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POLYMERIC BORON COMPOUNDS

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In the three years since the publication of our earlier review of the scientific literature on polymeric compounds containing boron[1], the number of papers published in this field has considerably increased, as well as their penetration of the subject. Investigators no longer restrict themselves to reporting the production of a polymer, but now describe its properties, give the results of investigations which confirm its structure, and, in particular cases, draw conclusions regarding the features of behaviour which reflect the specific chemical nature of boron.

However, as a whole, the chemistry of polymeric boron compounds still lags far behind the monomeric chemistry of boron in time spent on it and in the vigour of its development. It is as though it were passing through an induction period of hidden development, which is necessary for the assimilation of the huge amount of original material made available by the monomer chemistry and for the working out of the basic methods for the production of the polymers.

In this review we follow the order of presentation of material used in our previous review.

Only a few polymers are known in which the main chain contains B–B bonds. Thus Kuchen and Brinkmann[2] reacted metallic sodium with phenylboron dichloride and obtained the linear polymer of composition $[(C_6H_5)B]_n$ having molecular weight 820, corresponding to $n = 9–10$. The product is a yellow amorphous powder which is slowly oxidised in air and darkens above 200°, and it was considered to be the phenyl derivative of the previously described linear polyboron hydride $[BH]_x$.[3] A polymer of analogous structure was obtained by the pyrolysis of tricyclohexylboron, with elimination of cyclohexene and cyclohexane[4]:

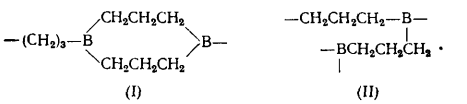
$$x\,B(C_6H_{11})_3 \xrightarrow{250^\circ} (BC_6H_{11})_x + x\,C_6H_{10} + x\,C_6H_{12}.$$

In their investigation of the chemical reactions of diboron tetrachloride, Holliday and coworkers obtained a solid polymeric boron subchloride $[BCl]_n$ from it by pyrolysis[5], and reacted it with epoxyethane to obtain tetrakis-(2-chloroethoxy)diboron $B_2(OCH_2CH_2Cl)_4$ which decomposes on heating to give the polymer $(BOCH_2CH_2Cl)_n$.[6]

According to a British patent[7], tetraethoxydiboron $B_2(OCH_2CH_3)_4$ is also converted into a polymer on heating at 100°.

The pyrolysis of decaborane gives hydrogen and a condensation product $B_{20}H_{24}$, which can evolve further hydrogen and is converted into a non-volatile solid boron hydride[8].

New polymers containing B–C bonds in the main chain have been described. These are most simply prepared by hydroboration of unsaturated compounds; thus by the action of diborane on triallylboron Mikhailov and Pozdnev[9] obtained a solid polymer which they consider contains both cyclic (I) and acyclic (II) units:



(I) (II)

According to patent data a polymer of structure (I) can be obtained by the hydroboration of allene [10].

A solid polymer insoluble in ether has been prepared from 1,2-diphenyldiborane and cyclopentadiene [11]. The polymers, in which all three valencies of the boron are bonded to carbon, are very readily oxidised in the air; they have no independent application, therefore, and are known only as intermediate products in the conversion of dienes into the corresponding glycols, generally $\alpha\omega$-glycols, or into the polymethylene diboronic acids $(HO)_2B(CH_2)_nB(OH)_2$. [12]

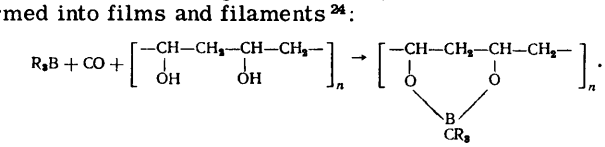
Solid polymers stable to heating and containing boron and carbon in the main chain can be obtained by reacting lower esters of orthoboric acid or boron halogenides with phenylene-1,4-di(magnesium bromide) [13] or by pyrolysing diphenylboron chloride in the presence of aluminium chloride [14]. These polymers have the structure $(-C_6H_4BOH-)_n$.

The production and properties of polymers with a carbon main chain and with boron in side-chains have been more fully investigated. Such compounds can be prepared by polymerising vinyl derivatives of borane or boric acid and its esters or anhydrides. Methylvinylborane and ethylvinylborane can polymerise spontaneously during their preparation [15]. *p*-Vinylbenzeneboronic acid polymerises on heating or in the presence of free-radical initiators. The polymer is a polyelectrolyte, soluble in aqueous alkali and in many organic solvents containing 5–10% of water, stable on heating to 300°, but losing water above this temperature to give boric anhydride [16]. The cyclic tris-(*o*-vinylphenyl)boroxin can also polymerise [17].

The polymerisation of the dibutyl ester of vinylboronic acid under the action of atmospheric oxygen or heat has been studied by Mikhailov and Aronovich, who concluded that molecular oxygen forms a copolymer with the partially hydrolysed vinylboronic ester. The dibutyl ester was also copolymerised with ethyl vinyl ether and with styrene [18].

Vinylbenzeneboronic ester polymers and copolymers with vinyl acetate, acrylonitrile, styrene, and vinyl chloride have been recommended for moulding, the preparation of laminar plastics, and as coatings, impregnants, and adhesives [19-21]. Polymers of vinylboronic, divinylborinic and propenylboronic acid and their copolymers with isocyanates can be used as boron-containing plastics[22]. Polymers are known in which boron in a side-chain is attached to the main carbon chain through oxygen. Kolesnikov and coworkers prepared the mixed anhydride of dibutylborinic and methacrylic acids: $(n\text{-}C_4H_9)_2B\text{–}OCOC(CH_3)=CH_2$ and its polymer and copolymers with methyl methacrylate and styrene. They obtained viscous liquid, waxlike, or vitreous polymers, insoluble in the usual organic solvents but soluble in dimethylformamide [23].

A new and original preparation of substituted boric acid anhydrides was developed by Hillman; by carrying out this reaction in the presence of poly(vinyl alcohol) he obtained a water-insoluble polymer stable towards hydrolysis and soluble in the usual organic solvents, and which can be formed into films and filaments [24]:



A polyester has been prepared by boiling boric acid with a hydrolysed copolymer of vinyl acetate and alkenes, of hydroxyl group content 17.3%, in xylene [25].

Carbon-chain polymers with boron in side-chains have also been described in Braun's review [26].

Methods for the preparation of B–N polymers are being vigorously developed. New methods for the production of boron nitride have been described: by reaction between boric acid and urea [27] and between diborane and hydrazine in the flame of a special burner [28].

In the reaction between hydrazinium sulphate and lithium tetrahydroborate, Goubeau and Ricker [29] obtained first the borine–hydrazine complex $BH_3.H_2NNH_2$; on heating this was converted into the hydrazobisborane $H_2B.HN.NH.BH_2$, and further pyrolysis produced the unstable compound $(HBN)_n$, still containing N–N bonds, and which is liable to explode.

The action of hydrazine on tris(dimethylamino)boron gives a readily hydrolysed polymer of composition $B_2(HNNH)_3$. [30]

From the reaction between diboron tetrachloride and hydrazine, Holliday obtained the new boron nitride $(B_2N_2)_n$, in which the B–B and N–N bonds are still retained. This nitride is less stable thermally than the two previously known nitrides [6].

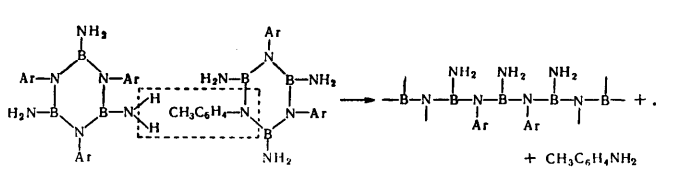
Linear B–N polymers are still very few, although much effort has been devoted to their preparation. The conditions for preventing ring formation in the reaction between primary amines and organoboron dichlorides have been most fully investigated by Gerrard. Using butylamine or isobutylamine and phenylboron dichloride, he showed that the alkyl group of the amine sterically hinders ring formation, so that the only reaction product is a linear polymer with B–N bonds; this is a solid substance, readily hydrolysed in boiling water [31,32].

In analogous investigations with 1,2-diphenyldiborane and amines or organoboron diamines, Korshak *et al.* [33] were only able to prepare linear polymers with very short chains, for example, using cyclohexylamine, the dimer:

$$(C_6H_{11})\,NHB\,(C_6H_5)\,N\,(C_6H_{11})\,B\,(C_6H_5)\,NH\,(C_6H_{11}).$$

An attempt to increase the length of the molecule by polycondensation of this dimer by heating to 260° only led to its decomposition. The comparatively large radical on the nitrogen apparently produces steric hindrance to chain lengthening as well as to ring formation [33].

It has not been shown possible to produce linear B–N polymers by opening the ring of borazoles with polymerisation of the resulting biradical, although two patents recommend carrying out this reaction in the presence of alkaline catalysts [34,35]. Recently Gerrard *et al.* [36] pyrolysed *BB'B''*-triamino-*NN'N''*-tri-*p*-tolylborazole and found that the borazole ring opened with the formation of a branched polymer with linear units as a result of transamination:

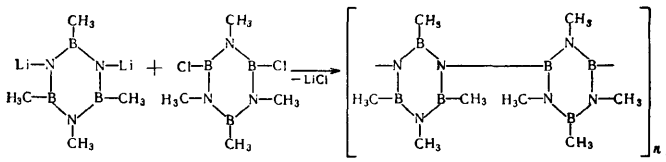


The polymer dissolves in some organic solvents and is not hydrolysed by atmospheric moisture.

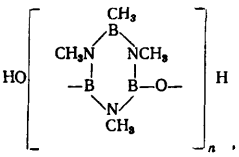
Considerably more is known of polymers in which the main chain consists of borazole rings joined either directly

by covalent bonds, or by amino-nitrogen, a polymethylene, or arylene chain, or hetero-organic or inorganic chains.

By condensing *NN'*-dilithiotetramethylborazole with *BB'*-dichlorotetramethylborazole Wagner and Bradford[37] obtained a polymer of molecular weight 1382 and softening point 155°:

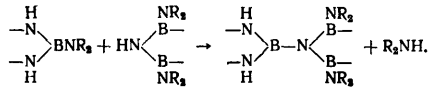


By quantitative hydrolysis of *BB'*-dichlorotetramethylborazole they also obtained the polymer of structure:



of molecular weight 3512 and m.p. 180–200°; the presence of a B–O–B bond was proved by infrared spectroscopy[37].

In their study of the pyrolysis of *B*-(dialkylamino)borazoles, Gerrard and coworkers[38] observed the formation of a B–N bond between different rings:

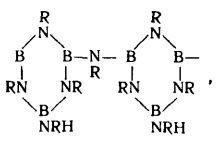


The ability of borazoles having unsubstituted nitrogen to undergo polycondensation was also observed by Meller, who obtained non-volatile vitreous products by heating *BB'*-di-n-butyl-*B"*-chloroborazole and *BB'B"*-tris(triphenylsiloxy)borazole[39].

The action of ionising radiation on *BB'B"*-trimethylborazole has given a polymer of $M = 1100$, soluble in organic solvents, and in which the main chain contains borazole rings; it was thought that the borazole radicals produced by the radiation react with further borazole molecules to form the polymer, with elimination of H_2 and CH_4.

The formation of individual linear units by elimination of rings is also possible[40].

The previously known polymer consisting of borazole rings joined by amino-nitrogen:



was described by Lappert[41].

A detailed investigation of the transamination of *B*-aminoborazole has been made by Niedenzu and Dawson, who obtained *BB'B"*-trihydrazinoborazole, which when heated is converted into a highly cross-linked polymer[42,43].

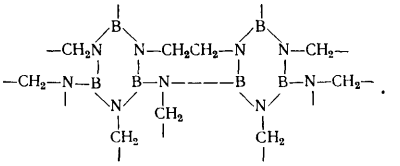
Polyborazoles in which borazole rings are joined by a hydrocarbon chain have often been described. The most important of these are the products of the polymerisation of *BB'B"*-triallyl-*NN'N"*-triphenylborazole and *NN'N"*-triphenyl-*BB'B"*-trivinylborazole and the copolymerisation of these with vinyl monomers. Because of the trifunctionality of the borazole monomers, the main hydrocarbon chains include borazole rings also.

Pellon and coworkers[44] have conducted a systematic investigation of the polymerisation of such monomers and the effect of steric factors; they obtained gel-like polymers of comparatively low molecular weight.

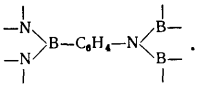
The production of solid polymers and copolymers of *BB'B"*-triallyl-*NN'N"*-triarylborazoles and *BB'B"*-trivinyl-*NN'N"*-trialkylborazoles has been described in American patents[45,46].

Ruigh has studied the polymerisation of *BB'B"*-tris-(2-chlorovinyl)borazole; by carrying out the reaction in boiling acetone, he obtained a solid vitreous polymer, probably of linear structure[47].

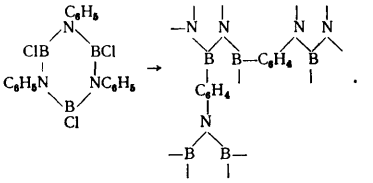
By reacting thioborates with ethylenediamine, Shchegoleva *et al.*[48] obtained a polymer which apparently has the structure:



Methods of joining borazole rings using bifunctional compounds have been developed by Gerrard and coworkers. By heating *BB'B"*-trichloro-*NN'N"*-triphenylborazole at 300°, HCl was given off and a polymer was produced which infrared spectroscopy showed to contain B–C bonds, so that the polymer was assigned the structure[31]:

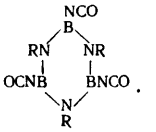


However, Gerrard later refined his results, and came to the conclusion that the borazole ring opens during the pyrolysis, the reaction more accurately proceeding[36]:



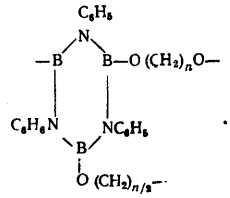
An attempt to obtain polyborazoles by pyrolysis of complexes of boron halides with diamines, in particular the 2 : 1 complex formed between boron trichloride and *p*-phenylenediamine, gave an infusible and insoluble polymer of composition $[ClBNC_6H_4NBCl]_n$. Whether the polymer was linear or polycyclic could not be diagnosed from the complex infrared spectra observed[49].

Lappert and Pyszora prepared a number of boron isocyanates and isothiocyanates, including a borazole with isocyanate-groups on the boron atoms[50]:



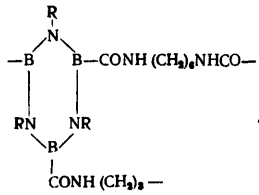
With hexamethylenediamine or phenylenediamine this gave three-dimensional polymers which were insoluble in organic solvents and boiling water[51].

Polycondensation between *NN'N"*-triphenylborazole and diols or polyols, with elimination of hydrogen, enabled Korshak *et al.* to obtain a number of rubberlike polymers, both of linear structure and of the branched structure:

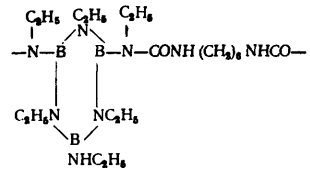


These polymers are very unstable towards hydrolysis, and decompose when kept in contact with air[52].

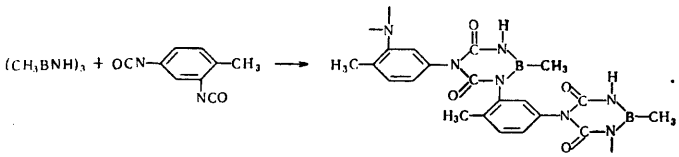
The migration copolymerisation of *NN'N"*-trimethylborazole and *NN'N"*-triphenylborazole with hexamethylene diisocyanate produces high-melting polymers, of low sensitivity to atmospheric moisture, of the structure[53]:



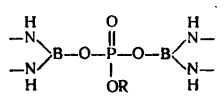
BB'B"-triethylamino-*NN'N"*-triethylborazole has also been copolymerised with hexamethylene diisocyanate, producing a linear polymer, melting at 185–200°, of the structure[54]:



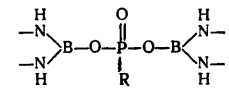
The borazole ring of *BB'B"*-trimethylborazole is decomposed on reaction with 4-methyl-1,3-phenylene diisocyanate with the formation of a polymer[55]:



High-melting thermostable polymers, sensitive to atmospheric moisture, have been obtained in which borazole rings are joined by phosphoryl or phosphonyl radicals; thus Gerrard and coworkers[56] condensed chloroborazoles with phosphoric esters to produce a polymer containing the unit:

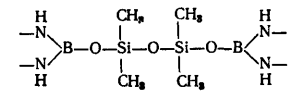


Phosphonic esters have given polymers with the unit[57]:

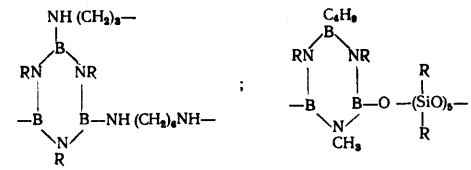


(R = H, C_2H_5, CCl_3, or Cl).

Korshak *et al.*[58] obtained a similar polymer from *BB'B"*-trichloroborazole and dibutyl methylphosphonate. By condensing *BB'B"*-trichloroborazole with tetramethyldisiloxanyl dibutyl ether, they produced a polymer melting above 300° and with a reduced viscosity in cresol of 0.16. It is unaffected by atmospheric moisture. The borazole rings in this polymer are joined by siloxane bridges[58]:



Polycondensation of *BB'B"*-tri-n-butylthio-*NN'N"*-trialkylborazoles and *B*-n-butyl-*B'B"*-di-n-butylthio-*NN'N"*--trialkylborazoles with hexamethylenediamine and various diols, including siloxanediols, led Mikhailov and Galkin[59] to obtain a number of interesting three-dimensional and linear polymers:

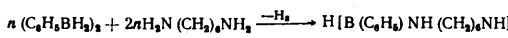


Those obtained from hexamethylenediamine were infusible and thermostable, but could be hydrolysed; those containing siloxane bridges are not hydrolysed in the air.

Various polymers of different structure and properties in which the main chain consists of B, N, and C atoms have been described, generally linear but sometimes cross--linked.

In their investigation of the donor properties of nitrogen in the ethylenediamine–diborane complex, Holliday and Jeffers[60] found the latter to give off hydrogen and to be converted into a polymer. Krause refers to similar polymers in his review of boron compounds[61].

Korshak *et al.* showed[62] that 1,2-diphenyldiborance gives linear polymers on reaction with hexamethylenediamine, *p*-phenylenediamine, or *NN'*-diisopropylhexamethylenediamine:

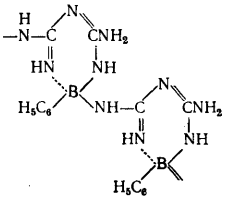


The presence of N–H bonds was shown by infrared spectroscopy and by reaction with isocyanates.

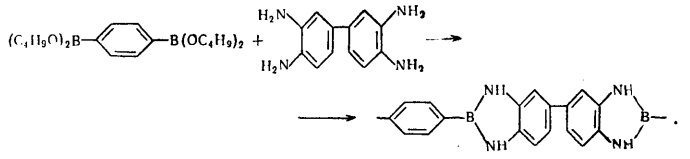
Free benzeneboronic acid can also react with diamines; with ethylenediamine it forms a brown water-soluble vitreous polymer melting at 80°.[63]

Organoboron diamines are also able to react by transamination with diamines, giving resinous products whose structure and properties have been little studied[64,65].

The transamination reaction between phenylbis(dimethylamino)boron and biguanide has been described; the infusible and insoluble polymer obtained has the structure[66]:



A very thermostable polymer has been obtained by condensing dibutyl benzene-1,4-diboronate with an aromatic tetramine as shown:



The polymer loses 25% of its weight when heated to 800° in nitrogen[67].

A solid high-molecular product, very sensitive to atmospheric moisture, has been prepared by the polymerisation of dimethylboron isocyanate $(CH_3)_2BNCO$.[68]

Linear polyboroureas have been obtained by copolymerising organoboron diamines with hexamethylene diisocyanate:

$$R'NH-\underset{R}{B}-NHR' + OCNR''NCO \longrightarrow -N-\underset{R'}{B}-\underset{R'}{N}-CONHR''NHCO-.$$

The solid vitreous products have melting points ranging from 50° to 200°, depending on the substituents on the boron and nitrogen. They are unaffected by moist air, but most are hydrolysed in boiling water[69].

The production of three-dimensional polymers of analogous structure from tri(alkylamino)borons and diisocyanates has been proposed in patents; suggested uses include the formation of films and shaped objects[70,71].

Ruigh and coworkers[72] copolymerised benzeneboronic acid with diisocyanates. Hexamethylene diisocyanate gave a hard film of poly(hexamethyleneurea), from which all the boron could be extracted by methanol in 70 hours without destroying the film.

According to other patents, free boric acid can also produce polymers with isocyanates[73]:

$$2\,H_3BO_3 + 3OCNRNCO \longrightarrow [B_2(NRN)_3H_4]_n + CO_2.$$

Most information on B–P polymers is still contained in patents. A few papers have described methods for the production of linear polymers. The pyrolysis of borane–secondary phosphine complexes first gives the linear polymer $-PR_2-BH_2-$, which on heating above 200° is almost completely depolymerised, with formation of cyclic trimers. According to Burg, this reaction is caused by the P → B donor bond from unit to unit along the whole length of the open chain of the molecule, so that at one end there should be a $R_2PH \rightarrow B$ bond, and at the other a free pair of electrons on phosphorus. At elevated temperature the donor bond may be displaced three units along the chain, and the terminal R_2P of the grouping can close the ring of the trimer[74]. With depolymerisation by such a mechanism, blocking the terminal groups with tertiary amines or phosphines suffices to render the linear polymer stable to heating above 250°.[75]

Linear and cyclic phosphinoborines have been prepared from trimethylsilylphosphine and diborane or dialkylboron halides:

$$(CH_3)_3SiPR_2 + R'_2BCl \longrightarrow (R_2PBR'_2)_n + (CH_3)_3SiCl.$$

The Si–P bond is easily broken, and many alkyl- and aryl-phosphinoborines can be obtained in high yield[76].

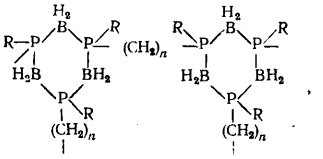
Attempts to prepare phosphinoborines by reacting the dimethylaminophosphines $P[N(CH_3)_2]_3$, $CH_3P[N(CH_3)_2]_2$, and $(CH_3)_2PN(CH_3)_2$ with BR_3, BF_3, or BCl_3 have been less successful; in most cases the corresponding complexes were not produced, but exchange took place, for instance CH_3PCl_2 and $(CH_3)_2PCl$ were obtained in the reaction with BCl_3.[77]

Burg and Brendel[78] have suggested a method for producing linear bis(trifluoromethyl)phosphinoborine $[(CF_3)_2PBH_2]_n$, which is thermally and chemically stable.

Primary phosphines have a greater tendency to form linear B–P polymers, because of the presence of hydrogen atoms on the phosphorus; Burg and Wagner have proposed methods for the production of such polymers[79], which on heating lose hydrogen and take on a cross-linked, reticular structure[80].

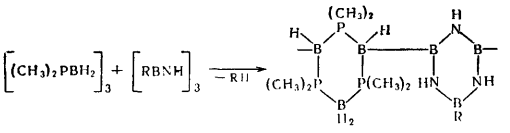
Pyrolysis of the phenyldichloroborine–phenylphosphine complex gives a polymer $[-P(C_6H_5)B(C_6H_5)-]_n$ which is thought to be linear[81]; according to patent data, this polymer melts at 142–144° and is readily soluble in alcohol[82].

Patents describe the preparation of polycyclic phosphinoborines of the type



in which the rings are joined by polymethylene or phenylene bridges; they are obtained from secondary biphosphines $HRP(CH_2)_nPRH$ and diborane or from difunctional boranes $X_2B(CH_2)_nBX_2$ and phosphines R_3P.[83]

Trimeric dimethylphosphinoborine has been condensed with *B*-substituted borazoles:



(R = C_4H_9 or C_6H_5) to give solid infusible polymers insoluble in the usual solvents[84].

It has recently been found that higher boron hydrides can be used to obtain B–P polymers of increased chemical and thermal stability. Thus Burg has prepared the polymer $\{B_2H_5(CH_3)_2P[N(CH_3)_2]_{0.4}\}_x$ by reacting pentaborane B_5H_9 with $(CH_3)_2NP(CH_3)_2$. This polymer becomes thermoplastic above 200° and is an excellent dielectric[85].

Condensation polymerisation of bis(chlorodiphenylphosphine)decaborane with bis(hydroxydiphenylphosphine)decaborane has produced a polymer of molecular weight 27 000:

$$n\,ClP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2Cl + n\,HOP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2OH + 2n\,(C_2H_5)_3N \longrightarrow$$
$$\longrightarrow [-OP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2-]_{2n} + 2n\,(C_2H_5)_3N.HCl.$$

Heating to 320° does not affect the inorganic main chain, but even at 270° hydrogen is given off (probably from the decaborane residues).

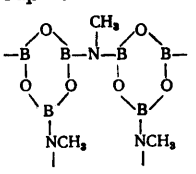
Reaction of bis(azidodiphenylphosphine)decaborane with 1,2-bis(diphenylphosphino)-ethane or -benzene also gives polymers[86]: (R = C_2H_4 or C_6H_4)

$$N_3P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2N_3 + P(C_6H_5)_2RP(C_6H_5)_2 \longrightarrow$$
$$\longrightarrow 2_nN_2 + [=P(C_6H_5)_2-R-P(C_6H_5)_2=N-P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2-N=]_n.$$

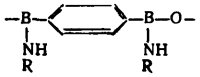
The production of phosphine–borane complexes and cyclic phosphinoborine trimers, including those substituted on both phosphorus and boron, has been described in several patents[87–91].

Boron- and halogen-containing cyclic phosphinoborines have been obtained by heating dialkylphosphinoborines with excess of alkyl halide in the presence of aluminium halides. The products are high-melting and, like the non-halogenated phosphinoborines, chemically inert[92]. The borohalogenation of polymeric phosphinoborines has been claimed[93].

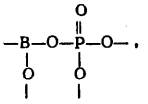
Polymers containing B–O (anhydride) bonds have been described; thus polycondensation of *BB'B"*-tri(methylamino)boroxole has given a polyboroxole, stable to heat but susceptible to hydrolysis, in which the individual rings are joined by an imino-group[94]:



Tetrabutyl benzene-1,4-diboronate condenses with amines and diamines to give high-melting air-stable polyaminopolyanhydrides[95]:

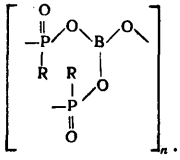


A boric and phosphoric mixed anhydride polymer, stable to hydrolysis and having the reticular boron phosphate structure:



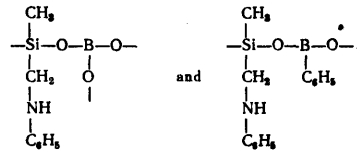
has been prepared by Gerrard and coworkers[96] by pyrolysing the complex $(RO)_3P{=}O.BCl_3$ at up to 1000°.

Phosphonic esters react with boron trichloride to produce analogous polymers which are high-melting and hydrolysed by aqueous alkali[56]:



Boric acid and its alkyl esters have been very successfully used for modifying siloxane rubbers, the anhydride bonds B–O–Si being formed[97–99]; in particular, the introduction of $-O-\underset{|}{B}-OC_4H_9$ groups improves the stability towards thermal oxidation, the elasticity, and other properties of polysiloxanes[100].

Borosiloxane elastomers can be protected against ease of hydrolysis by irradiation[101] or by the introduction of polar groups into the polymer chain; for instance, polymers containing phenylaminomethyl groups bonded to silicon are more stable to hydrolysis than poly(boro-organosiloxanes) not containing amino-groups[102,103]:



Organic boron–silicon polymers suitable as components of thermostable adhesives have been obtained by the polycondensation of boric acid with phenyltriethoxysilane and methylphenyldiethoxysilane[104].

A method has been proposed for the preparation of the vinyl-, methylvinyl-, and divinyl-polysiloxane borates of composition (for the vinyl compound) $[CH_2{=}CHSiO_3B]_n$, which are polymeric powders insoluble in the usual solvents and hydrolysed by water[105].

Polyesters of boric acid with polyols and hydroxyamines and mixed polyesters of boric and certain dicarboxylic acids have been described. The polyesters of boric acid with polyols are thermostable substances, but are not high-melting and are sensitive to hydrolysis by atmospheric moisture; they are completely hydrolysed in boiling water. The polyesters of boric acid with hydroxyamines are stable to hydrolysis, and many are soluble in water[106].

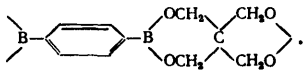
Oligomeric polyborates of aldoses, ketoses, and pentoses containing 8–10% of boron and stable when heated to 200–230° have been prepared[107].

Polyesters of boric acid with glycol or hydrogenated castor oil have been recommended as lubricants[108], and a polyester of boric acid with glycerol has been suggested as a vitreous binder[109].

Polymers from esters of polyepoxy-acids and boric acid, which are not hydrolysed by hot water, have been proposed as foam plastics and as protective and flame-resistant coatings[110].

trans-Cycloalkanediols give non-volatile polymeric esters with butaneboronic acid, but the *cis*-diols have only produced the monomeric cyclic esters[111].

Polyesters of aliphatic and aromatic diboronic acids are known, and are more stable to hydrolysis because of the intramolecular rings which they contain; thus moist air does not affect the polyester produced from benzene-1,4-diboronic acid and pentaerythritol, of the structure[112]:



Polyesters of diboronic acids with tetrakis-(2-hydroxyethyl)polymethylenediamines are completely stable to

hydrolysis and are fairly thermostable, and can be used for the production of films and fibres [113-115].

Polymers containing B–S bonds have been reported comparatively recently. These vitreous polymers of composition $(RSBH_2)_n$ (where R = CH_3, C_2H_5, and n-C_4H_9) were prepared by reacting diborane with the appropriate mercaptan. The methylthioborane polymer is stable on storage, but the ethyl and butyl compounds became converted into the corresponding trimers [116]. The polymers react with olefinic hydrocarbons to produce dialkaneborinic esters [117], *e.g.*:

$$[C_4H_9SBH_2]_x + 2xCH_2 = CH_2 \longrightarrow x\,(C_2H_5)_2\,BSC_4H_9.$$

Up to the present no commercially acceptable boron-containing polymeric materials have been described which possess the whole range of desired properties, *i.e.* more stable to heat than purely organic compounds, satisfactorily stable chemically and to hydrolysis under conditions of use, and suitable for fabricating or for direct use. Most of the known polymeric boron compounds are solid, thermostable (but infusible), insoluble materials which are not workable, and they are also insufficiently stable towards hydrolysis. However, there are no grounds for doubting that polymers could be obtained which satisfy all these basic demands. This is indicated by the ability of boron atoms to form stable covalent bonds with O, N, P, C, and H atoms and with other boron atoms, the ease of formation of coordination bonds, as a consequence of the high electron unsaturation, and the tendency to form numerous cyclic structures, which is due to the valency characteristics of boron. These are favourable indications that thermostable polymers could be produced. The ease of hydrolysis may be suppressed by making use of donor–acceptor bonds, cyclisation, and steric factors.

Organoboron polymers will probably find wide application. Polymers with a high boron content, for example those based on higher boron hydrides, may be of use as protective media against irradiation by slow neutrons. The thermoplastic linear polymers consisting of linked boroxole, borazole, or phosphinoborine rings can be used for the production of fibres, films, coatings, and adhesives, and, because of their high adhesion to glass, as compositions in heat-resistant glass–plastic materials. Polymers which can form reticular structures may be used as thermally reactive binders, for example in Triplex. Trimeric cyclic and polymeric phosphinoborines are of value as high-quality dielectrics.

There is much significant material on boron-containing polymers in previously published reviews and monographs [6,36,61,75,118-120].

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COMPOUNDS WITH CONJUGATED DOUBLE BONDS

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I. INTRODUCTION

The term "compound with conjugated double bonds" applies to a wide variety of organic substances, both monomeric and polymeric, and showing large differences in physical and chemical properties. We shall use it to describe a compound containing a fairly large number of carbon–carbon double bonds alternating with single bonds. The double bonds may include hetero-atoms, *i.e.* atoms with free electron pairs (such as N, O, S), without perturbing the conjugated system. These substances are intensely coloured, have a relatively high electrical conductivity, and show anomalous magnetic properties (electron paramagnetic resonance signals and static paramagnetism). We may arbitrarily classify these compounds into two general groups: 1) polymers with conjugated bonds and hetero--atoms in the conjugated chain, and 2) organic dyes. The second group includes polynuclear aromatic hydrocarbons, although these do not give an electron paramagnetic resonance signal.

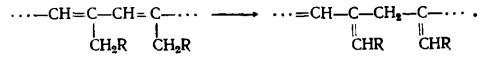
The special magnetic and electrical properties of polymers and other compounds with conjugated double bonds have received attention from many investigators in recent years[1–5]. In this review an attempt is made to expand systematically the results of the various investigators in this field, but monomeric or polymeric chelate compounds[6], polymers with a chain of metal atoms, or recently synthesised (and of independent interest) polymers with conjugated triple bonds[7] will not be considered here.

II. METHODS OF PREPARATION

The preparation of dyes has been reviewed recently[8,9]. Polymers with conjugated double bonds are prepared by a variety of methods, the most important of which are listed below.

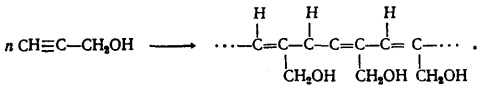
Polymerisation of acetylene hydrocarbons. Acetylene can be polymerised to give a system of conjugated bonds by various catalysts: aluminium ethoxide containing $TiCl_4$, titanyl or vanadyl acetylacetonates[10–12], sodium tetrahydroborate with a nickel halide[13] or an organophosphorus complex[14]. Polymerisation occurs between +80° and -80°; the number of units in the black, insoluble polymers is 12–15. Benzene is also formed in good yield.

The aliphatic homologues of acetylene undergo an analogous polymerisation[15], but they do not give conjugated systems, probably because of the isomeric rearrangement.



This type of rearrangement has also been reported in poly(cyclohexylacetylene) prepared by thermal polymerisation[16].

The polymerisation of acetylene can be induced by radiation at very low temperatures, giving a brown *cis*-polymer in the liquid phase and a dark red, insoluble *trans*--polymer in the solid phase[17]. Radiation polymerisation of propynol in the liquid or solid phase produces a dark red *trans*-polymer:



Phenylacetylene can be polymerised either by heating in an argon atmosphere or in the presence of air[18,19] for 6–12 h, or in the presence of a catalyst[19,20] at 80°. Initiators have little effect on the yield of the polymer, which does not exceed 30%. According to the polymerisation temperature used (150–400°), the resulting polymers vary in colour from yellow to black, the molecular weight also increasing with the depth of colour. The yield of polymer increases very significantly at polymerisation pressures of 98 and 588 MN m^{-2}†, reaching 66–67% at temperatures as low as 120°. The mean molecular weight of the polymer[21] can reach 1200. Alternatively, the yield of polymer can be increased by raising the polymerisation time to 18 h or by heating in solution in xylene or chlorobenzene

† 98 066.5 N m^{-2} = 1 kgf cm^{-2}, in accordance with the SI international system of units [for the SI system see Russ.J.Inorg. Chem., 8, 1481, 1484 (1963) (Ed. of Translation)].