluble only in concentrated sulphuric acid.

III. POLYIMIDAZOLES

In the case of polyazoles not containing fused rings—in contrast to polybenzazoles, where until recently attention has been paid mainly to benzimidazole derivatives—most of the work has been done on the synthesis of polythiazoles, the first information on which appeared during the Second World War. Few papers have been concerned with the synthesis of polyimidazoles, and we have found none on that of polyoxazoles.

Brown and Aftergut[64] prepared polyimidazoles of general formula



where M is a bivalent metal. The products were insoluble in organic solvents, infusible, and quite thermostable, showing no loss in weight when heated in nitrogen to 500–575°C.

A polymer possessing semiconductor properties was obtained by the pyrolysis of 2,4,5-tri-iodoimidazole and 1,2,4,5-tetraiodoimidazole[65].

IV. POLYTHIAZOLES

Erlenmeyer and his coworkers[66,67] were the first to obtain polythiazoles, but they did not examine the properties of the products. Mulvaney and Marvel[68], and somewhat earlier some Japanese investigators[69], continued Erlenmeyer's work on the synthesis of polythiazoles. Several papers have appeared recently reporting detailed investigations of the properties of polymers of this type, information on which is given in Table 3.

TABLE 2. Polybenzoxazoles and polybenzothiazoles.

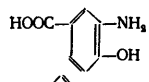
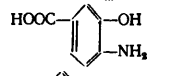
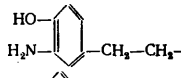
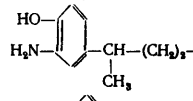
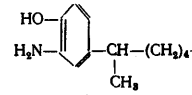
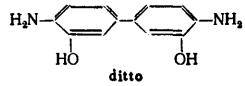
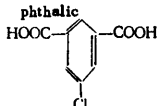
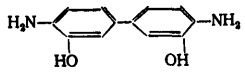
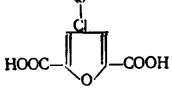
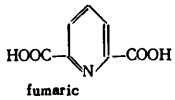
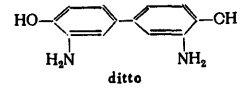
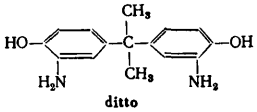
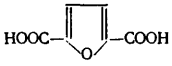
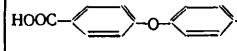
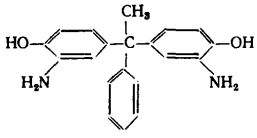
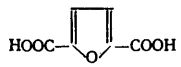
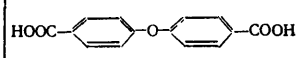
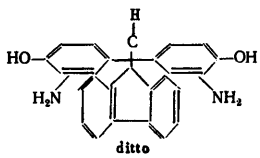
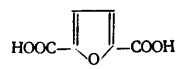
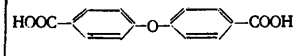
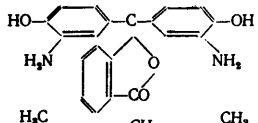
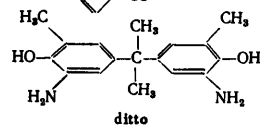
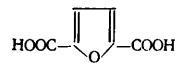
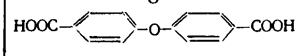
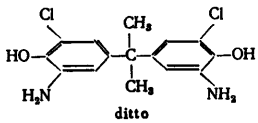
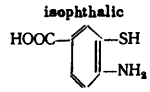
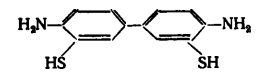
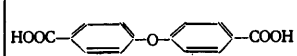
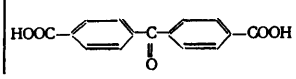
Polymer No.	Formula or name of initial components: bis-o-aminophenol or bis-o-aminothiol	Formula or name of initial components: acid	Reduced viscosity in H_2SO_4, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	Structure*	Solubility** in: HCOOH	Solubility** in: DMF	Solubility** in: other organic solvents	Ref.
1	—		2.21	—	450	am.	—	—		30
2	—		1.40	—	500	cr.	—	—		30
3	—		0.4—1.5 (*m*-cresol)***	—	—	—				16
4	—		—	—	—	—				16
5	—		—	—	—	—				16
6		sebacic	0.40	250° (softens slightly)	300°	—	+	am.	*m*-cresol	16, 29
7	ditto	terephthalic	1.36	—	500—550	am.	—	—		29
8	»	isophthalic	1.50	—	500	am.	—	—		29
9	»	phthalic	0.93	—	—	—	—			23
10	»		0.20	—	—	—			H_2SO_4 (75%)	23
11			—	—	—	—				59
12	ditto		—	—	—	—				59
13	»	fumaric	—	—	—	—				59
14		sebacic	1.34	250° (softens slightly)	300	am.				29
15	ditto	terephthalic	1.60	—	—	am.	—	—		29
16	»	isophthalic	2.09	—	450—500	am.	—	—		29
17		adipic	0.32	—	420	am.	×	+	chloroform, THF***, pyridine	60, 61
18	ditto	sebacic	0.38	—	420	am.	—	+	ditto	24
19	»	$HOOC-CH_2-O-CH_2-COOH$	0.18	—	250	am.	×	×		60, 61
20	»	terephthalic	0.16	—	510	lcr.	+	+	chloroform	60, 61
21	»	isophthalic	0.15	—	500	am.	+	+	chloroform, THF, pyridine	60, 61
22	»		0.12	—	450	am.	—	+	ditto	60, 61
23	»		0.21	—	420	am.	—	—	»	60, 61
24		adipic	0.26 (cresol)	—	350	am.	×	+	chloroform, THF, pyridine	60, 61
25	ditto	sebacic	0.3 (cresol)	—	350	—	+	+	ditto	60, 61
26	»	$HOOC-CH_2-O-CH_2-COOH$	0.22 (cresol)	—	200	—	—	+		60, 61
27	»	terephthalic	0.12 (cresol)	—	300	—	—	—	»	60, 61
28	»	isophthalic	0.15 (cresol)	—	320	—	—	+	»	60, 61

TABLE 2 (cont'd).

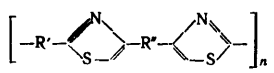
Polymer No.	Formula or name of initial components: bis-o-aminophenol or bis-o-aminothiol	Formula or name of initial components: acid	Reduced viscosity in H_2SO_4, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	* Structure	Solubility** in: HCOOH	Solubility** in: DMF	Solubility** in: other organic solvents	Ref.
29	» »		0.11 (cresol)	—	320	—	—	+	» »	60, 61
30	» »		0.12 (cresol)	—	350	—	—	+	» »	60, 61
31		adipic	0.28 (cresol)	—	400	am.	—	—	chloroform, THF	60, 61
32	ditto	sebacic	0.27 (cresol)	—	400	lcr.	—	×	chloroform, THF, pyridine	60, 61
33	»	HOOC–CH_2–O–CH_2–COOH	0.25 (cresol)	—	300	am.	—	—		60, 61
34	»	terephthalic	0.15 (cresol)	—	400	am.	—	×	chloroform, THF, pyridine	60, 61
35	»	isophthalic	0.18 (cresol)	—	400	am.	—	×	ditto	60, 61
36	»		0.15 (cresol)	—	300	am.	—	+	»	60, 61
37	» »		0.15 (cresol)	—	350	am.	—	×	»	60, 61
38		sebacic	0.17	—	330	am.	—	—		24
39		adipic	0.32	—	400	lcr.	+	+	chloroform, THF, pyridine	60, 61
40	ditto	sebacic	0.34	—	300	lcr.	+	+	ditto	60, 61
41	»	HOOC–CH_2–O–CH_2–COOH	—	—	200	am.	×	×		60, 61
42	»	terephthalic	0.17 ($CHCl_3$)	—	400	am.	—	×	»	60, 61
43	»	isophthalic	0.18 ($CHCl_3$)	—	400	am.	—	×	»	60, 61
44	»		0.15 ($CHCl_3$)	—	300	am.	—	+	»	60, 61
45	»		0.2 ($CHCl_3$)	—	300	am.	—	+	»	60, 61
46		sebacic	—	—	220	lcr.	—	—		60, 61
47	ditto	isophthalic	—	—	180	am.	—	—		60, 61
48	»		2.03 (H_2SO_4)	>450	500	am.				30
49		sebacic	0.31 (H_2SO_4)	—	300	cr.	+		cresol	29
50	ditto	terephthalic	1.02 (H_2SO_4)	—	550	am.	—	—		29, 62
51	»	isophthalic	0.43 (H_2SO_4)	466,527, 910(glass point)	600	am.	—	—		29, 62
52	»	HOOC–	0.62 (H_2SO_4)	288 (glass point)	—	—				62
53	»	HOOC–	0.36 (H_2SO_4)	—	—	—				62

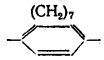
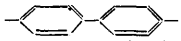
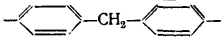
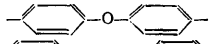
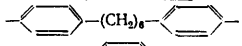
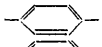
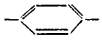
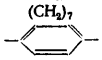
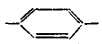
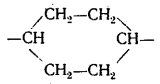
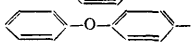
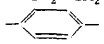
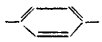
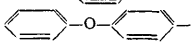
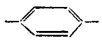
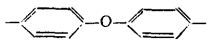
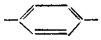
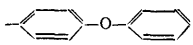
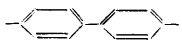
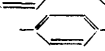
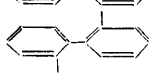
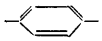
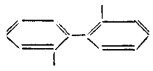
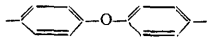
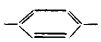
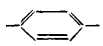
* Abbreviations: cr. = crystalline; lcr. = low degree of crystallinity; am. = amorphous polymer.

** Symbols: + = soluble; × = partly soluble; – = insoluble; DMF = dimethylformamide.

*** Intrinsic viscosity.

**** THF = tetrahydrofuran.

TABLE 3. Polythiazoles of general formula 

Polymer No.	R′	R″	Reduced viscosity in H_2SO_4, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in N_2	Ref.
1	—	—	—	—	—	66
2	—	$(CH_2)_4$	—	—	—	66
3	—	$(CH_2)_7$	—	—	—	66
4	—		0.23	>520	500—700	70, 71
5	—		0.24	>520	400 (20%)	80
6	—		0.47	>520	400 (20%)	70
7	—		0.38	>520	525 (40%)	70
8	—		0.40	440—448		70
9	CH_2		0.24	500	500 *	71
10	$(CH_2)_2$		0.87 (HCOOH)	164—265	290 *	71
11	$(CH_2)_4$	—	—	—	—	66
12	ditto	$(CH_2)_4$	—	—	—	66
13	»	$(CH_2)_7$	—	—	—	66
14	»		3.96 (HCOOH)	164—265	487—490 *	67, 68, 71
15	$(CH_2)_7$	—	—	—	—	66
16	ditto	$(CH_2)_4$	—	—	—	66
17	»	$(CH_2)_7$	—	—	—	66
18	$(CH_2)_8$		1.78 (HCOOH)	164—265	487—490 *	71
19			1.00	226	440 (20%)	72
20			0.30	>500	500 *	67, 68, 71
21	ditto		0.22	>500	500 *	71, 72
22			0.17	>500	500 *	68, 71
23	ditto		0.49	340	450 (20%)	71, 72
24			0.13	>500	500 *	71
25	ditto		0.33	>500	500 *	71
26			0.19	>500	500 *	71
27			0.52	164—265	500 *	71
28			0.59 (HCOOH)	164—265	500 *	71
29	$(CH_2)_4$; 		0.34	240		71

* In air.

Longone and Un[70] obtained polybenzothiazoles from a dithioamide and aromatic and mixed aliphatic and aromatic bis-α-bromoketones. All the polymers obtained were insoluble in organic solvents, including dimethyl sulphoxide, dimethylacetamide, and formic acid, but readily dissolved in concentrated sulphuric acid, and were infusible highly crystalline substances of high molecular weight. These polymers possess excellent thermal stability, but probably will not find wide practical application owing to difficulties arising in processing and their poor mechanical characteristics.

The most thorough study has been made by Sheehan el at.[71] They prepared a series of polythiazoles by the reaction

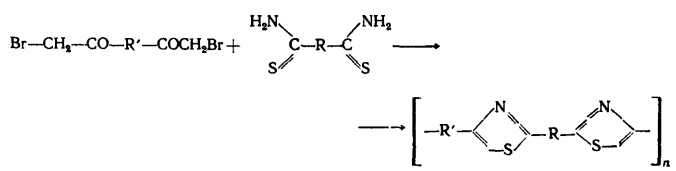


TABLE 4. Polypyrazoles.

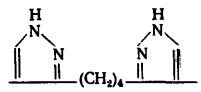
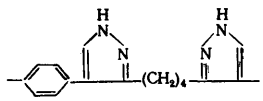
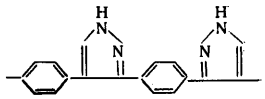
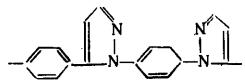
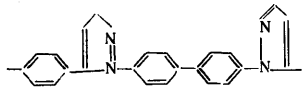
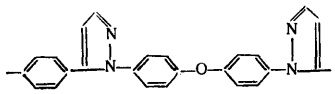
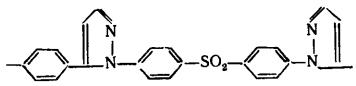
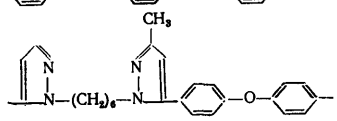
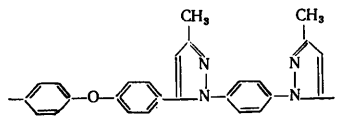
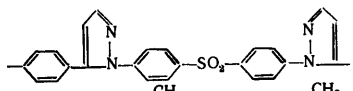
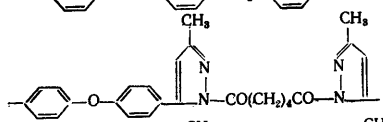
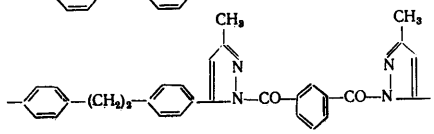
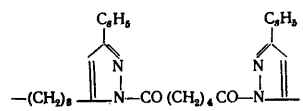
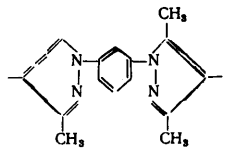
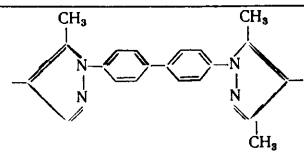
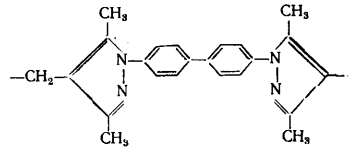
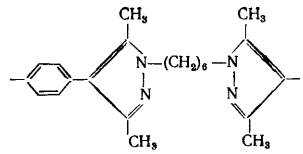
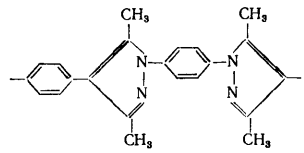
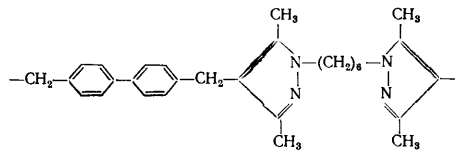
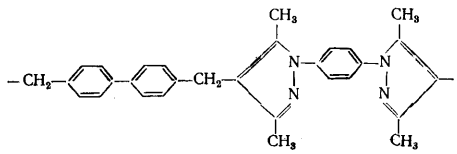
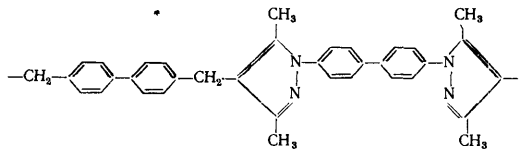
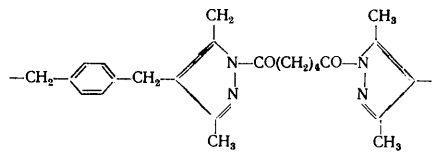
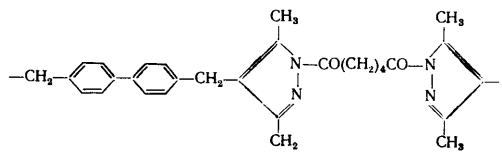
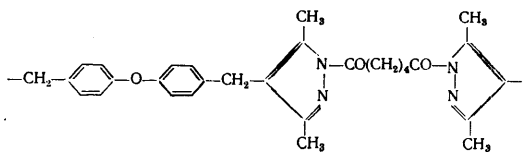
Polymer No.	Structural unit	Reduced viscosity in cresol, dl g^{-1}	Temperature, °C		Ref.
			melting	start of decomp. in air	
1		0.2	350—374	—	78
2		0.3	440	—	78
3		0.24	>500	—	78
4		0.13 (HCOOH)	—	600 (20%)	77
5		—	—	—	77
6		—	—	—	77
7		—	—	—	77
8		0.12	118—124	—	78
9		0.09	122—140	—	78
10		0.14	218—225	—	74
11		0.10	210—220	—	74
12		0.12	260—280	—	74
13		0.08	100—120	—	74
14		1.5—2.0 (HCOOH)		450 (in nitrogen)	76

TABLE 4 (cont'd).

Polymer No.	Structural unit	Reduced viscosity in cresol, dl g^{-1}	Temperature, °C: melting	Temperature, °C: start of decomp. in air	Ref.
15		0.54; 0.70 (H_2SO_4)	—	500	80
16		—	—	350	80
17		0.25	156—174	—	79
18		0.15	262—265	—	79
19		0.08	141—146	—	79
20		0.09	120—132	—	79
21		0.19	180—190	—	80
22		0.12	230—300	—	81
23		0.1	228—230	—	81
24		0.15	245—256	—	81

and concluded that only those polymers which had low heat-resistance possessed satisfactory mechanical properties. Other workers hold the same view[72].

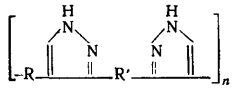
An interesting result of the work of Sheehan et al. is the preparation of polythiazoles based on *oo'*-bisbromoacetylbiphenyl, possessing satisfactory mechanical properties and high thermal stability (up to 500°C). They also obtained[73] a fibre-forming polythiazole.

The introduction of side-chains—methyl and carboxyl substituents—into the thiazole ring produces no appreciable improvement in the properties of the polythiazoles[71].

V. POLYPYRAZOLES

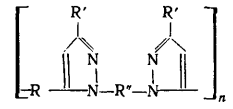
In 1963 Korshak et al.[74] described for the first time the preparation of polypyrazoles by the reaction of bis-β-diketones with dihydrazides of dicarboxylic acids. A later paper by Korshak et al.[75] has further elaborated methods for the synthesis of polypyrazoles. American workers have also published papers on the synthesis of polypyrazoles[76,77]. According to their structure these polymers can be divided into three main types.

Polypyrazoles of general formula



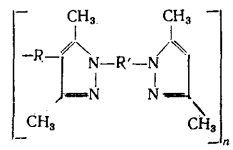
have been obtained by the method of Korshak et al.[78] from bisdiazo-compounds and *p*-diethynylbenzene or butadiyne. They were high-melting products of molecular weight around 10 000, soluble in dimethylformamide and cresol. Unfortunately, the authors gave no indication of the thermal stability of these polymers.

Polypyrazoles of general formula



have been obtained by the interaction of bis-β-diketones of the type $R'COCH_2CORCOCH_2COR'$ with various dihydrazines or dihydrazides[74,77,79-81]. In this case the reaction goes in two stages, involving the initial formation of a polyhydrazone, which then cyclises to produce the polypyrazole. The first stage can be conducted in a solvent[77,79]. With dihydrazides of dicarboxylic acids[74] polypyrazoles are obtained which can be regarded formally as *N*-substituted polyamides.

A third group of polypyrazoles corresponds to the general formula

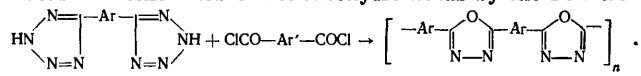


The heat-resistance of polymers of this type is lower than that of polypyrazoles containing no alkyl substituents, but their thermal stability must be expected to be higher owing to the absence of a mobile hydrogen atom in the pyrazole ring.

VI. POLYOXADIAZOLES

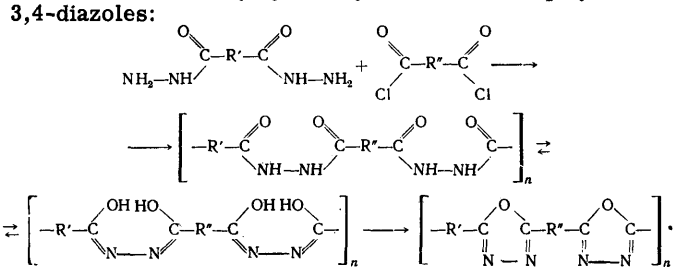
Most of the work on the synthesis of polyoxadiazoles has been done on the preparation of polyoxa-3,4-diazoles. Fully aromatic polyoxa-3,4-diazoles possess not only excellent resistance to heat, chemicals, and light but also good mechanical properties, which enables films and fibres to be made from them. Table 5 gives some properties of polyoxa-3,4-diazoles obtained by various methods.

Abshire and Marvel[86], elaborating the method of Sauer et al.,[87] prepared polyoxa-3,4-diazoles from bistetrazoles and chlorides of dicarboxylic acids by the reaction



However, the molecular weights of polymers obtained by this method were not very high.

Frazer and Wallenberger[85,88,89] proposed a two-stage method for the synthesis of polyoxadiazoles. Under conditions of low-temperature polycondensation in the first stage macromolecular polyhydrazides are obtained, which are then converted by cyclodehydration into the polyoxa-3,4-diazoles:



Films and fibres can be obtained from the melt only with those polyoxadiazoles which fuse below 350°C. Aromatic polyoxadiazoles which melt above this temperature are processed at the polyhydrazide stage, and cyclisation is accomplished in the finished goods.

A two-stage synthesis of polyoxa-3,4-diazoles has been used also by Korshak et al.[84,90,91], who obtained a polyoxadiazole containing ether links which was a promising material for the manufacture of a heat-resistant fibre.

It has also been proposed to obtain polyoxa-3,4-diazoles in the melt, starting from the corresponding polyhydrazides[82]. However, this method is restricted to a narrow range of aliphatic polyoxadiazoles.

Iwakura et al.[83] synthesised polyphenyleneoxa-3,4-diazoles in polyphosphoric acid or oleum solution, the latter solvent giving polymers of higher molecular weight. Soviet workers have also reported[92] the preparation of polyoxa-3,4-diazoles in oleum.

A paper has appeared recently[93] on the synthesis of polyoxa-2,4-diazoles by the series of reactions

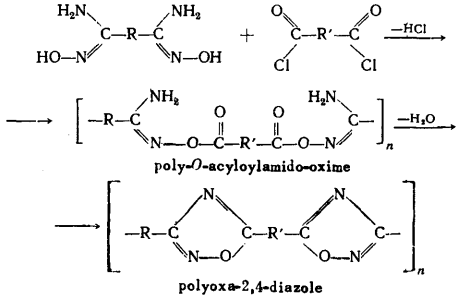
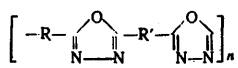
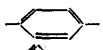
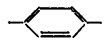
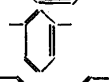
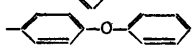
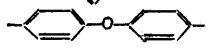
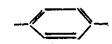
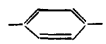
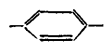
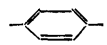
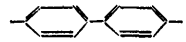
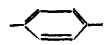
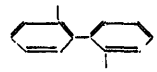
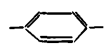
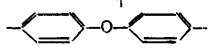
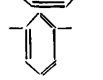
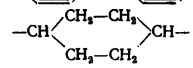
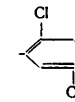
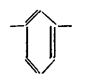
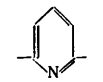
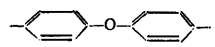
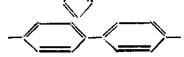
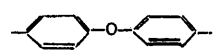


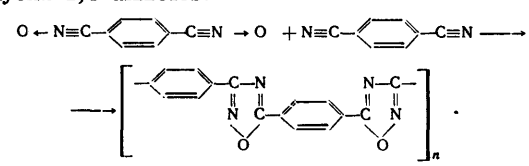
TABLE 5. Oxa-3,4-diazoles of general formula 

Polymer No.	R	R'	Reduced viscosity in H_2SO_4, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	Ref.
1	$(CH_2)_8$	$(CH_2)_8$	0.45 * (cresol)	90—110	300	82
2	$(CH_2)_9$	$(CH_2)_9$	0.40 * (cresol)	66—82	300	82
3	$(CH_2)_{10}$	$(CH_2)_{10}$	0.41 * (cresol)	64—100	300	82
4			3.7	—	450	83
5			2.2	—	450	83
6			0.95	370	430	84
7	—		0.60	—	—	85
8	—		0.1	—	—	85
9	$(CH_2)_4$	$(CH_2)_7$	0.3	—	—	85
10	$(CH_2)_4$		0.50	—	—	85
11	$(CH_2)_7$		0.15	—	—	86
12	$(CH_2)_8$		0.4	—	—	85
13			0.5	—	450	85
14			0.10	—	—	86
15			0.05	—	—	86
16			0.09	—	—	86
17			1.1	430	470	86
18			0.2	—	—	86
19			0.2	—	—	86
20			0.6	—	—	85
21			0.61	380	430	84
22			0.75	440	460	84

* Intrinsic viscosity.

However, the thermal stability of such a polymer is considerably poorer than that of the polyoxa-3,4-diazole of analogous structure.

Overberger and Fujimoto[94] obtained polymers containing oxazole *N*-oxide groups by the polymerisation of terephthalonitrile oxide. The copolymerisation of terephthalonitrile oxide with terephthalonitrile leads to the formation of polyoxa-2,4-diazoles:

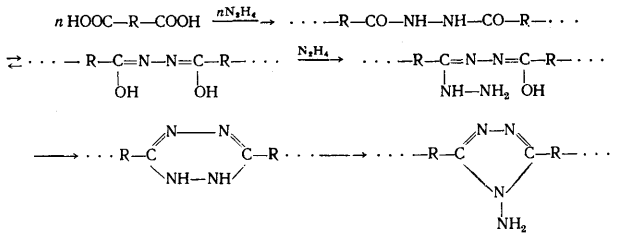


VII. POLYTRIAZOLES

There is a large published literature, consisting mainly of patents, on the synthesis of aliphatic polytriazoles.

In 1941 Prichard[95] described fibre-forming polymers obtained from dihydrazides of dicarboxylic acids. He was the first to point out the difference between the two reactions taking place on heating a salt of hydrazine and a dicarboxylic acid (equimolecular proportions of hydrazine and the acid) and on heating a dihydrazide of a dicarboxylic acid, i.e. 2 moles of hydrazine and 1 mole of the acid. Prichard suggested that in the latter case the polymer contains 1,2,4-triazole-4-amine rings. His work served as a basis for several investigations in this field, conducted during recent years by Moncrieff, Fisher, and their coworkers in England, and by Korshak, Chelnokova, and Shkolina in the USSR.

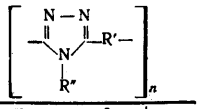
In the view of Fisher et al.[96] the formation of poly-1,2,4-triazole-4-amine can be represented by the scheme

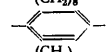
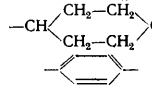
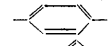
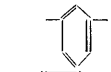
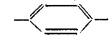


Polyaminotriazoles will not be discussed in detail in the present review, since the synthesis, the properties, and the applications of these polymers have been subjects of detailed consideration in the literature[97-100].

Table 6 gives the chief properties of homopolytriazoles of various structures. Korshak et al.[27] obtained also mixed poly-1,2,4-triazole-4-amines, which exhibit rather better solubility than do the homopolymers. These workers found that polyaminotriazoles are not subject to degradative exchange processes due to interchain exchange reactions.

TABLE 6. Polytriazoles of general formula



Polymer No.	R′	R″	Reduced viscosity in cresol, dl g^{-1}	Temperature, °C: melting	Temperature, °C: start of decomp. in N_2	Ref.
1	$(CH_2)_4$	—H	>0,5	220		101
2	$(CH_2)_8$	—H		180—240		102
3		—H				103
4	$(CH_2)_2$	—NH_2		360		96
5	$(CH_2)_3$	—NH_2	0.62	137—141		99
6	$(CH_2)_4$	—NH_2		300		104
7	$(CH_2)_5$	—NH_2		260		104
8	$(CH_2)_6$	—NH_2	0,4	300—315		99
9	$(CH_2)_7$	—NH_2	0,58	248—225		99
10	$(CH_2)_8$	—NH_2	0,91	225—260		99
11	$(CH_2)_9$	—NH_2				105
12	$(CH_2)_{10}$	—NH_2		245		105
13	$(CH_2)_{18}$	—NH_2	0,72	225—228	—	99
14	$(CH_2)_{20}$	—NH_2	0,83	210—213	—	99
15	$(CH_2)_2S(CH_2)_3$	—NH_2	—	150—155	—	106
16	$(CH_2)_4S(CH_2)_4$	—NH_2	—	160—165	—	106
17	$(CH_2)_5S(CH_2)_5$	—NH_2	—	206—208	—	106
18	$(CH_2)_2SO_2(CH_2)_3$	—NH_2	—	208—210	—	95, 106
19	$(CH_2)_4SO_2(CH_2)_4$	—NH_2	—	258—260	—	95, 106
20	$(CH_2)_5SO_2(CH_2)_5$	—NH_2	—	220—225	—	96, 106
21	$(CH_2)_2O(CH_2)_nO(CH_2)_2$	—NH_2	—	oil	—	107
22		—NH_2	—	—	—	108
23		—NH_2	—	—	—	108
24		C_6H_5	2.0 (HCOOH)	290—310	512	109
25		C_6H_5	2.0 (HCOOH)	240—250	512	109

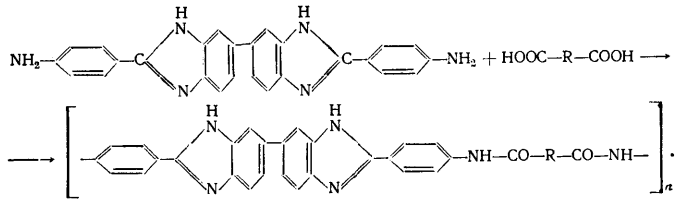
VIII. COPOLYMERS WITH AZOLE RINGS

Copolymers containing azole rings which have been described in the literature can be divided into two groups—cyclolinear copolymers, e.g. polyamides or polyesters containing benzimidazole rings, and cyclic copolymers, e.g. copolymers containing benzimidazole and pyromellitimide rings in the chain.

In copolymers of the first group several workers wished to combine the thermal stability characteristic of polyazoles with adequate solubility and other valuable properties inherent in linear polymers (polyamides, polyesters, etc.). However, the introduction of polyamide and polyester segments produced a substantial diminution in the thermal stability of the copolymers.

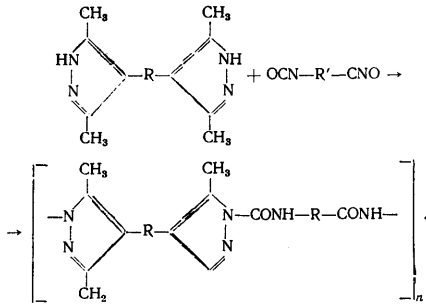
Korshak et al.[110,111] obtained aliphatic poly(amidobenzimidazoles) from diphenyl sebacate, biphenyl-3,3′,4,4′-tetra-amine or diphenylmethane-3,3′,4,4′-tetra-amine, and hexamethylenediamine. The melting point of the copolymers varied with the relative proportions of the initial diamine and the tetra-amine, passing through a minimum at 164°C in the case of biphenyl-3,3′,4,4′-tetra-amine. Increase in the polyamide content is accompanied by an increase in the crystallinity of the copolymers. The synthesis of benzimidazole polyesters from biphenyl-3,3′,4,4′-tetra-amine, hexane-1,6-diol, and diphenyl sebacate is accompanied by secondary reactions, which impair the properties of the final copolymer[111].

Iwakura et al.[112] described a series of polyamides obtained in polyphosphoric acid from dicarboxylic acids and a diamine containing benzimidazole rings:



The polyamide based on sebacic acid begins to decompose in air at 250°C whereas those based on aromatic dicarboxylic acids begin to decompose above 400°C.

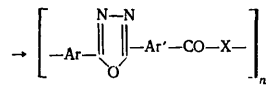
Polyamides containing pyrazole rings were obtained by Korshak et al.[79] by the reaction of dipyrazoles with hexamethylene and methylphenylene di-isocyanates:



These polymers possess viscoelastic properties over the range 200–300°C. They can be regarded as *N*-substituted polyureas. As Fedotova et al.[113] showed, the latter are not very heat-resistant and are amorphous polymers.

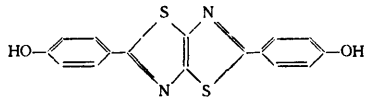
The synthesis of aliphatic polyamides containing triazole rings has been described in several patents and has been reflected in a corresponding review literature[97–100]. Block copolymers of ε-caprolactam and polytriazoles were prepared by Iwakura et al.[101] and later by Grekov et al.[114]

Aromatic polyamides and polyesters of regular structure containing oxadiazole rings have been obtained[104,115] via the corresponding polyhydrazides:



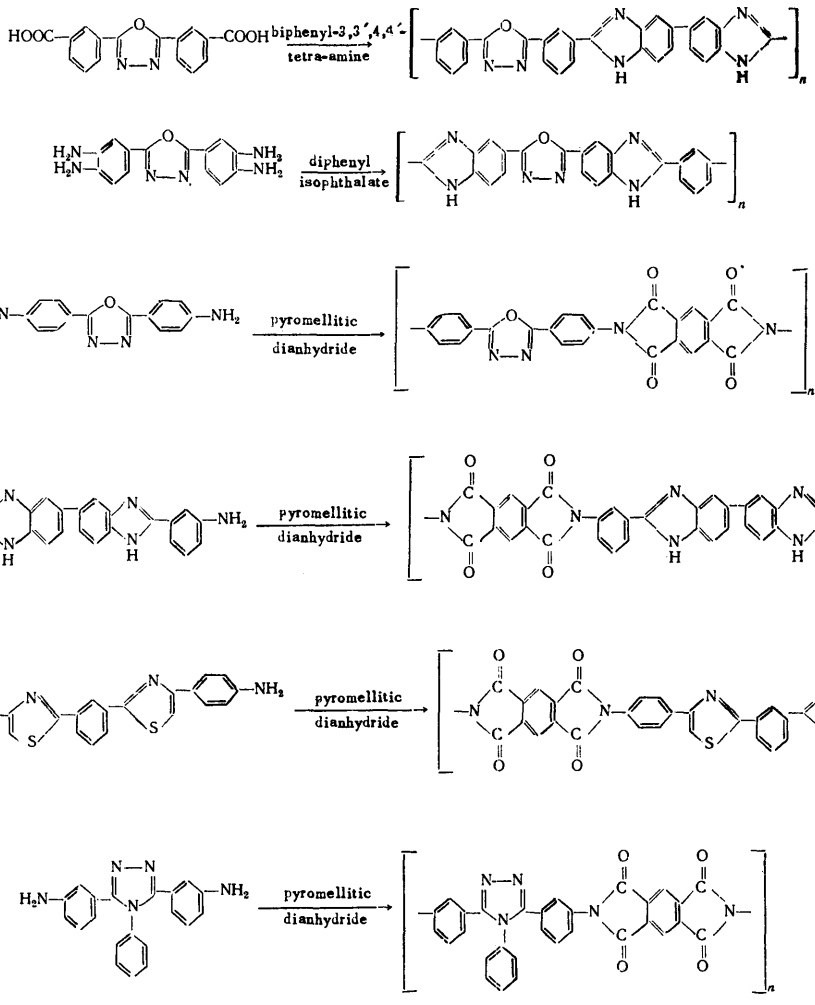
where X = NH or O. The polyamides and the polyesters softened over the ranges 400–470° and 300–400°C respectively.

Fox[116] accomplished the synthesis of various polyesters containing thiazolo[5,4-*d*]thiazole rings using a bisphenol having the structure



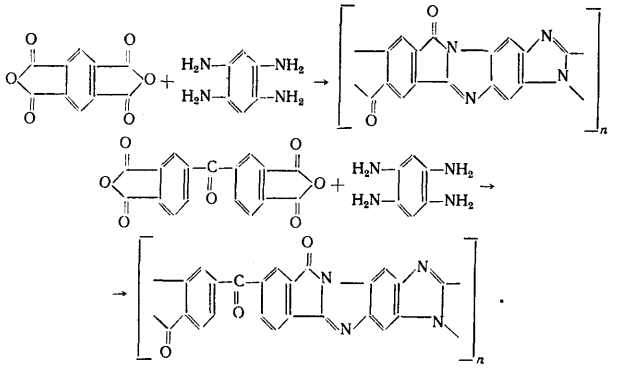
as starting material. When such a bisphenol is treated with carbonyl chloride or a bischloroformate, polycarbonates are produced, whereas treatment with chlorides of aliphatic dicarboxylic acids yields polyesters.

It is probable that the preparation of copolymers of the second group, containing different rings in the chain, will be more effective in preserving the thermal stability of the polyazoles. Unfortunately, very little work has been done in this field, so that it is difficult to reach final conclusions. However, a paper by Preston and Black[117] already substantiates this hypothesis. These workers prepared heterocyclic copolymers of ordered structure, the synthesis of which can be represented schematically as:



These copolymers are extremely thermostable, beginning to decompose in an inert atmosphere at 500–550°C. The authors did not examine other properties of the copolymers.

Adrova [118] reported the synthesis of copolymers containing benzimidazole and benzophosphorimidazoline rings. In the second group of copolymers can be included also the polyimidazopyrolones (polybenzimidazolimides, pyrrones) obtained [5] from aromatic tetra-amines and aromatic dianhydrides:



However, the properties of such polymers are influenced predominantly by the ladderlike or partly ladderlike structure.

IX. GENERAL PROPERTIES OF POLYAZOLES

At the present time the study of polyazoles has been concerned mainly with developing the synthesis of polymers having sufficiently high molecular weights, and considerably less attention has been paid to the properties of these polymers.

1. Chemical Properties

(a) Hydrolytic stability. Polyazoles are characterised by excellent resistance to hydrolysis, as a consequence of the presence of a stable aromatic heterocycle in the macromolecule. There are indications of hydrolytic stability and resistance to the action of acids and alkalis in such polymers as polybenzimidazoles [17,20], polybenzothiazoles and polybenzoxazoles [29], polyoxadiazoles [85], polythiazoles [71], aliphatic polyaminotriazoles [98,99], and polyphenyltriazoles [109].

Vogel and Marvel [17] showed that heating poly-2,2′-(*m*-phenylene)-5,5′-bibenzimidazolyl in 70% sulphuric acid produces only a slight diminution in the reduced viscosity. There is practically no hydrolysis when this polymer is boiled in 25% alkali solution for 10 h. Imai et al. [29] made an analogous investigation on polybenzoxazoles and polybenzothiazoles (Table 7). They found that polybenzoxazoles were less resistant to hydrolysis than were polybenzothiazoles, while the latter were less resistant than the corresponding polybenzimidazoles.

The chemical resistance of the polybenzimidazole based on biphenyl-3,3′,4,4′-tetra-amine and sebacic acid has been examined in some detail [20]. It is seen from Table 8 that no significant decrease in the weight of the specimens is produced by either hydrochloric acid or alkali. This indicates that the polymer is stable to acid and alkaline hydrolysis.

TABLE 7. Change in reduced viscosity of polymers as a result of hydrolysis in 5 *N* KOH or 10 *N* H_2SO_4 at 120°C for 5 h.

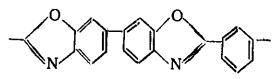
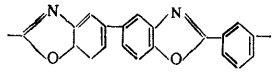
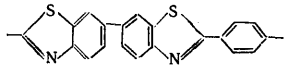
Structural unit	Hydrolysis		
	before	acid	alkaline
	1.50	0.44	0.76
	2.09	0.32	1.01
	1,02	0.61	0.97

TABLE 8. Chemical resistance of poly-2,2′-octamethylene-5,5′-bibenzimidazolyl.

Reagent	Concn. of reagent, %	Conditions		Initial polymer		Polymer after degradation	
		temp., °C	time, h	wt., g	η_{red} in HCOOH	wt., g	η_{red} in HCOOH
HCOOH	90	65	3	—	3.62	—	3.54
HCOOH	90	65	10	—	3.62	—	3.28
HCOOH	90	100	3	—	3.62	—	3.46
HCOOH	90	100	10	—	3.62	—	3.78
HCl	38	180	3	0,25	4.42	0.27	3.16
HCl	38	180	3	0.21	4.32	0.25	2.90
KOH	30	100	10	0,50	3.50	0.50	3.62
$HOOC(CH_2)_8COOH$	100	250	3	—	3.50	—	0.86
$H_2N(CH_2)_6NH_2$	100	190	3	—	3.50	—	2.88

Among all the polyazoles only the polybenzoborimidazolines [43,44] have proved to be unstable to hydrolysis, owing to the peculiarity of the borazole ring. With the polymer obtained from biphenyl-3,3′,4,4′-tetra-amine and tetra-acetyl diborate, for example, the intrinsic viscosity decreased to almost one-third after keeping over water in a desiccator for a week.

The results on the hydrolytic stability of the polyazoles show that it is determined primarily by the nature of the azole ring in the polymer.

(b) Resistance to other chemical reagents. Korshak et al. [27], in a study of polyaminotriazoles, referred to the exceptional stability of the azole ring towards various degradative agents. When two different polyaminotriazoles were heated together for a long time, no exchange reactions were detected, such as are characteristic of other classes of heterochain polymers [119–121].

The solubility of polyazoles in a narrow range of solvents (predominantly of polar type) governs their resistance to oils and organic solvents, but the literature contains no actual papers on this.

Copolymers of polyazoles of the first group will probably have considerably poorer chemical stability than have polyazoles or copolymers of polyazoles of the second group. Thus polyesters containing oxadiazole rings, unlike polyoxadiazoles, are decomposed by the action of sulphuric acid [122].

(c) Stability to heat and oxidation. The thermal stability of polyazoles has been assessed by the

method of thermogravimetric analysis. Although certain differences are possible between results obtained by different workers, caused by different experimental conditions, e.g. different rates of heating, this method is sufficiently reliable to yield comparative data on the thermal stability of polyazoles. It is seen from Tables 1–6 and Figs. 4–7 that all polyazoles made up of alternating azole and phenylene rings are characterised by approximately the same start of intense decomposition in air in the range 450–600°C, whereas polyazoles containing polymethylene or other aliphatic chains usually decompose in the range 300–400°C.

Several polyazoles (e.g. polybenzimidazoles) containing ferrocene or perfluoromethylene units break down at relatively low temperatures, owing to their structural peculiarities. Thus the poor thermal stability of polyperfluoromethylenebenzimidazoles is due to the ease with which hydrogen fluoride is formed from fluorine in the perfluoromethylene chain and hydrogen in the imidazole ring[48]. Nevertheless, a purely perfluoromethylene molecule, e.g. in polytetrafluoroethylene, possesses excellent thermal stability.

Work on the thermal stability of polymers[123] is based on the "cage" theory. On this theory the thermal stability is determined by the phase state of the polymer, so that it depends on the melting point. However, the results for polyazoles show that this principle is not always valid. Thus polythiazoles based on 2,2′-biphenylylene units melt at 164–265°C, whereas a polythiazole based on 4,4′-biphenylylene units does not melt up to 500°C, although all these polymers start to decompose at the same temperature of 500°C (Table 3).

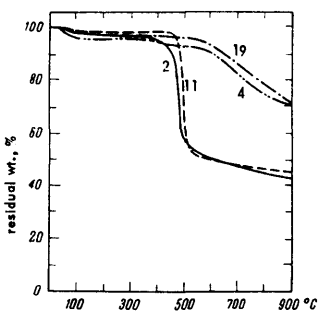


Fig. 4. Thermogravimetric analysis of polybenzimidazoles in air. Numbering of polymers from Table 1.

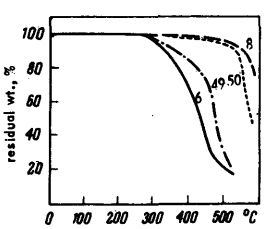


Fig. 5. Thermogravimetric analysis of polybenzothiazoles and polybenzoxazoles in air. Numbering of polymers from Table 2.

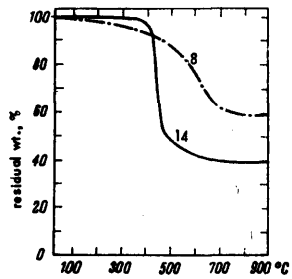


Fig. 6. Thermogravimetric analysis of polythiazoles in air. Numbering of polymers from Table 3.

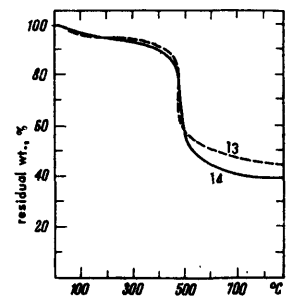
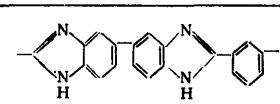
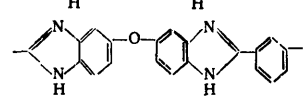
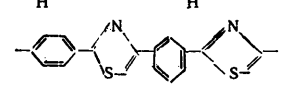
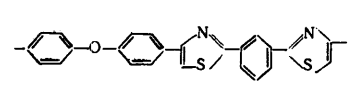
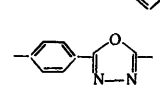
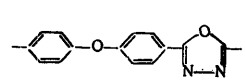


Fig. 7. Thermogravimetric analysis of polyoxadiazoles in air. Numbering of polymers from Table 5.

TABLE 9.

Structural unit	Temp. of start of decomp., °C	Solubility in* DMA	DMF	BA	Remarks
	500	+	×	–	
	500	+	+	+	
	500	–	–	–	does not form films or fibres
	450 (in N_2)	–	–	–	forms stable films
	450	–	–	–	
	430	+	×	–	forms films and fibres from soln.

* DMA = dimethylacetamide; DMF = dimethylformamide; BA = benzyl alcohol.

2. Physical Properties

Solubility. The problem of the thermal stability of polyazoles is closely linked with the preparation of polymers having satisfactory mechanical characteristics and sufficient solubility for goods to be manufactured from them. Polyazoles containing alternating azole and phenylene units often exhibit inadequate mechanical strength and solubility. Therefore various groups are introduced into the polyazole molecule which, without significantly lowering the thermal stability, increase the flexibility of the chain or produce an internal plasticising effect. The introduction of ether links between the phenylene units has proved to be the most successful. Table 9 gives data showing the effect of an oxygen bridge on the properties of polyazoles.

With the polybenzoxazoles as example Korshak et al.[60] showed that the introduction of bulky substituents into polymer molecules considerably improves their solubility. Such polybenzoxazoles dissolve in many organic solvents—chloroform, tetrachloroethane, tricresol, benzyl alcohol, pyridine, dimethylformamide, etc.—while possessing high thermal stability. The solubility is improved also by preparing mixed polymers, but the effect is rather smaller than with linear heterochain polymers, e.g. polyamides. Thus a polyaminotriazole based on sebacic and azelaic acids has a maximum solubility in ethyl alcohol of 8%,[27] and a polyamide based on hexamethylenediamine and the same acids is 100% soluble[124], whereas homopolyaminotriazoles and homopolyamides based on these acids are insoluble in alcohol.

X. USES OF POLYAZOLES

The chief property determining the use of polyazoles is their exceptional thermal stability. In this connection it must be borne in mind that aromatic polyazoles are more promising than aliphatic polyazoles in this respect, although the mechanical properties of the latter are better.

The first striking results on the application of aromatic polyazoles were achieved in the use of polybenzimidazoles as high-temperature and constructional adhesives, coatings, high-temperature fibres, thermal insulation, and binders for glass plastics[122,125-131].

Marvel[8] reported the fibre-forming and film-forming properties of the polybenzimidazole from biphenyl-3,3',4,4'-tetra-amine and diphenyl isophthalate. The unoriented film obtained from a solution of the polymer is dimethyl sulphoxide exhibited at 25°C the properties—tensile strength 0.7 g denier^{-1}, elongation 7%, modulus 35 g denier^{-1}—the corresponding values at 200°C being 0.5, 9%, and 15 respectively. After some orientation, filaments obtained from the solution had a strength of 4.5 g denier^{-1}, which they maintained in air up to 300°C.

Aliphatic polybenzimidazoles possess, together with adequate thermal stability, excellent mechanical properties, which enables them to be used for films, fibres, adhesive compositions, and other purposes. Thus the isotropic film from 2,2'-octamethylene-5,5'-dibenzimidazolyl possesses a tensile strength of 1200–1300 kgf cm^{-2}, an elongation of 18–20%, and good dielectric characteristics. On orientation the strength of the film reaches 5000 kgf cm^{-2}.[132]

It has been stated[65,133] that imidazole polymers can be used as semiconductor materials.

Reports have appeared recently of the use of other aromatic polyazoles. This applies primarily to polyoxadiazoles[134,135], from which it has proved possible to obtain a fibre having excellent thermal stability, chemical resistance, and good mechanical characteristics. The properties of the fibre do not change up to 200°, and only 40% loss in strength occurs at 300°C.

Holsten and Lilyquist[109] showed that polytriazoles also yield excellent thermostable filaments and films. This was to be expected, since aliphatic aminotriazoles have long been known as excellent fibre-forming materials.

The large amount of work which has been done on the structure of polythiazoles[71,73] has enabled products to be obtained having satisfactory mechanical properties and great thermal stability, suitable for the manufacture of films and fibres.

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POLYMERS BASED ON FERROCENE

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I. INTRODUCTION

Ferrocene is the most accessible and stable—and hence the most thoroughly investigated—representative of a novel type of organometallic compound. Several detailed reviews[1-3] have appeared on ferrocene and its derivatives. The aromatic character of ferrocene, its structural peculiarities, the high reactivity, and the thermal stability—unusual for organometallic compounds—have attracted the attention of many research workers, and explain the attempts to use various of its derivatives for the synthesis of polymers.