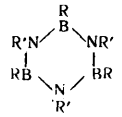
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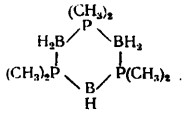
POLYMERIC COMPOUNDS OF BORON

V. A. Zamyatina and N. I. Bekasova

Little information is available in the scientific and patent literature about polymers of boron, although it is known[1] that they are of great importance because of their resistance to heat and the action of hydrocarbons. Of special interest are polymers containing in the main chain atoms of boron and nitrogen, –B–N–B–N–, or boron and phosphorus, –B–P–B–P–[2], although up to the present the only systematic descriptions of such compounds which have been published are of cyclic representatives with low molecular weights, namely the borazoles,



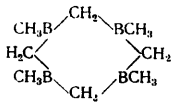
(where R and R′ can be H, alkyl, or aryl), and the phosphinoborines,



Very little is as yet known about linear polymers whose molecular chains consist of atoms of boron and nitrogen or of boron and phosphorus. In most cases the properties of polymeric compounds of boron have been inadequately described, and often no information is given on their molecular weight, melting points, solubility, or resistance to oxidation and hydrolysis. In addition to work on the preparation of polymeric compounds containing boron, the following review covers also investigations concerned with

monomeric compounds of boron during the course of which the formation of polymers has been observed.

Polymers containing B–B bonds in the main chain are unknown, apart from the polyboranes [3], although the possibility of their preparation has been suggested [4,5]. Only a few organic polymers whose main chain consists of boron and carbon atoms are known. Thus Goubeau and Epple [6], who heated trimethylboron in an autoclave to 400°–600° and observed the elimination of methane, obtained, in addition to 1,3,5,7-tetramethyl-1,3,5,7-tetraboracyclooctane,

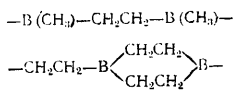


a coloured solid of the composition $(B_2C_3H_6)_x$. At 600° it splits off further methane and hydrogen, forming a polymer of the empirical composition $(BCH_2)_x$, to which these workers ascribe a cross-linked structure. The disproportionation of other trialkylborons is also accompanied by the formation of polymers; thus tri-n-hexylboron on being boiled under reflux undergoes the following reaction:

$$x\mathrm{B(C_6H_{13})_3} \rightarrow [\mathrm{B(C_6H_{13})}]_x + 2x\mathrm{C_2H_{12}} + x\mathrm{H_2}.$$

The polymer $[B(C_6H_{13})]_x$ proved to be a mixture of solid substance having the composition $[BHB(C_6H_{13})]_x$, containing 20% of boron, and a liquid $[B_2(C_6H_{13})_2(C_6H_{12})]_x$ with a molecular weight of ~600 [7].

Schlesinger *et al.* [8] obtained a quantitative yield of *B,B'*-tetrachloroethylenediborine $Cl_2BCH_2CH_2BCl_2$ by the action the action of ethylene on tetrachlorodiborane. On treatment with dimethylzinc, this compound is converted into the corresponding *B,B'*-tetramethyl compound, $(CH_3)_2BCH_2.CH_2B(CH_3)_2$, which on pyrolysis splits off trimethylboron to form vitreous polymers of the type



Pyrolysis of the original *B,B'*-tetrachloroethylenediborine yields hydrogen, methane, ethane, boron, trichloride, and a solid polymeric boron subchloride $(BCl)_n$ [9]. Similar observations have recently been published by Holliday and Massey [10].

By heating the tetrahydrofuran compound of triphenylethynylboron, Krüerke [11] isolated a reddish-violet polymeric solid stable to the action of water:

$$\mathrm{B(C{\equiv}CC_6C_5)_3.OC_4H_8} \xrightarrow{85^\circ} \mathrm{C_4H_8O} + \text{polymer}.$$

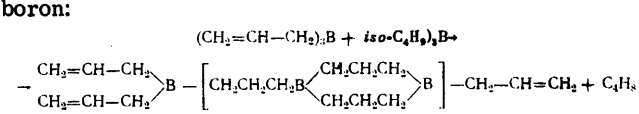
Its molecular weight and structure were not determined.

The formation of polymeric products was observed also in the synthesis of bisdi-n-butylborylacetylene $(n\text{-}C_4H_9)_2B\text{–}C{\equiv}C\text{–}B(n\text{-}C_4H_9)_2$. [12]

Pyrolysis of diphenylboron chloride in the presence of aluminium chloride yielded a solid polymer which did not melt below 300° [13]. The pyrolysis was accompanied by the formation of an equivalent amount of benzene:

$$m(\mathrm{C_6H_5})_2\mathrm{BCl} \rightarrow \mathrm{C_6H_5(BClC_6H_4)}_{m-1}\mathrm{BClC_6H_5} + (m-1)\mathrm{C_6H_6}.$$

During the sublimation of boron tricyanide $B(CN)_3$, Chaigneau [14] observed the formation of a polymer which became darker at 130°. The action of an electric discharge on a mixture of boron trichloride and carbon monoxide led to the formation of a polymeric film with a softening temperature of 115° [15]. Mikhailov and Tutorskaya [16] observed the formation of polymeric derivatives of 1,5-diboracyclooctane by the interaction of triallylboron and triisobutylboron:



The polymer formed a gelatinous mass, which was swollen by ether and benzene. The same workers noted that the anhydride of 2-propeneboronic acid can be polymerised by slow distillation [17]. Topchiev *et al.* suggested a new method for synthesising triallylboron and trivinylboron [18]. They investigated the chemical changes undergone by these compounds, and proposed using the resulting monomers, in particular 2-propeneboronic esters, as starting materials for the synthesis of boron-containing polymers [19].

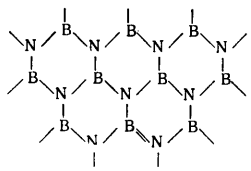
Normant and Braun synthesised substituted ethyleneboronic and ethyleneborinic acids of the types $>C{=}C(\text{–})\text{–}B(OH)_2$ and $(>C{=}C(\text{–})\text{–})_2BOH$ and a substituted trivinylboron, $(>C{=}C(\text{–})\text{–})_3B$. They note that compounds containing the vinyl groups $CH_2{=}CH\text{–}$ and $CH_2{=}C(CH_3)\text{–}$ rapidly polymerise in the air [20]. β-Chloroethyleneboronic acid, which has been known for some time [21,22], is recommended for copolymerisation with vinyl monomers [23].

The synthesis of *p*-vinylbenzeneboronic acid, its esters, and its anhydride has been described. These compounds polymerise readily in the presence of the ether compound of boron trifuloride and of peroxides, as well as in the liquid state [24,25]. Lennarz and Snyder report that the polymer of *p*-vinylbenzeneboronic acid is a white powder slightly soluble in aqueous alkali; it does not melt below 300°, but at 300°–350° it decomposes slightly and darkens [26]. Bis(*p*-vinylbenzene)borinic acid $(CH_2{=}CHC_6H_4)_2BOH$ was copolymerised with styrene and other vinyl compounds; the resulting insoluble resins could be used to extract aminoethyl alcohol from solutions. It was readily regenerated in aqueous media, releasing free aminoethyl alcohol [27].

Considerably more work has been published describing polymers containing B–N links in their structure. The simplest polymer of boron and nitrogen is boron nitride, which has been known for a long time. Wöhler and St. Deville [28] as well as Moissan [29] established that boron combines with nitrogen at 1230° to form a white solid having the composition BN. This compound can be obtained also by the action of urea [30] or ammonia [31] on boron trioxide at red heat. The purest boron nitride is obtained by the pyrolysis of boron imide $B_2(NH)_3$ [32], as well as by the action of ammonia on boron tribromide [33] or trichloride [34]. Soviet investigators have suggested preparing boron nitride by the action of ammonia on boric acid in the presence of ammonium chloride at 1200° [35]. The kinetics of the formation of boron nitride by the action of nitrogen on elemental boron have been studied by Sleptsov and Samsonov [36].

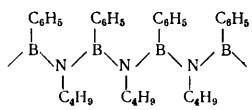
Boron nitride is a white powder melting at about 3000° under pressure; it is slowly hydrolysed on boiling with water, forming boric acid and ammonia; like graphite it

has a hexagonal structure:



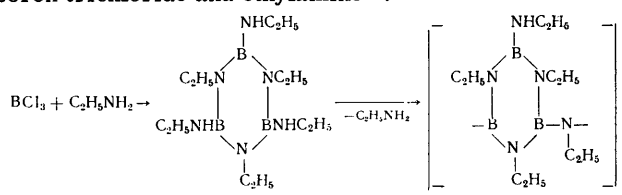
Until recently boron nitride found no great practical use. However, interest in this compound increased rapidly when it became known[37] that the hexagonal form passes into a cubic form on heating to 1800° under a pressure of 85 000 atm, the change being from a solid resembling graphite to a hard crystal surpassing diamond in mechanical strength. Cubic boron nitride withstands heating to 2000°, being only slightly oxidised at the surface; it is a good dielectric.

Numerous attempts to prepare a linear polymer with a main chain consisting of boron and nitrogen atoms have generally led to the formation of the cyclic trimer borazole. However, a polymer of this type has now been prepared by Gerrard. Using phenylboron dichloride and n-butylamine or isobutylamine as starting materials, he was able to prevent ring formation by steric hindrance, and obtained a linear polymer containing 20–40 atoms of boron and nitrogen in the chain:

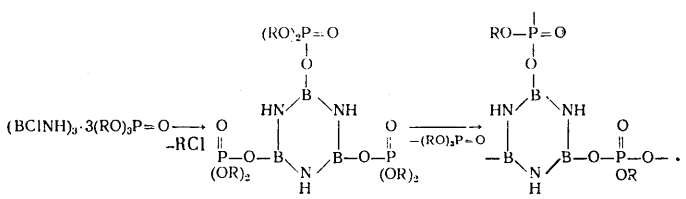


This polymer melts at about 150°, and remains stable on heating to 400°, but is readily hydrolysed[38].

The view has been expressed[1,39,40] that borazole and its *N*- and *B*-substituted derivatives, being very heat-resistant substances, might be used to synthesise polymers of high melting point which are heat resistant. Hexaphenylborazole, for example, melts at 413°–415° without decomposition[41–43]. Some polymers of this type have already been obtained; Lappert obtained a brittle substance of high melting point, sensitive to hydrolysis, by the interaction of boron trichloride and ethylamine[44]:

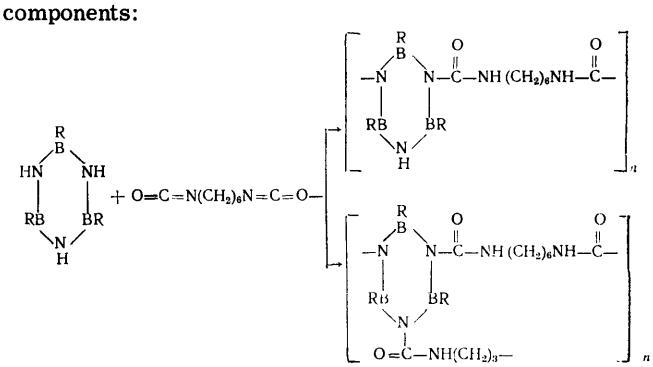


Analogous syntheses have been described by other workers[45,46]. A similar type of polycondensation is the elimination of alkyl chloride and alkyl phosphate from the complex of trichloroborazole with a trialkyl phosphate:



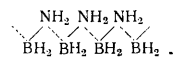
The poly(alkyl borazole orthophosphate) which is obtained does not dissolve in the usual organic solvents, is slowly hydrolysed in water, and is stable up to 400°. At higher temperatures breakdown of the borazole rings occurs[38].

Another type of condensation is observed on the prolonged heating of *B*-trichloro-*N*-triphenylborazole to 600°. This compound loses nearly all its chlorine as hydrogen chloride and is converted into a brittle black substance stable to the action of sulphuric acid, alkali, and hydrogen peroxide[38]. Korshak *et al.*, by the migration copolymerisation of *B*-substituted borazoles with hexamethylene diisocyanate, obtained a series of copolymers of linear or three-dimensional structure depending on the proportions of the components:



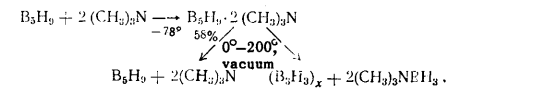
The copolymers are transparent vitreous substances with softening temperatures depending on the nature of the substituent attached to the boron[47].

In a study of the reaction of diborane with ammonia, Burg *et al.*[48], as well as other investigators[49,50], obtained in addition to borazole an insoluble solid with the composition $(BNH_4)_x$, which may possibly have the structure

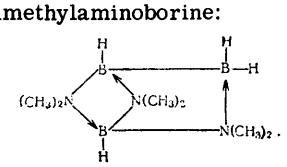


This polymeric aminoborine was isolated also by Schaeffer and Basile[51] when studying the reaction between lithium amide and diborane. The properties of the polymer were not described. However, no mention is made of this polymer in subsequent papers either by these authors or by other investigators; and it is possible that its linear structure has not been confirmed[52]. Pyrolysis of the complex of borazole with methanol led to the isolation of a polymeric material with a composition close to $[(CH_3O)BNH]_x$ together with trimethoxyborazole[53].

With the aim of preparing aminopolyboranes, Burg[54] investigated the reaction of pentaborane with trimethylamine, which can be represented by the scheme



The polymer $(B_3H_3)_x$ includes a small amount of excess trimethylamine which, in Burg's opinion, is responsible for its thermoplastic properties above 100°. At ordinary temperatures the polymer is a hard and brittle material in conformity with its cross-linked structure. Burg studied also the reaction between pentaborane and bisdimethylaminoborine, $[(CH_3)_2N]_2BH$, which yields, together with other products, triaminotriborane, a coordination compound consisting of one molecule of dimethylaminodiborane and a molecule of bisdimethylaminoborine:



Triaminotriborane melts at 95°, boils at 220°, and remains unchanged on being heated to 300°. On being heated to 360°, it becomes still more stable, and apparently polymeric. Zhigach *et al.* investigated the pyrolysis of the complex of pentaborane and di- and tri-alkylamines, and found that formation of alkylamino derivatives of diborane and borine is accompanied by that of a solid polymer containing B, H, C, and N [55].

Goubeau and Zappel[56], heated trimethylboron with ethylenediamine and trimethylenediamine in sealed tubes to 250°. In addition to cyclic borazans and borazens, they obtained polymeric oils and solids soluble in water with decomposition. On further heating these were converted into a vitreous mass unaffected by air, water, or acids. These authors write the reaction as follows:

$$2(CH_3)_3B + NH_2CH_2CH_2NH_2 \xrightarrow[250°]{-2CH_4} (CH_3)_2B{=}NHCH_2CH_2NH{=}B(CH_3)_2 \xrightarrow[-2CH_4]{450°} \text{polymer}.$$

It has been reported also that a vitreous polymer having the composition C_3H_7NBH, which is stable in the air, can be obtained by heating monoisopropylaminoborine to 300° [57]. This polymer does not dissolve in water or dilute acids, and is a good dielectric. The results in the earlier patents[58,59], which describe the preparation of boron-containing resins by heating boric or phenylboronic acid with diisocyanates in a non-aqueous solvent, were not subsequently confirmed[60]. The resins proved to be formed by reaction of the diisocyanates with the water eliminated by the dehydration of the boric or boronic acids, and contained boron only as impurity.

Unusually high thermal stability is shown by organic boron–phosphorus polymers, which have been prepared and investigated by Burg and his collaborators[61]. By the interaction of diborane and dimethylphosphine, they obtained a cyclic trimer, $[(CH_3)_2PBH_2]_3$, which is stable up to 400° and is very inert chemically. According to Burg[62], the great thermal stability of such compounds is explained by the boron–phosphorus bond being strengthened by some interaction between the electrons of the B–H bond and neighbouring phosphorus atoms. In an attempt to strengthen this delocalisation of electrons, Burg and Brendel[63] replaced the methyl groups attached to the phosphorus by the more electronegative fluorocarbon groups. The stronger inductive effect was accompanied, however, as these authors had foreseen, by a weakening of the ordinary σ bond between boron and phosphorus, which resulted in the weakening of the ring. The trimer and tetramer of bis(trifluoromethyl)phosphinoborine $(CF_3)_2P.BH_2$, obtained by these workers, were stable only up to 200°; above this temperature pyrolysis occurred with the formation of BF_3, H_2, and solids containing no boron.

In his later work[64] Burg evidently obtained both cyclic and linear polymers starting from the borine complexes of tetramethyldiphosphine. Pyrolysis of the diborine complex $(CH_3)_4P_2.2BH_3$ (170°–200°) gave a 75% yield of the cyclic trimer $[(CH_3)_2P.BH_2]_3$ and a 15% yield of the polymer $[(CH_3)_2PBH_2]_x$. The monoborine complex $2(CH_3)_4P_2.2BH_3$ under similar conditions eliminated hydrogen and dimethylphosphine to form cyclic trimers and tetramers in 42.3% yield. The thermoplastic white residue was stable up to 300°, but when heated at 330° for 20 h, it was largely converted into the trimer and tetramer. In an attempt to increase the yield of polymer, Wagner and Caserio[65] carried out the pyrolysis in the presence of triethylamine (10% and more). They put forward the following reaction scheme:

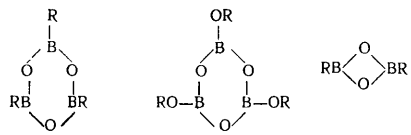
$$(CH_3)_2HP{\cdot}BH_3 \xrightarrow{200°} (CH_3)_2PBH_2 + H_2\,,$$
$$(CH_3)_2PBH_2 + (C_2H_5)_3N \rightarrow (CH_3)_2P{\cdot}BH_2{\cdot}N(C_2H_5)_3\,,$$
$$(CH_3)_2PBH_2{\cdot}N(C_2H_5)_3 + n\,(CH_3)_2PBH_2 \rightarrow [(CH_3)_2PBH_2]_n(CH_3)_2P{\cdot}BH_2{\cdot}N(C_2H_5)_3.$$

The end group of the triethylamine complex is not conducive to cyclisation, and the yield of polymer was therefore increased to 49%. Its molecular weight was 6000, and its melting point 170°. These workers ascribe a linear structure to the polymer; they regard a macrocyclic structure with an eighty-membered ring as improbable.

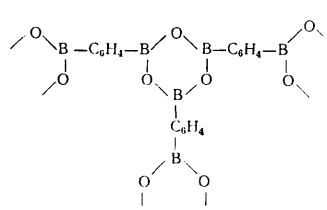
In 1959 a patent was granted to Burg and Slota in which they proposed to obtain cyclic phosphinoborines by heating disubstituted phosphinyl chlorides with sodium tetrahydroborate in the dimethyl ether of diethylene glycol[66]. These starting materials are considerably more readily available and more convenient to handle than phosphines and diborane. Detailed investigations in this field have already been described[67]. Burg studied also the reaction of pentaborane with trimethylphosphine, aminophosphines, and diphosphines. He obtained several transparent polymers of complex composition, which after removal of volatile impurities were found to be high-melting and thermostable[68].

Polymeric compounds containing boron–oxygen links in the main chain include polyanhydrides and polyesters. These materials are very stable to heating, but the overwhelming majority of them are readily hydrolysed, which hinders their practical application. Synthetically they form the most easily accessible and the cheapest class of boron-containing polymers, and therefore research in this field is being tenaciously pursued. Individual representatives of this group which are quite stable to hydrolysis have been obtained.

Boron oxide is a polymer[69], vitreous B_2O_3 having a tetrahedral structure. Linear polyanhydrides containing a $-\overset{|}{B}-O-\overset{|}{B}-O-$ chain, resembling the chain of siloxanes, have not yet been obtained. The anhydrides of alkane- and arene-boronic acids or of alkylboric acids ["*O*-alkyl-" (Ed. of Translation)], the boroxoles, are usually cyclic trimers or dimers [70–75]:

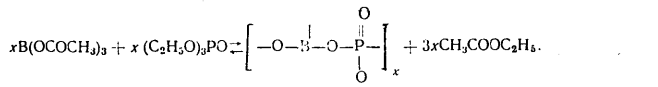


Boroxoles are very stable to heating. Thus, for example, tri-n-butylboroxole, which boils at 259°, remains unchanged on being heated to 600°. Above this temperature it evolves ethylene and gives a non-volatile product containing $>BCH_2\text{-}CH_3$ groups [76]. The action of heat on benzene-1,4-diboronic acid yielded a polymeric anhydride with the structure

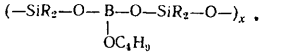


It does not melt, does not sublime, and remains unchanged on being heated in air to 350° or in a vacuum to 450° [77]. A similar polymer was obtained from benzene-1,3-diboronic acid [78].

An infusible but strongly hygroscopic and readily hydrolysed mixed polyanhydride of boric and phosphoric acids obtained by the reaction of boron triacetate with triethyl phosphate has been described [79]:



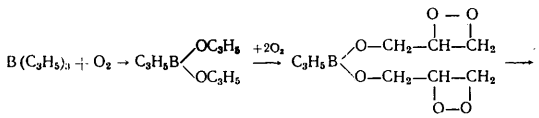
Heterofunctional polycondensation of alkyl- or aryl--dialkoxysilanes with triacetoxyboron, and of alkyl- or aryl-diacetoxysilanes with butyl borate, yielded organoborasiloxanes, the molecular chains of which contained silicon, oxygen, and boron [80]:

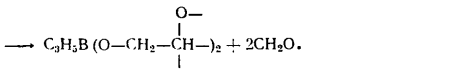


These polymers are stable on heating, but are readily hydrolysed by water with the formation of boric acid and an organosilicon polymer. Other investigators [81,82] have also studied the preparation of such polyanhydrides.

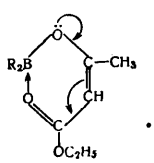
Polyesters of boric and substituted boric acids have been known for a comparatively long time, being readily prepared by simple esterification or "transesterification". Several of them are used as adhesives, plasticisers, and textile sizes. Reaction of ethyl borate with methylene glycol diacetate yielded polyborylformal [83], a solid which hydrolyses in the air. Similar instability in the presence of moisture is shown by poly(ethylene glycol borate) [84,85], the polyester obtained by heating glyceryl borate in a vacuum [86], and by the products of the polycondensation of boric acid with catechol, resorcinol, and pyrogallol [87,88].

Topchiev *et al.* [89] obtained a branched polyester of 2-propeneboronic acid by the oxidative polymerisation of triallylboron:



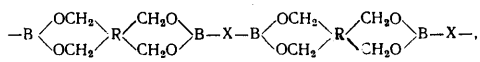


A polyester resistant to hydrolysis was synthesised by Kamenskii *et al.* [90] by condensing trisdiacetonyl borate with furfural. After being hardened in the presence of alkali, the polymer did not melt below 400°. The resistance of this polyester to the action of water may be explained by the formation of a coordinate link between the carbonyl of the diacetonoxy group and a boron atom. An example of this type of stability is provided by the esters formed by dialkylborinic acids with ethyl acetoacetate [91]:

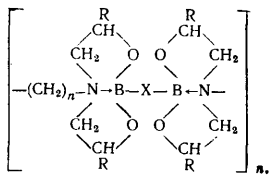


A broad investigation of the hydrolysability of boric esters was carried out by Steinberg and Hunster [92]. They synthesised a large number of alkyl and aryl borates, including many for the first time, and studied their rates of hydrolysis in water and in aqueous dioxan. These workers derived several rules which could be utilised in the synthesis of polyesters of boric acid.

Several new polyesters are described by Bamford and Fordham [93], some of which are quite stable in moist air. Polyesters of *p*-phenylene- and polymethylene-diboronic acids with pentaerythritol and tetrakishydroxymethylcyclopentanone of general formula



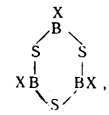
are infusible and stable to heat and hydrolysis when X = = p-C_6H_4. If, however, X = $[CH_2]_n$, fibre-forming polyesters obtained are of relatively low melting point and less resistant to hydrolysis. Chelate polyesters of diboronic acids with tetrakishydroxyalkylated polymethylenediamines have also been described:



When n = 2, R = CH_3, and X = p-C_6H_4 the polyester remains unchanged in boiling water, and darkens slightly on being heated to 300°. The intramolecular coordination between boron and nitrogen atoms in this polymer is probably responsible for its great stability to the action of water [94].

Several hydroxylated carbon-chain polymers modified with boric acid are known, *e.g.* poly(vinyl borate) [95], and the products obtained by the reaction of boron oxide with hydroxylated polymers of conjugated dienes or hydroxylated natural rubber [96]. These products are employed in the manufacture of moulding powders, sealing compounds, and varnishes.

Polymeric compounds of boron containing sulphur and arsenic have been obtained. Thus the reaction between diborane and hydrogen sulphide yielded a polymer of composition $(BHS)_n$, containing the B–S bond and probably having a linear structure. It forms a colourless transparent film, readily hydrolysed by water [97]. Wiberg and Sturm [98,99] synthesised several cyclic borasulpholes with the structure



where X = H, Cl, Br, OCH_3.

Pyrolysis of the addition product of diborane and dimethylarsine yielded trimers, tetramers, and polymers having the composition $[(CH_3)_2AsBH_2]$, analogous to phosphinoborines, but less stable to heat and chemical reagents [100].

The above brief review of polymeric compounds of boron shows that this branch of high-polymer chemistry has only just begun to evolve. Synthetic methods have been little

developed, the properties of the polymers are not always described, and the polymers themselves are rarely available, since many of them have been prepared only in gram quantities. The requirements of modern technology, however, demand that research shall be continued on the polymeric compounds of boron, as theoretical considerations suggest that it may be possible to make materials of high melting point, which are stable to heat and to chemical agents. The most promising compounds are evidently the phosphinoborines, which are expected to have good mechanical properties.

Polymers containing borazole rings in the main molecular chain will probably have very rigid three-dimensional structures. It would appear from individual examples that linear polymers containing −B−N− and −B−P− chains do not have high melting points, are less heat resistant, and in the case of phosphinoborines tend to change into cyclic compounds of low molecular weight at high temperatures.

The properties of polymers containing the −B−C− bond have hardly been described at all; the fundamental disadvantage of many of them is the readiness with which they are oxidised by atmospheric oxygen. Although the polyanhydrides and polyesters of boric and substituted boric acids show a general tendency to be readily hydrolysed, isolated representatives of these polymers are completely stable both to hydrolysis and to oxidation and the action of high temperatures.

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THE CHEMISTRY OF RARE-EARTH AND ACTINIDE SULPHIDES

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INTRODUCTION

The rare-earth and actinide sulphides are of interest on account of the combined effects on the outer *s* and *d* electrons (in the metal) of the electronegative sulphur atom and of the incomplete metal 4*f* and 5*f* orbitals, which are themselves unable to take part in bonding. As a result, the bonds in these compounds are always heterodesmic and sometimes even predominantly ionic, rather than covalent or metallic, and this leads to important and useful physical properties. Sulphides with metallic bonding and structure have the hardness, high melting point, and large heat of formation characteristic of interstitial compounds. Those rich in sulphur have semiconductor properties and relatively low melting points, are less hard, and dissociate more readily on heating in a vacuum. Some sulphides, inert to molten metal, are used as refractory materials; others will be used as high temperature semiconductors, large resistances, and anti-emission materials. This article reviews the electronic structure, chemical and physical properties, and applications of these compounds, in order to facilitate further study of them.

STRUCTURE AND PROPERTIES

The rare-earth and actinide sulphides have the general formulae MS, M_5S_7, M_3S_4, M_2S_3, and MS_2; the rare earths and plutonium form oxysulphides M_2O_2S, and the remaining actinides form oxysulphides MOS. These resemble sulphides in their properties, structure, and bonding. X-Ray investigation of the structures of the lanthanum, cerium,