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NEW METHODS FOR SYNTHESIS OF THERMALLY STABLE POLYMERS HAVING RINGS IN THE CHAIN

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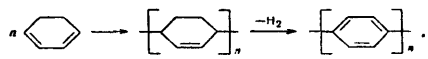
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Various thermally stable polymers are required for wide application in modern technology. Most of the known polymeric materials have a low thermal stability. Research on the synthesis of polymers stable to high temperatures is therefore being expanded and new methods are being discovered. One of the possible ways of making heat-resistant polymers which are also thermally stable is to synthesise polymers containing homocyclic (carbon) and heterocyclic rings in the main chain[1,2]. Progress in the last two years on the synthesis of new heat-resistant and thermally stable polymers, having rings in the main chain, is reviewed here.

I. POLYMERS HAVING BENZENE RINGS IN THE MAIN CHAIN

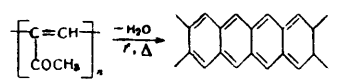
Recent work has shown conclusively that polymers constructed only of benzene rings have very high thermal stability. Such polymers, obtained by polycondensation and polymerisation are, as a rule, of low molecular weight. Marvel and Hartzell[3] attempted to obtain high-molecular-weight polyphenylene, starting from polycyclohexadiene. With a Ziegler catalyst 1,3-cyclohexadiene gave a linear polycyclohexadiene soluble in benzene and with molecular weight ~10 000. This polymer was converted, by dehydrogenation with chloranil, to polyphenylene, which does not melt up to 530° in a nitrogen atmosphere:



The polymer was heated in air at 230°–240° for 72 h without noticeable change.

Replacement of all the hydrogen atoms in polyphenylene by fluorine gives polyperfluorophenylene[4] which has even greater thermal stability.

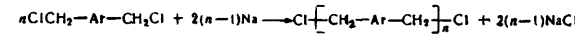
Nesmeyanov *et al.*[5] observed an interesting polycondensation of 1-chlorobut-1-ene-3-one to a polymer, which on further heating *in vacuo* underwent cyclopolymerisation (with loss of water) to form a polymer of the acene series, which had high thermal stability and interesting magnetic and electrical properties:



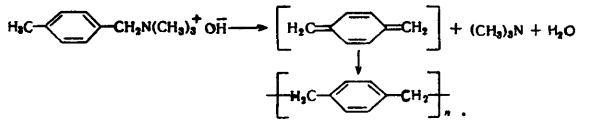
Polymers constructed entirely of benzene rings have high thermal stability but are brittle, so that their practical use is hindered. New methods have appeared, in recent years, for the synthesis of polymers having flexible elastic links (CH_2, S, O, etc.) in the main chain as well as benzene rings. There are, for example, the reactions of perarylation[6], polyrecombination[7], migration polymerisation of aromatic hydrocarbons with two isopropenyl groups[8], cyclic polymerisation[9,10], and reactions in macromolecular chains[11].

Poly-*p*-xylylene, which has high thermal stability and satisfactory mechanical properties, attracted attention long ago, but until recently there were no good reproducible methods for its synthesis or that of its analogues. Vansheidt *et al.*[12] used the Wurtz reaction for this purpose; the reaction of sodium metal with bischloromethyl derivatives of

aromatic hydrocarbons in dioxan at 25° yielded polycondensation products as white powders with various degrees of crystallinity:

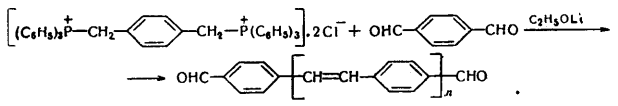


Young showed[13] that macromolecular poly-*p*-xylylene can be obtained in good yield (80%) from the reaction of 50% aqueous solutions of *p*-methylbenzyltrimethylammonium bromide (or chloride) with sodium hydroxide:

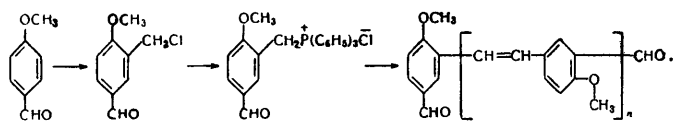


The poly-*p*-xylylene so obtained dissolves readily in chlorinated paraffins or benzyl benzoate, forming, at 300°, solutions with intrinsic viscosity $[\eta] = 1.0-2.0$.

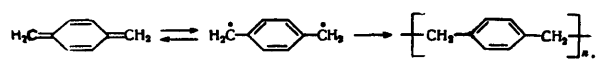
McDonald and Campbell[14] used the Wittig reaction for the synthesis of poly-*p*-xylylidene and its analogues. The reaction of *p*-xylylenebis(triphenylphosphonium) chloride with terephthalic aldehyde in the presence of lithium ethoxide gives poly-*p*-xylylidene, which is yellow and melts above 400°:



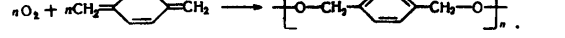
Similarly, starting from anisaldehyde, a poly-*p*-xylylidene with m.p. about 180° and intrinsic viscosity $[\eta] = 0.31$ was obtained:



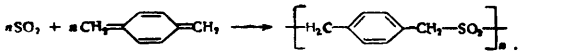
Errede *et al.*[15] developed an original method for obtaining solutions of *p*-xylylene in hexane. Pyrolysis of *p*-xylene at 1000° *in vacuo* gives the *p*-xylylene pseudoradical which is introduced into the solvent at -78°. Under these conditions the *p*-xylylene does not lose its reactivity for a long time. At -78° its half-life is 22 h, but at -36° it exists for only 12 min. When a solution of *p*-xylylene is kept for a very long time at -78°, polymerisation takes place to form poly-*p*-xylylene with molecular weight 200 000 and more:



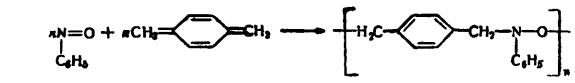
In hexane solution at -78° *p*-xylylene is very active and forms copolymers[16]. With oxygen it gives a polymeric peroxide which decomposes explosively at 100°:



Copolymerisation of *p*-xylylene and SO_2 takes place easily to form an insoluble copolymer, which can be melted at 200° under 500 atm pressure giving transparent flakes:

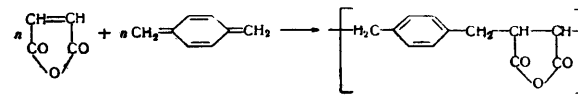


p-Xylylene forms copolymers with various nitroso--compounds (*e.g.* nitrosobenzene, *p*-nitroso-*NN*-dimethylaniline, α-nitroso-β-naphthol) which have interesting compositions and properties:



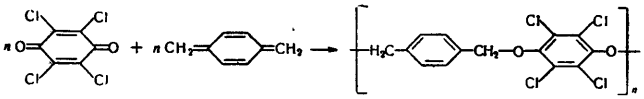
These are soluble in organic solvents and melt or soften at 200°.

p-Xylylene also gives copolymers with maleic anhydride, diethyl maleate, diethyl fumarate, acrylonitrile, n-butyl acrylate, and styrene:

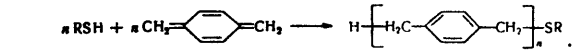


All of them are thermoplastic.

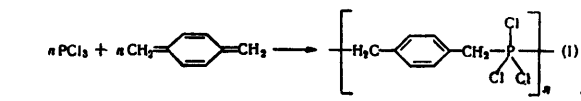
An interesting copolymer is that of *p*-xylylene and chloranil, with softening point 195°–200°:



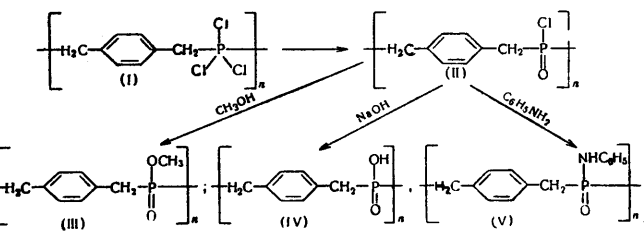
With mercaptans, macromolecular telomers are formed:



The copolymerisation of *p*-xylylene and PCl_3 is unusual, polymers having phosphorus atoms in the principal chain being produced[17]:



Under the influence of moisture, polymer (I) easily loses two chlorine atoms to form polymer (II); when treated with methanol this forms the polymeric ester (III), softening point 150°, which can be compressed to transparent films. When polymer (II) is treated with alkali, a salt is obtained, and hence the corresponding polymeric acid (IV), which can be used as an ion-exchange resin. Polymeric amides (V) are obtained by treating polymer (II) with aniline or hexamethylene diamine:

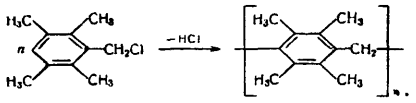


Similar reactions take place easily between *p*-xylylene and the compounds PBr_3, PI_3, $C_6H_5PCl_2$, and $(C_6H_5)_2PCl$, but not $POCl_3$ and $(C_6H_5)_3P$.

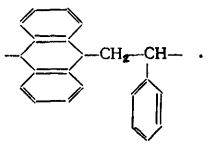
Preparation of poly-*p*-xylylene from *p*-chloromethyltoluene has been proposed[18], by passing the latter, at 102°

and reduced pressure, through a gypsum tube heated to 750°; the polymer is deposited in a receiver, in 65% yield.

A highly branched polybenzyl was obtained by polycondensation of benzyl chloride. Polycondensation of chloromethyldurene in the presence of a ferric oxide catalyst at 100° gives[19] a polymer with m.p. 260°–280°:

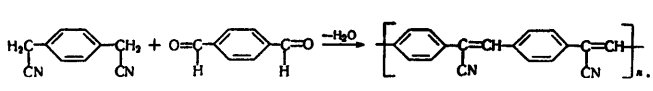


Imoto[20] states that the copolymer of anthracene and styrene had high thermal stability:

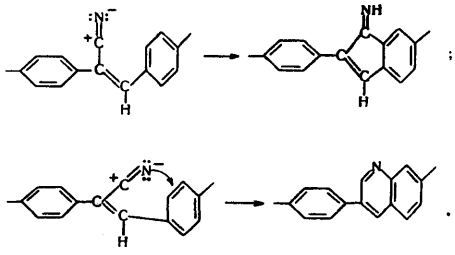


On heating to 305° for 4 h, the loss in weight amounted to 5.5–13.1%.

The polymer of acenaphthylene (M = 200 000), obtained in the presence of the boron trifluoride ether complex, undergoes no change on heating to 280°. Lentz and Handlovits[21] have developed a method of preparing polycyanoterephthalidene by the condensation polymerisation of α,α'-dicyano-p-xylene and terephthalic aldehyde:

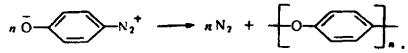


Polycyanoterephthalidene is insoluble, infusible, and has exceptional thermal stability. On heating to 450° for 3000 sec, the polymer loses ~15% of its weight, and ~25% on heating to 500° for 6000 sec. The infra-red spectra of the polymers heated at 450° and 500° differ from those of the original polymers. Possibly cyclisation occurs to form an iminoindene structure or a quinoline residue in the chain:

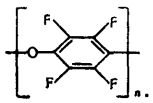


The thermal stability of the polymer increases after heating at 550°; when heated again at this temperature for 30 min, it loses not more than 2% in weight.

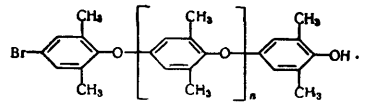
Polymers are known which contain an etheric oxygen atom, –O–, in the chain as well as rings. An interesting method for their preparation is the decomposition of derivatives of benzene-1,4-diazooxide:



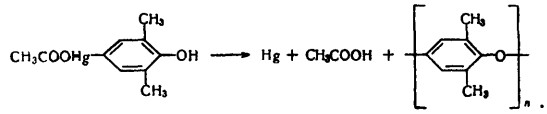
Dewar and James[22] showed that, in the thermal decomposition of 3,5-dibromobenzene-1.4-diazooxide in chlorobenzene solution at 70°, nitrogen is liberated and a polymer with softening point 200°–220° is formed. Decomposition of tetrafluorobenzene-1,4-diazooxide gives, similarly, the elastomer[23]



Staffin and Price[24] used 2,6-disubstituted phenols to obtain macromolecular 2,6-disubstituted p-phenylene ethers. A benzene solution of 2,6-dimethyl-p-bromophenol was shaken at room temperature with alkali in the presence of lead dioxide as oxidising agent to give the polymer

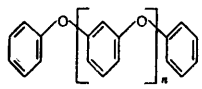


This polymer is soluble in organic solvents, its intrinsic viscosity [η] is 0.43 and softening point 260°. It has a rigid chain structure and possesses great thermal stability. According to Madorskii's data[24], the loss in weight on heating at 320° for 30 min amounted to 1%, 13% at 370°, and 69% at 420°. Attempts were made to obtain the same polymer by decomposing 4-(acetoxymercury)-2,6-dimethylphenol at 200°:



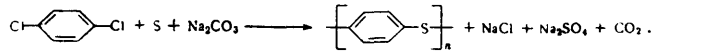
Only 12% of soluble polymer was obtained, the major part having a cross-linked structure.

Phenoxypoly(m-phenoxylene)benzenes with great thermal and radiation stability were obtained by Ullman's method[25]:

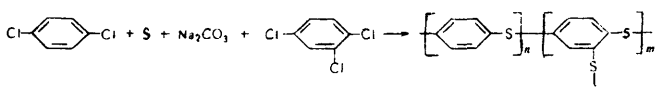


The polymers with a low degree of polymerisation (n = = 2 to 5) are high-boiling liquids (b.p. 463°–650°), useful as lubricating oils.

Polymers are also known with sulphur atoms, –S–, in the main chain as well as rings. Lentz and coworkers[26] described a new method of producing thioether polymers by the high-temperature (250°–350°) condensation of polyhalogenoaromatic compounds with alkali or alkaline-earth sulphides:



Linear crystalline poly(phenylene sulphide) had m.p. 285°. Linear, soluble or cross-linked, insoluble polymers with great thermal stability at 400°–500° and resistance to chemical reagents are obtained similarly:



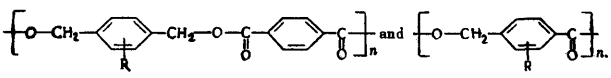
Organoarsenic polymers have also been synthesised[27]; they are prepared by the reaction of dilithium aromatic

derivatives with aromatic chloroarsines. Most of these polymers are soluble in alcohol and ether. The polymers synthesised and their properties are listed in the Table.

Korshak and Vinogradova[28] and Conix[29] described the preparation of various polyesters from dibasic aromatic acids and bisphenols. Aromatic polyesters have very great thermal stability (up to 500°), high solubility, and are capable of forming films.

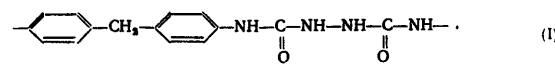
Another group of polymers with high thermal stability and fibre-forming properties are aromatic polyanhydrides[30]. Those of terephthalic acid are especially stable, decomposing above 400°. They are resistant to concentrated acids and *aqua regia*.

Mitin *et al.*[31] carried out polymerisation of aromatic dialdehydes by the Cannizzaro–Tishchenko reaction in non-aqueous medium. In the presence of aluminium ethoxide as catalyst terephthalic aldehyde in the melt forms a transparent amorphous linear polymer, soluble in chloroform, with molecular weight 100 000 to 120 000 (determined by light scattering):

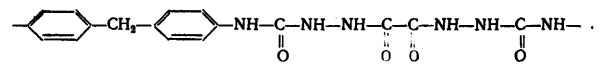


The m.p. of the polymers of some aromatic dialdehydes are: terephthalic aldehyde 120°, isophthalic aldehyde 80°, 2,5-dimethylterephthalic aldehyde 140°, and 4,4′-diformylbiphenyl 250°.

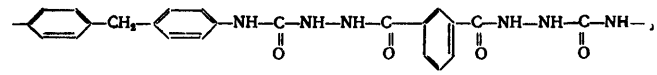
Starting from diisocyanates and dihydrazides or hydrazine, Campbell and coworkers[32] obtained new polymers containing benzene rings in the chain. The reaction of methylenebis-*p*-phenylene diisocyanate with hydrazine hydrate in dimethylformamide solution gives a transparent viscous solution of polymer (I) with the structure:



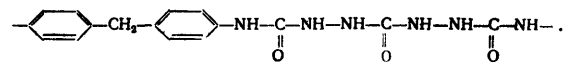
The polymer forms tough flexible films and fibres stable up to 300°. It is stable to the action of light: after 200 h exposure, the film remains tough and flexible. When (I) reacts with oxalyl dihydrazide in dimethyl sulphoxide solution, a polymer with an unusual link structure is obtained:



From a solution of such a polymer, tough films showing 200% elongation at 200° and stable up to 270° can be obtained. Isophthalyl dihydrazide condenses easily with (I) in dimethyl sulphoxide solution to form the polymer

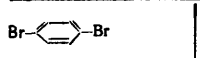
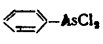
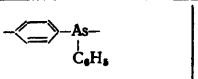
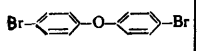
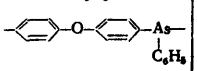
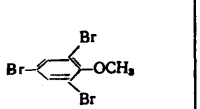
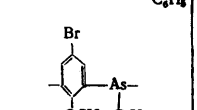
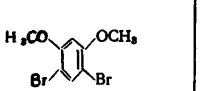
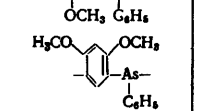
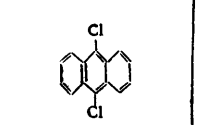
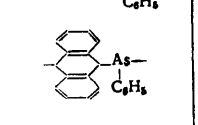
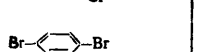
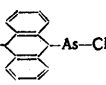
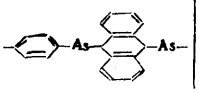


which has an intrinsic viscosity, $[\eta]$, of 1.7 and gives tough films with 31% elongation at rupture, and melting at 250°. Carbonyl hydrazide $NH_2NHCONHNH_2$ reacts easily with (I) forming a polymer with the structure



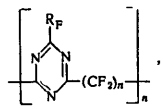
Its intrinsic viscosity, $[\eta]$, is 0.33 and it melts with decomposition at 260°. A polymer with greater thermal stability and a higher degree of polymerisation is obtained in the reaction of carbonyl hydrazide with 3,3′-dimethyl-4,4′-biphenylene diisocyanate; it has an intrinsic viscosity. $[\eta]$, of 1.46, and m.p. 280°.

TABLE. Synthesis and properties of arsenic-containing polymers.

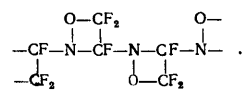
Aromatic halogen compound	Chloroarsine	Polymer	M.p. of polymer, °C	Mol. wt. of polymer
			40	6000
	»		140	2000
	»		300	2000
	»		220	1900
	»		270	2000
			250	13 300

II. POLYMERS HAVING HETEROCYCLIC RINGS IN THE MAIN CHAIN

Polymers containing no hydrogen, which possess great chemical and thermal stability, are very interesting. By the condensation of perfluoroamidines and perfluorodiamidines, Brown[33] obtained elastomers with triazine rings and CF_2 groups in the main chain:



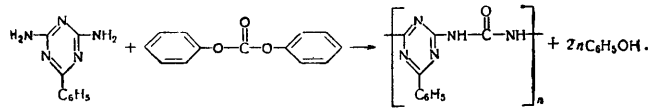
where R_F is perfluoroalkyl. The elastomer is stable at 350°–410° and loses weight (30–50%) only when kept at 470° for 30 min. It possesses exceptional chemical stability: its main properties did not change after it had been boiled with fuming nitric acid for 24 h. In the polymerisation of trifluoronitrosoethylene $CF_2=CF-N=O$, Griffin and Haszeldine[34] observed the formation of poly(perfluoro-1,2-isooxazetidin-2,3-ylidene) with the unusual chain structure



When heated for 2 h at 400°, the elastomer changed into a solid yellow polymer with liberation of carbonyl fluoride:

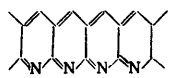
$$=CF-N=CF-N=CF-N= \cdot$$

A polymer with very high thermal stability is obtained[35] by polycondensation of diaminophenyltriazine with diphenyl carbonate:



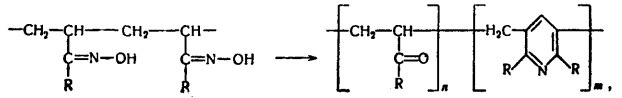
It is soluble in sulphuric acid and melts at 350°.

By a special heat treatment of polyacrylonitrile, Topchiev and coworkers[36] obtained a cyclic polymer with the structure



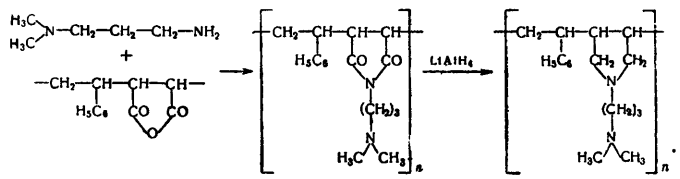
Polymers of this type have exceptional thermal stability; they do not burn when introduced into a flame, and they possess interesting semiconductor properties.

Under the action of an alcoholic solution of hydrogen chloride, ketoximes of poly(methyl vinyl ketone) and poly(phenyl vinyl ketone) form[37] a copolymer which has pyridine, as well as ketone, residues in the main chain:

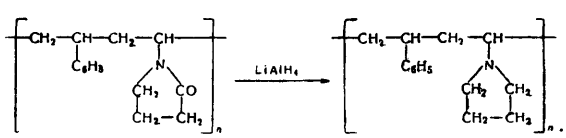


where R is methyl or phenyl. The copolymers are soluble in chloroform, with intrinsic viscosity $[\eta] = 0.11-0.14$. They are thermally stable, losing ~3% in weight when heated at 225° for 12 h.

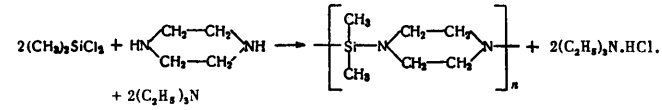
Reduction of some copolymers with lithium aluminium hydride produces new copolymers containing pyrrolidine residues in the main chain[38]. The copolymer formed by the reaction of γ-dimethylaminopropylamine and the copolymer of styrene with maleic anhydride, when reduced with lithium aluminium hydride, gives a copolymer of a substituted pyrrolidine:



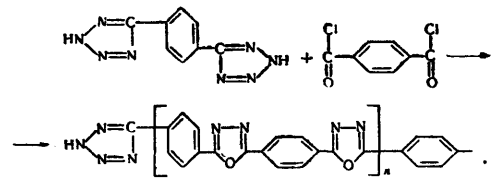
The copolymer of styrene and vinylpyrrolidone is also easily reduced to a copolymer of styrene and vinylpyrrolidine:



The reaction of dimethyldichlorosilane with piperazine in ether, in the presence of triethylamine as catalyst, gives a polymer with silicon atoms and piperazine rings in the main chain[39]:

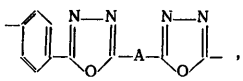


Marvel and coworkers[40] synthesised polymers containing oxadiazole, thiazole, triazole, and benzoimidazole rings in the chain. Those containing oxadiazole are formed when bis(tetrazolyl)benzenes are boiled in pyridine with diacyl chlorides. *p*-Bis(tetrazolyl)benzene and terephthaloyl chloride give a polymer soluble only in concentrated sulphuric acid:



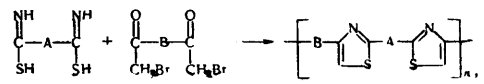
where n is 17–50. This polymer has high thermal stability; the loss of weight when it is heated for 12 h at 350° does not exceed 10%.

Polymers having repeated oxadiazole rings interlinked by aliphatic or aromatic groups (A) are thermally very stable. For example, the polymer

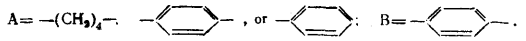


with A = $(CH_2)_7$ is soluble and its formic acid solution yields brittle films. It is thermally stable and softens at about 270°.

Polymers containing the oxazole ring were obtained from bis(tetrazolyl)benzene and pyridine-2,6-dicarboxylic acid; they are black, soluble in formic acid and phenol, and their solutions yield brittle films. The weight loss of the polymer on heating in the air for 12 h at 350° was ~28%. Introduction of triazole rings into the polymer chain raises the solubility of the polymers[41]. The polymers, obtained by the reaction of bis(tetrazolyl)benzene with *NN'*-diphenylisophthaloyliminochloride, are black and soften at 235°–300°. Marvel introduced the thiazole ring into the polymer chain by condensation of the corresponding dithioamides with bis(α-bromoketones):



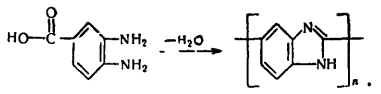
where



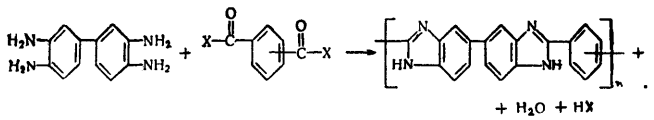
These polymers are thermally very stable up to 300°.

Polymers having benzoimidazole rings in the main chain possess exceptionally high thermal stability; this is apparently connected with the aromatic nature of the benzoimidazole rings. Marvel and coworkers[43] developed methods for the preparation of polybenzoimidazoles and a

series of model compounds. Condensation of 3,4-diaminobenzoic acid in boiling sulphuric acid produces green poly-2,5(6)-benzoimidazole, soluble only in concentrated sulphuric acid and unstable when heated to 350°:

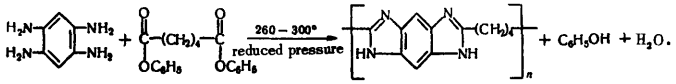


Polybibenzoimidazoles have recently been obtained by the reaction of *oo'*-diaminobenzidine with diphenyl esters of dicarboxylic acids:



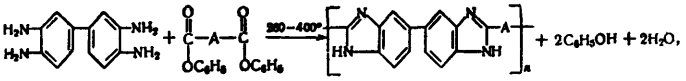
where X = OC_6H_5. Solutions of the poly[2,2'-(*p*-phenylene)--5,5'-bibenzoimidazole] so obtained, a yellow powder soluble in formic acid and concentrated sulphuric acid, yield brittle films. It has great thermal stability, losing 2% in weight when heated for 7 h at 350° in a nitrogen atmosphere. Poly[2,2'-(*m*-phenylene)-5,5'-bibenzoimidazole], yellow and more flexible than the *p*-isomer, also has high thermal stability.

Among other polymers with heterocyclic rings in the main chain, the polydiimidazobenzenes are of interest. The general method for their synthesis can be demonstrated by the example of poly(2,6-tetramethylenediimidazobenzene):

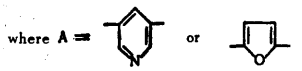


They are bluish grey and their solutions in formic acid yield transparent films.

Interesting properties are possessed by poly[2,2'-(3,3'--pyridylene)-5,5'-bibenzoimidazole] and poly[2,2'-(2,2'--furylene)-5,5'-bibenzoimidazole], prepared by the general method.

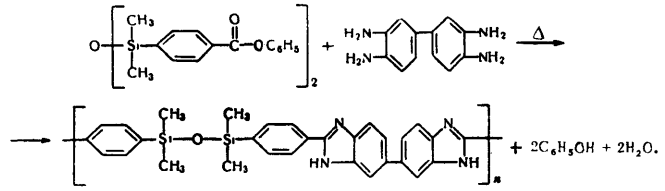


where



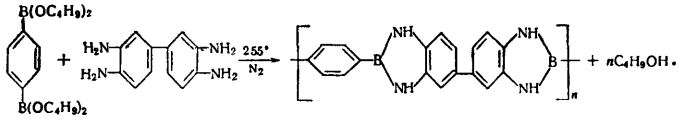
Poly[2,2'-(3,3'-pyridylene)-5,5'-bibenzoimidazole] has very great thermal stability; weight is lost only on heating to above 500°. In contrast to other *m*-phenylene polymers, it displays some crystallinity. Poly[2,2'-(2,2'-furylene)-5,5'--bibenzoimidazole] is orange and softens at 480° with a little decomposition.

Siloxane derivatives of benzoimidazole polymers were obtained[42] in the reaction of *oo'*-diaminobenzidine with a diphenyl ester of a disiloxane:



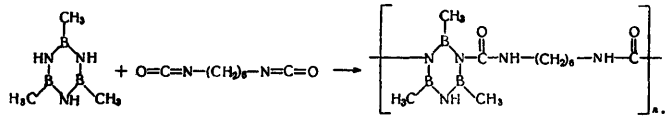
The polymer is soluble in formic and concentrated sulphuric acids, has high thermal stability, and melts above 420°–450°.

The borimidazoline polymer[42], obtained in the reaction of tetrabutyl benzene-1,4-diboronate with *oo'*-diaminobenzidine, has very interesting properties:

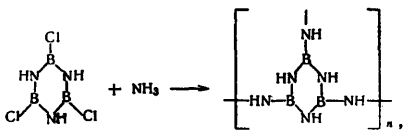


It is soluble in sulphuric acid and dimethyl sulphoxide, and has exceptionally high thermal stability. When heated to 800° in a nitrogen atmosphere (rate of heating 150 deg h^{-1}), the polymer lost ~25% in weight, but above 600° the weight loss was less than 10%.

Interesting properties are also possessed by polymers which have borazole rings in the main chain. Korshak and coworkers[44] obtained a glassy copolymer in the reaction of trimethylborazole with hexamethylene diisocyanate:

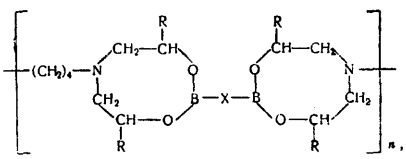


Polycondensation of trichloroborazole with ammonia[45] gave a white amorphous powder:



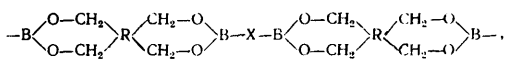
which does not change on heating to 300°.

The reaction of alkylenediboronic [benzenediboronic? (Ed. of Translation)] acids with tetra(hydroxyalkyl)polymethylene diamines resulted in interesting polyesters[46] with the structure

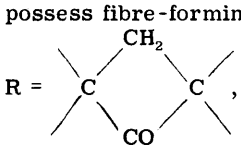


where R = CH_3, X = $-C_6H_4-$. These polymers withstand boiling in water for 4 h and are thermally stable up to 300°.

The products of the polycondensation of the diboronic acids and tetrols [pentaerythritol and tetra(hydroxymethyl)-cyclopentane], with the structure

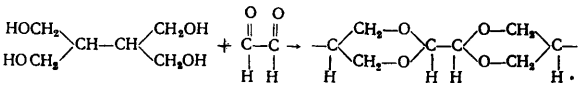


possess fibre-forming properties. When X = $-C_6H_4-$ and



, the softening point of the polymer is 240°.

Recently[47] a new class of linear polycycloacetals was reported. The reaction of dialdehydes with tetrahydric alcohols, which contain two 1,2- or 1,3-diol groupings, easily produces linear polycycloacetals, in which each unit contains a ring:



In this reaction the dialdehydes and tetrols can be considered as bifunctional compounds. The reaction of more stable acetals of aliphatic aldehydes of the general formula $(C_2H_5O)_2CH(CH_2)_nCH(OC_2H_5)_2$ with various tetrols, such as pentaerythritol or $(HOCH_2)_2CH(CH_2)_mCH(CH_2OH)_2$, where $m = n = 6-10$, gives yellow or white solid polymers, m.p. 146°–205°, which are soluble in chlorinated hydrocarbons and have film- or fibre-forming properties. The dielectric constant of these polymers is 2.1–2.4, the dielectric loss 0.03, and the resistivity $10^{16}-10^{17}$ ohm cm.

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THE SATURATED CYCLIC SULPHIDES OF PETROLEUM AND THEIR SYNTHESIS

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