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POLYCARBORANES

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Great progress has recently been made with polymers containing boron, and several reviews of this work have appeared[1-5]. The polymer chemistry of boron has recently been enriched with a new class of compounds—the so-called polycarboranes.

Carboranes—products of the reaction between decaborane and acetylenic compounds—are obtained via the intermediate product in the interaction of decaborane with Lewis bases (nitriles, amines, amides, isocyanates), with subsequent displacement of the base by the action of acetylene and its derivatives:

$$B_{10}H_{14} + 2CH_3CN \longrightarrow (CH_3CN)_2B_{10}H_{12} + H_2$$

$$(CH_3CN)_2B_{10}H_{12} + RC{\equiv}CR' \longrightarrow RC\!-\!CR' + 2CH_3CN + H_2 .$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \diagdown B_{10}H_{10} \diagup$$

The formation of carborane derivatives was described simultaneously by Soviet[6,7] and by American[8-18] research workers.

X-Ray examination as well as theoretical calculations of possible structures of several carboranes[19-25] suggest that a system of ten boron atoms is combined with two carbon atoms to form an icosahedron in which the C–C σ-bond is oriented at right angles to the plane of the 6,2,4,9-positions of the boron atoms in the decaborane unit (Fig. 1). In conformity with the recommendation of the Committee on Nomenclature of the Division of Inorganic Chemistry of the American Chemical Society[26] the name "carboranes" is used to denote compounds containing the system



in which the carbon atoms are regarded as heteroatoms and are numbered 1 and 2.

When carborane is heated above 475°C [18] it isomerises into a new compound, which has been termed "neocarborane". It is assumed that the thermal isomerisation involves transformation of the icosahedral structure with a strained C–C bond into the stable regular structure of neocarborane, which is free from strain. In such an icosahedral structure the carbon atoms are completely analogous to the boron atoms, and form three-centre bonds

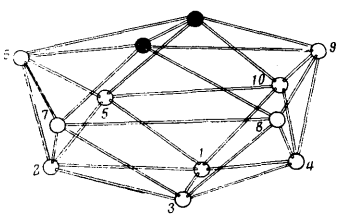


Fig. 1. Structure of the carborane molecule.

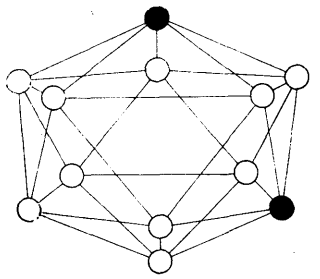


Fig. 2. Structure of the neocarborane molecule.

with the nearest boron atoms (Fig. 2). Neocarboranes resemble carboranes in their properties. However, the infrared spectra differ markedly (Fig. 3), as also certain physical and chemical properties (lower polarity, lower melting points, inability to form cyclic compounds, etc.).

Comparison of the infrared spectra of neocarborane and carborane reveals considerable differences in the range 1250–900 cm^{-1}. The high peak at 1212 cm^{-1} characteristic of carborane is completely absent from the spectrum of neocarborane. The bands in the region of 1149, 1043, 1015, and 995 cm^{-1}, which are characteristic of carborane, disappear from the spectrum of neocarborane, and new bands appear in the region of 1158, 1069, 1022, and 991 cm^{-1}.

Carborane derivatives can be prepared both from acetylenic compounds and also by converting some carborane derivatives into others. A series of monomers have been obtained based on carboranes (diols, dicarboranic acids, dichlorides, diesters, di-isocyanates, vinyl derivatives, acrylates, epoxides, silanes, etc.), which are used for the preparation of various carborane polymers[9,11,12,14-17].

The present paper describes methods for obtaining various polymers of carborane, and also their properties.

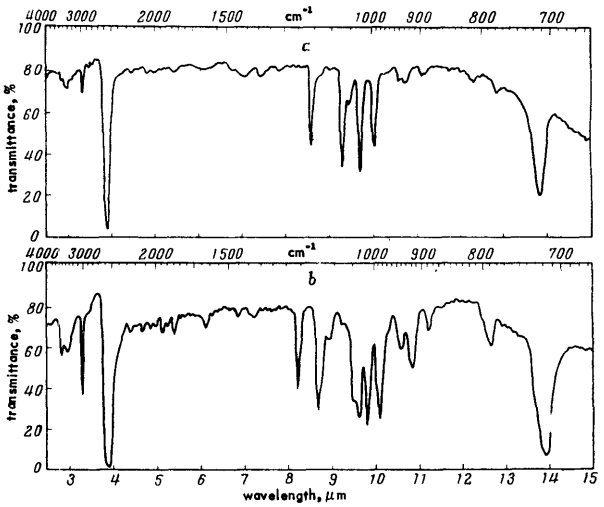
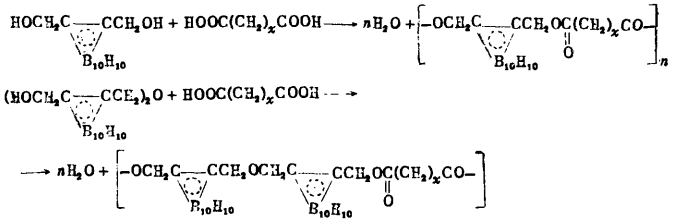


Fig. 3. Infrared spectra of: *a*) neocarborane; *b*) carborane.

Among the polymers of carborane which have been described, the polyesters are widely represented in the literature[27-29]. Numerous carborane derivatives[27]—diols, acids, acid chlorides, esters—have been used for the synthesis of polyesters. The latter has been accomplished by the polycondensation of organic and fluorinated organic diols of carborane with dibasic acids or with their chlorides. Polyesters of molecular weight 2000–3000 have been prepared by the polycondensation of carboranediols with various dicarboxylic acids or chlorides:



The polymers obtained and their properties are listed in Table 1.

TABLE 1. Properties of carborane polyesters.

Diol	Dibasic acid	Properties of polyesters		Ref.
		M*	m.p., °C	
$HOCH_2C(B_{10}H_{10})CCH_2OH$	HOOC—COOH	1160	brittle, softens at 72–74°C	29
ditto	HOOC—CH_2—COOH	1530	brittle, softens at 63–66°C	29
»	HOOC—$(CH_2)_2$·COOH	2600	brittle, flows at 90–91°C	28
»	$HOOC(CH_2)_3COOH$	3600	flows at 63°C	27
»	ditto	3600	plastic, flows at 78°C	28
»	$HOOC(CH_2)_4COOH$	2650	flows at 66°C	28
»	ditto	3000	plastic, flows at 81°C	27
»	$HOOC(CH_2)_7COOH$	2300	viscous liquid (88 P) at 100°C	28
»	ditto	3200	flows at 22°C	27
»	$HOOC(CH_2)_8COOH$	2400	viscous liquid (78 P) at 100°C	27
»	ditto	3200	flows at 28°C	28
»	$ClOC(CH_2)_2COCl$	1907	vitreous substance	27
»	$ClOC(CH_2)_4COCl$	2040	amber-coloured plastic	27
	$ClOCC_6H_4COCl$	—	brittle, softens at 270°C	27
$HOCH_2C(B_{10}H_{10})CCH_2OH$	$HOOC(CF_2)_2COOH$	2500	61°C	26
ditto	$HOOC(CF_2)_3COOH$	3000	50°C	28
»	$HOOC(CF_2)_4COOH$	3400	55°C	28
»	$ClOC(CF_2)_3COCl$	2540	plastic, flows at 57°C	27
$(HOCH_2C(B_{10}H_{10})CCl_2)_2O$	$ClOC(CF_2)_3COCl$	960	brittle, melts at 200°C	27
	$ClOC(CF_2)_8COCl$	1600	softens at 74°C	27
$(HOCH_2CH_2C(B_{10}H_{10})CCH_2)O$				
ditto	$HOOC(CH_2)_2COOH$	2800	hard, brittle, softens at 90°C	27
»	$ClOC(CH_2)_4COCl$		hard, brittle, flows at 70°C	27
»	$HOOC(CH_2)_8COOH$		brittle, 200 P at 100°C	27

* Molecular weight determined by cryoscopic or precision ebullioscopic methods.

Inspection of the melting points of the carborane polyesters has revealed (though not very clearly, because of the incompleteness of the homologous series) the "evenness factor" discovered by Korshak and Vinogradova[30], consisting in the fact that polyesters of polymethylenedicarboranic acids having an odd number of carbon atoms melt at lower temperatures than both compounds of the polyester having an even number of carbon atoms in the molecule. This phenomenon is explained by polar effects in the dicarboxylic acid and diol molecules.

Examination of Table 1 shows that the replacement of CH_2 by CF_2 groups also lowers the softening point of a carborane polyester.

The carborane group consists of a sphere of effective van der Waals radius 4 Å. It is strongly electrophilic. Difficulties arising in the synthesis of the polymers and the properties of the products are determined both by steric and by electronic factors.

The effect of the carborane group on the properties of the polymers was studied on the polyadipates[31] obtained by the polycondensation of adipic acid with 1,2-bishydroxymethylcarborane, butane-1,4-diol, and butyne-1,4-diol. The first of these products was a viscous liquid, exhibiting no tendency to crystallise. The analogous organic polymers of equivalent molecular weight were crystalline waxes. Hence it can be concluded that the carborane group impedes the dense packing of the molecules and the subsequent crystallisation of the polymer. Investigations have shown[27] that the polyesterification of carboranediols proceeds considerably more slowly than that of organic diols. Thus a polyadipate of molecular weight 2500 can be obtained from butane-1,4-diol and adipic acid in 24 h, whereas synthesis of a poly(carborane adipate) at the same temperature lasts 5 days. This is indicated also by the fairly low rate constants given in Table 2 for the formation of a poly(carborane adipate)[32].

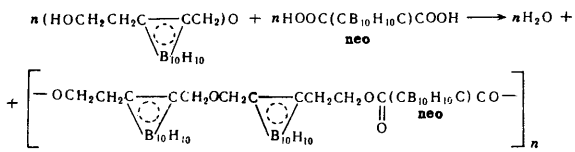
If both diol and dicarboxylic acid contain a carborane group, the adverse effect of the two carborane groups is so great that either no polymeric compound is obtained at all or else the resulting polymer has a low molecular weight.

It is possible that increasing the distance between the carborane system and the functional groups of the molecule will tend to diminish the influence of the steric factor of the carborane unit. Table 1 shows that, when bishydroxymethylcarborane is replaced by bis-(2-hydroxymethylcarboran-1-ylmethyl) ether, which contains two carborane groups, the molecular weight of the product decreases from 2500 to 960. When, however, bis-(2-hydroxyethylcarboran-1-ylmethyl) ether is used, i.e. when the distance between the carborane nucleus and the hydroxyls in the molecule is increased, the molecular weight of the compounds is somewhat higher (1600 instead of 960).

TABLE 2. Rate constants of the formation of carborane adipate polyester.

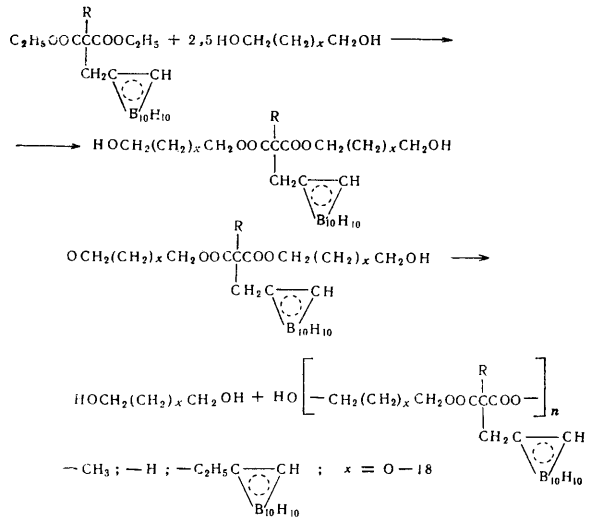
Temp., °C	Rate constant, mole g^{-1} min^{-1}
170	$7.46 \cdot 10^{-4}$
190	$1.59 \cdot 10^{-3}$
205	$2.48 \cdot 10^{-3}$

Interaction of bis-(2-hydroxyethylcarboran-1-ylmethyl) ether with neocarboranedicarboxylic acid according to the equation



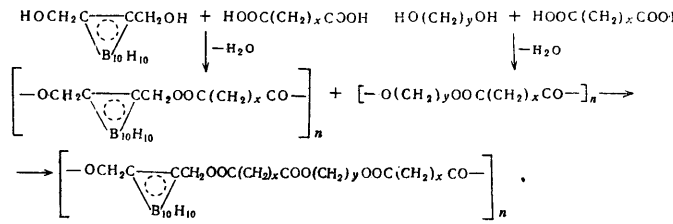
yields vitreous polymers of molecular weight 1730 and softening point 125°C. The resulting neocarborane polyesters are more crystalline than the carborane polymers, probably as a consequence of more compact packing of the molecules.

The steric and inductive effects of carborane groups which inhibit polymerisation may be exhibited when these groups are present in the side-chain. Thus polycarboranemalonates can be obtained by the esterification of carboranemalonates with glycols[27]. The process involves formation of an intermediate addition product of the diol and the carborane diester, followed by its self-condensation to a linear polymer accompanied by elimination of the glycol:



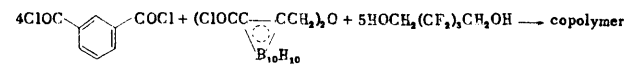
The products are vitreous materials of relatively low molecular weight. Attempts to increase the molecular weight were unsuccessful even when solvents of high boiling point were used and the molar ratio of the reactants was varied.

To obtain polymeric compounds having lower softening points and pour points, ternary copolymers were synthesised from bishydroxymethylcarborane, diethylene glycol, and dicarboxylic acids[28]. The mixed carborane polyesters were prepared by first synthesising polyesters of low molecular weight by the interaction of bishydroxymethylcarborane and a polymethylenedicarboxylic acid (adipic or glutaric acid), and also of diethylene glycol with the dicarboxylic acid, and then bringing about polyesterification between the two polyesters of low molecular weight to yield the mixed carborane polyester of higher molecular weight:



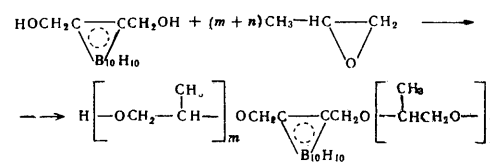
The copolymers were liquids of viscosity 33–35 P and molecular weight 2000–2200.

Ternary copolymers have been synthesised[27] from terephthaloyl and carboranedicarbonyl chlorides and a fluorocarbon diol:



The molecular weight of the product is 2500. The polymer softens at 35°C, possesses elastic properties over the range 35–56°C, and is converted above 56°C into a sticky liquid. The molecular weight of another copolymer obtained also from terephthaloyl chloride, together with 1,2-bishydroxymethylcarborane and hexafluoropentanediol, is 3300.

Oligomeric compounds having low softening points and pour points have been obtained by the migration copolymerisation of bishydroxymethylcarborane with alkyloxirans[33]. The migration copolymerisation of the former component with propylene oxide at 75–100°C and 3–5 atm yields a polyoxypropylenecarboranediol which is a liquid of viscosity 22 P comprising 5–6 structural units:



Fractionation of the polymer by adsorption chromatography[34] showed it to be polydisperse with a mean molecular weight of 500.

Attempts to increase the molecular weight of the polymer by varying the temperature of the synthesis or increasing the molar ratio of propylene oxide to bishydroxymethylcarborane were unsuccessful: the carborane units probably tend to inhibit polymerisation. However, the rates of formation of the polyoxypropylenecarboranediol are considerably higher than the rates of formation of carborane polyesters of dicarboxylic acids[32,35] (Table 3).

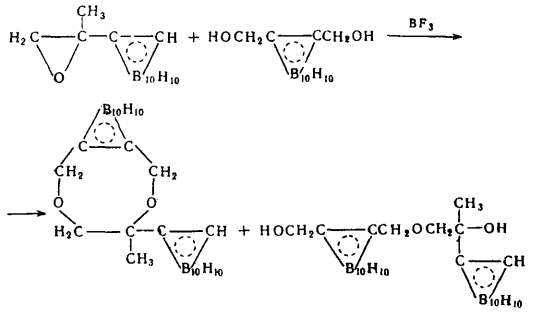
TABLE 3.

Temp., °C	Formation rate constant, mole g^{-1} min^{-1}	
	polyoxypropylenecarboranediol (Ref. 38)	poly(carborane adipate) (Ref. 33)
75	0.000344	—
120	0.00413	—
130	0.00788	—
140	0.0277	—
170	—	0.000746
190	—	0.00159
205	—	0.00248

Thermographic and thermogravimetric studies have been made to obtain information on the thermal stability of the polyoxypropylenecarboranediol. The results show that vigorous decomposition of the product begins above 250°C, and is accompanied by exothermic peaks at 330° and 435°C, probably associated with oxidising processes.

The Reviewers have made attempts to prepare a polymer by the migration polymerisation of 2′-methyloxiran-2′-ylcarborane, a product of the oxidation of isopropylcarborane with perfluoroacetic anhydride. In the presence of traces of water a resinous polymeric compound of molecular weight ~ 1000 was obtained. It proved impossible to prepare a substance of higher molecular weight. It is probable that the steric and inductive effects of the carborane nucleus are also operative here, tending to inhibit polymerisation of the 2′-methyloxiran-2′-ylcarborane.

The reaction between 2′-methyloxiran-2′-ylcarborane and bishydroxymethylcarborane is also adversely affected by the carborane system[36]. In the presence of boron trifluoride cyclic—not polymeric—compounds are formed:

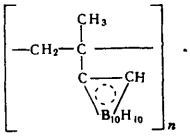


It is probable that the distance between the carborane system and the epoxy-group must be increased in order to diminish the steric effect of the carborane group. It has been remarked[31] also that attempts to polymerise 2′-methyloxiran-2′-ylcarborane have not always yielded positive results.

Carboraneurethane elastomers have been prepared by the interaction of di-isocyanates with carborane polyesters of polymethylenedicarboxylic acids[28] and also with polyoxypropylenecarboranediol[33]. The di-isocyanate is taken in slight excess over the stoichiometric quantity in order to form allophanic and biuret cross-links, which improve the mechanical properties of the elastomers. To increase the frequency of the vulcanisation network and improve the elastic properties it is proposed in certain cases[28] to introduce various polyols (glycerol, castor oil, 1,1,1-trishydroxymethylpropane, etc.) into the linear polyurethane polyester. The carboraneurethane elastomers obtained possess superior elastic properties.

Attempts have been made to obtain carborane elastomers by the polymerisation of carborane monomers, such as vinyl-, isopropenyl-, butenyl-, and allyl-carboranes. However, attempts to obtain polymers by the radical or ionic polymerisation of these compounds were unsuccessful.

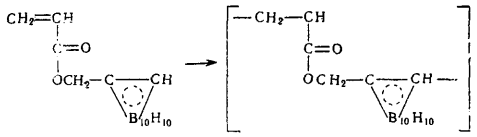
Information appeared later[37] on the polymerisation of isopropenylcarborane in the presence of 5% of aluminium chloride at 150–170°C, with the formation of a solid product of molecular weight 1790, soluble in benzene and melting above 300°C. The infrared spectra of the polymer corresponded to polyisopropenylcarborane



Trimeric isopropenylcarborane has been obtained[37] by using 50 wt.% of di-t-butyl peroxide as catalyst. With a smaller amount of the peroxide polymerisation was not observed.

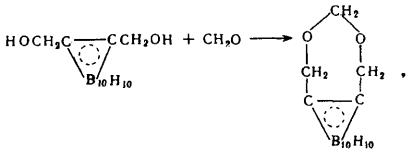
Isopropenylcarborane has been copolymerised with methyl acrylate in the presence of azoisobutyronitrile to form a polymer which softens at 45–50°C.[37] The polymerisation has been reported[38] of 1-vinylcarborane, 1-methyl-2-vinylcarborane, and 1-isopropenyl-2-methylcarborane in the presence of phenyl-lithium in ethereal solution.

Investigations have been made on the polymerisation of carboranylmethyl acrylate[27]. Radical bulk polymerisation gave a homopolymer, a brittle solid which became rubberlike at 165°C:



Copolymers of carboranylmethyl acrylate with various fluorinated acrylates have been obtained[27] by radical bulk and emulsion polymerisation.

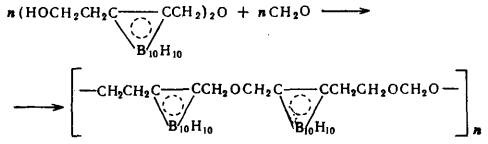
Cyclic and polymeric dialkoxymethanes have been described[27], resulting from the interaction of carboranediols with formaldehyde or with dipropoxymethane. The character of the products depends on the conditions of the reaction and the nature of the glycol used, either 1,2-bishydroxymethylcarborane or 2-carboranylpropane-1,2-diol. 1,2-Bishydroxymethylcarborane reacts with formaldehyde to yield linear polymers. Cyclic products are formed by bulk polymerisation in the presence of toluene-*p*-sulphonic acid:



Attempts to open the ring with formation of a linear dialkoxymethylene polymer were unsuccessful. The stability of the ring can be explained both by the stability of cyclic methylenedioxycarboranes and by steric hindrance to formation of a carborane polymer chain. It has been found that 1,2-substituted carboranes readily form three-membered exocyclic rings. This tendency to form cyclic structures is explained by the diminished bond length and the relatively acute external angle at which the group is attached to the carborane system.

Dimers and trimers (of molecular weight 400 and 700 respectively), or mixtures thereof, have been obtained by the interaction of 1,2-bishydroxymethylcarborane with formaldehyde in the presence of hydrochloric acid. The products were assigned a linear structure on the basis of their infrared spectra, which contained absorption bands due to terminal hydroxy-groups (2.88 μm). Other evidence of a linear structure is provided by the reaction of these products with adipoyl chloride, which results in a polymer of molecular weight 2839.

A polymer of molecular weight 4400 has been obtained by the interaction of bis-(2-hydroxyethylcarboran-1-ylmethyl) ether with formaldehyde:



The linear structure of the polymer is confirmed by the presence in the infrared spectrum of an absorption band at 2.95 μm, corresponding to terminal hydroxy-groups, and also by the interaction of the polymer with 4-methyl-1,3-phenylene di-isocyanate to give a rubberlike polymer.

However, neither cyclic nor polymeric products could be obtained from bis-(2-hydroxymethylcarboran-1-ylmethyl) ether. This fact also indicates steric hindrance by the carborane groups, inhibiting polymerisation.

Materials exhibiting high thermal stability can be obtained on the basis of carborane polymers. The production of thermostable polymers is based on a chemical bond of high energy between the atoms constituting the main polymer chain and the groups surrounding it. However, the types of bonds leading to polymers which are stable to heat are very limited. Table 4 gives the energies of rupture [sic] of a few chemical bonds.

It may be supposed that carborane polymers containing the above types of bonds as well as the carborane group will have enhanced thermal stability. Indeed, polymers containing B–O bonds together with carborane groups are stable above 400°C. Such polymers have been obtained[28] by the interaction of boric acid with 1,2-bishydroxymethylcarborane and also with 2′-methyloxiran-2′-ylcarborane. They are solids of molecular weight 1000–1200, which have softening points of 118–87°C.

Thermographic and thermogravimetric studies have been made on the thermal stability of the polymers. They show that vigorous decomposition of the product begins above 300°C. At 400°C the polymers lose about 10% of their original weight. At 800°C the losses in weight amount to 21.2%. The process is accompanied by exothermic effects over the range 490–540° and also at 725°C, probably associated with structural changes in the polymer.

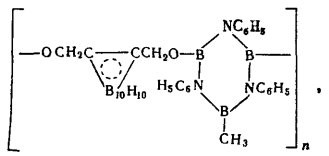
Interest has grown recently in the use of cyclic compounds of boron and nitrogen—the borazoles—for the synthesis of thermostable polymers[41]. The reason is the great thermal stability of the borazole ring, resulting from the fact that the σ-bond between boron and nitrogen atoms is supplemented by a coordinate link produced by displacement of the electron density of the lone pair of electrons from the nitrogen to the boron[42,43].

TABLE 4. Energy of rupture* of chemical bonds[39,40].

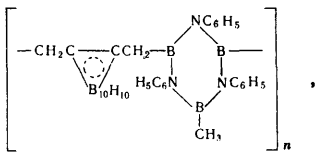
Bond	Bond energy, kcal mole^{-1}
B—O	119.3
B—N	104.3
B—C	100.0
Si—O	89.3
P—O	81.7

* Presumably the Reviewers have bond dissociation energies in mind (Ed. of Translation).

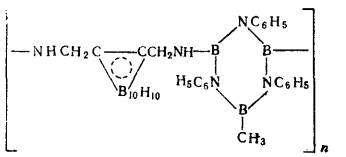
Polymers resistant to heat and to chemical reagents have been prepared from borazole and carborane compounds[44]. Polymers have been obtained from *B*-methyl-*N*-triphenylborazole together with 1,2-bishydroxymethylcarborane



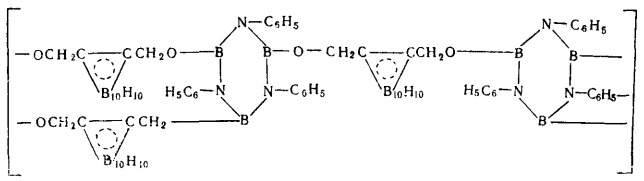
bischloromethylcarborane



or bisaminomethylcarborane



and from *N*-triphenylborazole together with 1,2-bishydroxymethylcarborane



Polymers obtained by polycondensation in the melt are brittle, transparent, pale yellow substances having molecular weights ≫ 2000. In contrast to most polyborazoles, which are readily hydrolysed in air, these polycarborane-borazoles are completely resistant to atmospheric moisture. The resistance to hydrolysis is probably influenced by steric hindrance due to the carborane groups. The structure of the polymers was assessed from their molecular weights and their infrared spectra.

Fig. 4 gives the infrared spectra of *N*-triphenylborazole *1*, bishydroxymethylcarborane *2*, and the oligomer *3* obtained from them. It is seen that the band at 1401 cm^{-1}, corresponding to the cyclic B–N bond in *N*-triphenylborazole *1* is preserved in the spectra of the oligomer *3*. The band at 2590 cm^{-1}, corresponding to the B–H bond in the carborane rings of bishydroxymethylcarborane *2* also occurs in the spectra of the oligomer. Hence it may be concluded that the oligomer consists of carborane and borazole rings.

The thermal stability of these polymers has been investigated. The heat-resistance was determined by recording thermomechanical compression curves with P = 50 g (Fig. 5). The greatest heat-resistance is shown

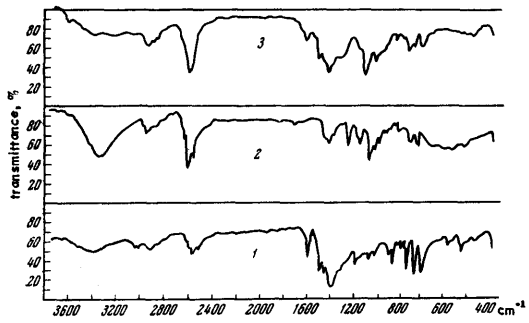


Fig.4. Infrared spectra of: 1) *N*-triphenylborazole; 2) bishydroxymethylcarborane; 3) oligomer obtained from them.

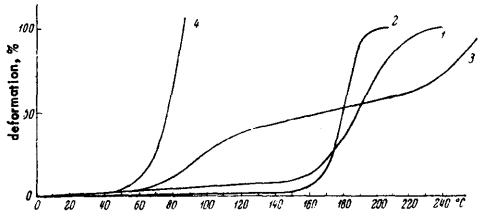


Fig.5. Thermomechanical curves of polymers based on: 1) *N*-triphenylborazole and bishydroxymethylcarborane; 2) *B*-methyl-*N*-triphenylborazole and bishydroxymethylcarborane; 3) *B*-methyl-*N*-triphenylborazole and bisaminomethylcarborane; 4) *B*-methyl-*N*-triphenylborazole and bischloromethylcarborane.

by polymers obtained from 1,2-bishydroxymethylcarborane with *N*-triphenylborazole *1* and with *B*-methyl-*N*-triphenylborazole *2*. The softening points of these polymers lie in the range 150–160°C. Those of polymers obtained from *B*-methyl-*N*-triphenylborazole with bisaminomethylcarborane *3* and with bischloromethylcarborane *4* are respectively 60° and 45°C.

The thermal stability of a polymer was determined from the change in weight of a specimen when heated in air (Fig. 6). The greatest stability is exhibited by polymers based on 1,2-bishydroxymethylcarborane with *N*-triphenylborazole *1* and with *B*-methyl-*N*-triphenylborazole *2*. When the polymers are heated in air to 400–450°C the loss in weight is ~ 1% (Fig. 6). The improved thermal stability of the polymers is possibly due to the presence of the thermostable borazole and carborane groups linked by a B–O bond, which has a high energy (Table 4). Polymers obtained from *B*-methyl-*N*-triphenylborazole with bisaminomethylcarborane *3* and with bischloromethylcarborane *4* begin to decompose vigorously above 150°C.

Phosphinocarboranes, obtained by the action of dilithium carborane on chlorophosphines containing 1–3 chlorine atoms, are highly resistant to heat and hydrolysis[45]. The product from dilithium carborane and phosphorus trichloride gives with sodium azide a compound $(B_{10}H_{10}C_2PN_2)_2$,

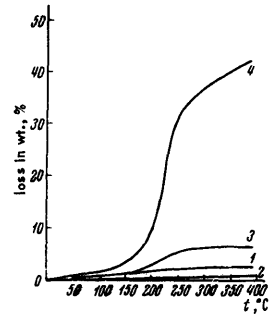
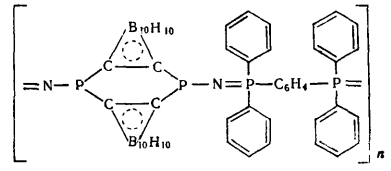


Fig.6. Thermal stability curves of borazole–carborane polymers. Numbering of curves as for Fig.5.

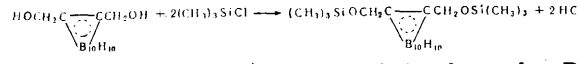
which copolymerises with $[(C_6H_5)_2P]_2C_6H_4$ to form a polymer having the structure



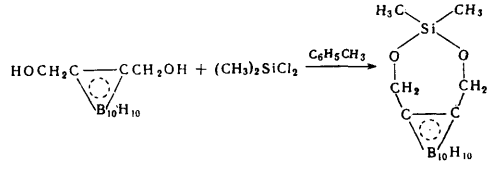
Recent investigations by the Thiokol Chemical Corporation, an American firm, show[46] that polymers highly resistant to oxidation and heat can be obtained by introducing carborane groups into a polybenzimidazole chain. Thus the sodium salt of polybenzimidazole reacts with 1-bromomethylcarborane to give the very stable polymer, polycarboranylmethylbenzimidazole. Thermogravimetric studies have shown losses of 18% and up to 25% of the original weight when the polymer is heated to 900°C in nitrogen and in air respectively.

Extremely interesting information[8,12] has been obtained on thermally stable carborane polymers containing silicon, which remain unchanged when heated to 450–500°C. Monomeric silicon-containing carboranes can be obtained[47] by the reaction of silicon chlorides with alkenylcarboranes. These reactions are catalysed by chloroplatinic acid and ferric chloride.

Reactions have been described[48] between carboranediols and methylchlorosilanes. The reaction of 1,2-bishydroxymethylcarborane with trimethylchlorosilane is represented by the equation

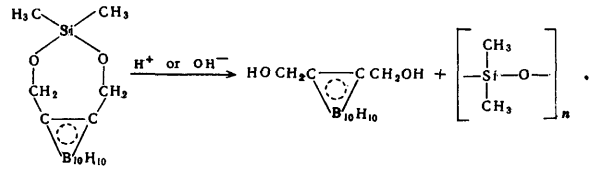


bis(trimethylsiloxymethyl)carborane being formed. Dimethyldichlorosilane reacts with the carboranediol to give a seven-membered cyclic compound



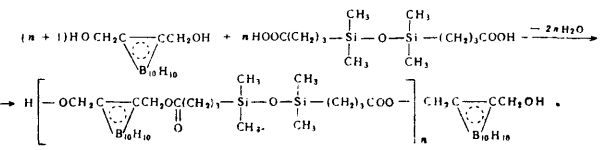
which consists of white crystals of molecular weight 260 and melting point 100°C. Attempts to open the ring to obtain a linear polymer were unsuccessful even when a catalyst was used (toluene-*p*-sulphonic acid or caustic potash),

the product being hydrolysed to the original carboranediol with formation of a polydimethylsiloxane:



An analogous compound has been synthesised[49] by the interaction of 1,2-bishydroxymethylcarborane and dimethyldichlorosilane.

The same workers[49] obtained also a series of linear carboranesiloxane polymers by the reaction between dichloropolymethylsiloxanes and 1,2-bishydroxymethylcarborane. The properties of the compounds obtained are listed in Table 5. These workers prepared carboranesiloxane oligomers by the polycondensation of bishydroxymethylcarborane with 5,5,7,7-tetramethyl-6-oxa-5,7-disilaundecane-1,11-dioic acid:



Carboranesiloxane oligomers are transparent colourless liquids of viscosity 80–90 P and molecular weight ~1000, soluble in aromatic hydrocarbons and chlorinated hydrocarbons but insoluble in alcohols and water. Thermogravimetric examination showed that the oligomers were stable up to 350°C.

Organosilicon carborane oligomers have been obtained[50] by the interaction of epoxyalkylsilanes with bishydroxymethylcarborane.

A study has been made of the migration copolymerisation of epoxypropoxypropyltriethoxysilane with bishydroxymethylcarborane. In the first stage of the process a linear polymer is formed by interaction of the epoxy-groups with the hydroxy-groups of the carborane (curves *1*, *2*, *3* at 160°, 180°, and 190°C respectively). In the second stage, when the content of epoxy-groups reaches its minimum value, the ethoxy-groups undergo alcoholysis (curves *4*, *5*, *6*, at 160°, 180°, and 190°C respectively); their content in the reaction mixture drops sharply, and the product passes from a viscous liquid to an elastic state (Fig. 7).

The resistance of the polymers to deformation on being heated was examined by determining thermomechanical curves with loads of 50 g and 100 g (Fig. 8, curves *1* and *2*). This work showed that, unlike most polymers, the product, with rise in temperature, passes into an infusible state without softening, the volume increasing at temperatures above 360°C. In view of the great thermal stability of the carboranesiloxane polymers obtained, coupled with their strong adhesion to glass and metals, and also the good dielectric properties inherent in carborane compounds, the polymers have been recommended for use as heat-insulating coatings.

There are indications that carboranesiloxane polymers having the carborane groups in side-chains possess greater thermal stability than do linear polymers having alternating carborane and siloxane units, in which the carborane groups are linked to a silicon atom directly through a methyl, methoxyl, ether, or ester group. Thus the synthesis has been described[31] of carboranesiloxane homopolymers and their copolymers with dimethylsilane having carborane groups in the side-chain, which are stable up to

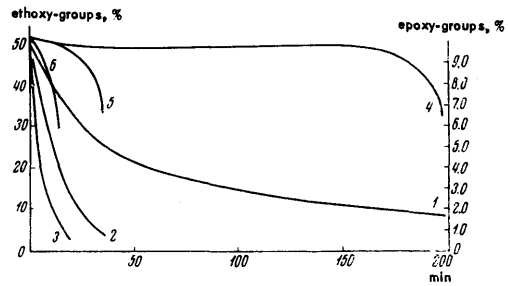
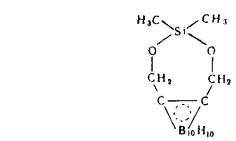
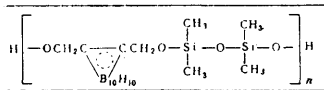
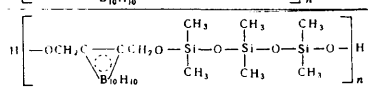
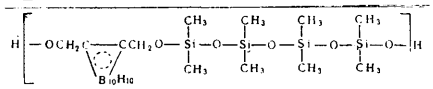


Fig. 7. Variation in quantities of epoxy-groups (1, 2, 3) and of ethoxy-groups (4, 5, 6) during reaction between epoxypropoxypropyltriethoxysilane and bishydroxymethylcarborane at temperatures of 160°, 180°, and 190°C respectively.

TABLE 5. Physicochemical properties of polydimethylsiloxymethylcarboranes.

Formula suggested for product	M	d_4^{20}	M.p., °C
	260	—	100
	580	1.5118	223.5
	900	1.4881	524
	1170	1.4726	821

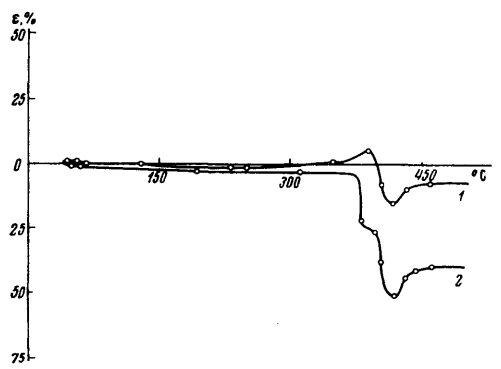
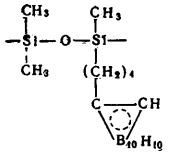


Fig. 8. Thermomechanical curves for the copolymer of epoxypropoxypropyltriethoxysilane with bishydroxymethylcarborane at loads of: 1) 50 g; 2) 100 g.

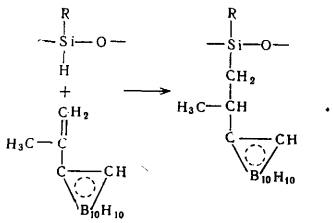
450°C. These polymers were obtained by hydrolysis and condensation reactions:†

The homopolymers have a low molecular weight owing to the formation of a large number of cyclic compounds. The copolymers are elastic solids of molecular weight ~ 13 000 and a pour point of ~ 100°C.



Thermogravimetric examination indicates that these carboranesiloxane polymers are stable up to 400–450°C in nitrogen and in air. The infrared spectra show that the carborane group remains unchanged at these temperatures. Investigation of the thermal degradation of the carboranesiloxane polymers shows that they are unaffected by heating at 350°C for 100–200 h.

Carboranesiloxane polymers have been described[51,52] with the carborane groups framing the main siloxane chain. They were obtained by the migration copolymerisation of alkenylcarboranes with polyalkylsiloxanes:



The resulting polymers are viscous or solid depending on the degree of substitution by carborane groups of hydrogen attached to the silicon atom. The solubility of the polymers in aromatic hydrocarbons and in alcohols diminishes with increase in their content of carborane groups.

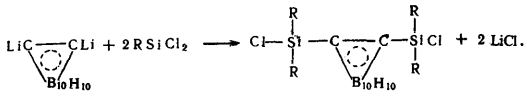
The investigations have shown that reaction between a polyalkylsiloxane and isopropenylcarborane takes place at temperatures above 200°C, hardly any reaction occurring below this temperature. However, the rates of formation of carboranesiloxane compounds are not very high even at high temperatures, as is indicated also by the formation rate constants (Table 6). The low rates of formation of carboranylsiloxanes are probably explained by steric and electronic factors due to the presence of the carborane group. Thermogravimetric analysis indicated that these polymers were stable in air up to 400–500°C.

TABLE 6. Rate constants of the formation of carborane–siloxane compounds.

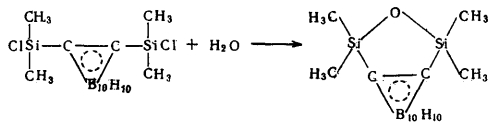
Compound	Rate constant, mmole g^{-1} min^{-1}, at		
	250°	270°	290°
Methylcarboranyloligosiloxane	$4.4 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$1.82 \cdot 10^{-4}$
Methylcarboranylcyclosiloxane	$6.25 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$1.92 \cdot 10^{-4}$

† Equations appear to have been omitted from the Russian text (Ed. of Translation).

Chlorosilyl derivatives of carborane in which the silicon atoms were directly attached to the carborane group were obtained via dilithium carborane[12]: e.g.



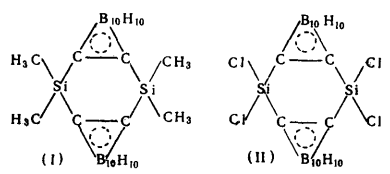
The hydrolysis of such compounds, in contrast to those described above, leads to the formation of cyclic carborane–organosilicon compounds, not the original carborane and a polysiloxane. Treatment of bischlorodimethylsilylcarborane with water yields a cyclic bisdimethylsilylcarborane:



The ammonolysis of bischlorodimethylsilylcarborane and also of bismethyldichlorosilylcarborane gave cyclic carboranedisilazanes[53]. Unlike ordinary silazanes, which react with water, the carboranesilazanes were stable to hydrolysis.

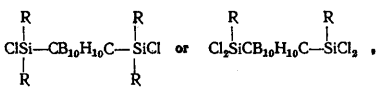
Cyclic carboranedisiloxanes and carboranedisilazanes are thermally stable up to 400°C. Above 500°C they decompose with the evolution of methane. Further rise in temperature to 600°C is accompanied by rapid decomposition with the evolution of hydrogen. Replacement by methyl groups of hydrogen attached to nitrogen improved the stability of the compounds.

Two types of thermally stable cyclic compounds

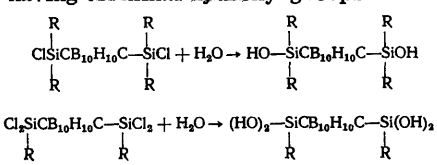


have been obtained[53]. Bisdimethylsilylenedicarborane (I) is stable to heat and hydrolysis up to 485°C. Bisdichlorosilylenedicarborane (II) does not react with water, but with ammonia the chlorine atoms are replaced by amino-groups, the carborane systems being preserved. Attempts to open the rings to give linear polymers were unsuccessful.

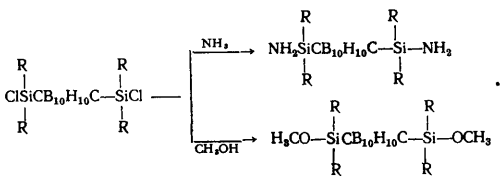
For the synthesis of thermostable carborane–organosilicon polymers, research workers turned to *m*-carborane (or neocarborane) systems, in which the positions of the carbon atoms exclude the possibility of the formation of exocyclic structures, while the stability at high temperatures is maintained. Chlorosilyl derivatives of neocarborane



were obtained via dilithium neocarborane[54]. Hydrolysis of these compounds yielded linear carborane–organosilicon compounds having terminal hydroxy-groups:

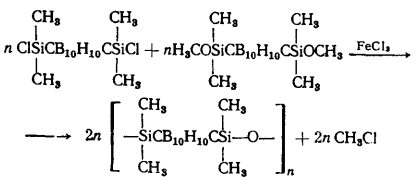


Treatment of bischlorosilylneocarboranes with ammonia and with methanol yields respectively bisaminosilyl- and bismethoxysilyl-neocarboranes:

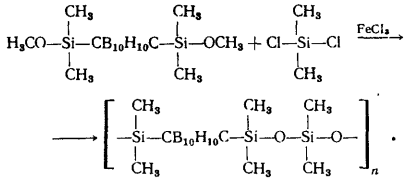


A series of silylneocarboranes have been obtained in this way [54].

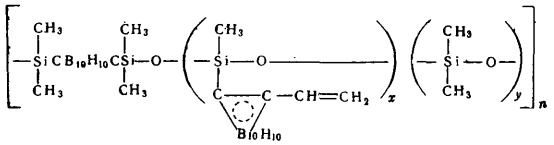
Polymers may be obtained [55] based on these compounds. The reaction of bischlorodimethylsilylneocarborane with bismethoxydimethylsilylneocarborane in the presence of iron(III) chloride at 140–190°C according to the equation



yields a polymer of molecular weight 16 000 and melting point 235–255°C, soluble in hot *N*-methylpyrrolid-2-one, decalin, chlorobenzene, and bromobenzene. Analogous polymers having different numbers of dimethylsiloxy-units have been obtained [55] by the interaction of bismethoxydimethylsilylneocarborane with dimethyldichlorosilane (or dichloropolymethylsiloxanes):



To obtain polymers by a free-radical mechanism, a few methyl groups (not more than 8%) were replaced by vinyl groups [55], especially for dichlorovinyl derivatives of carborane, yielding a polymer having the structure



The resulting polyneocarboranylenesiloxanes exhibited thermal stability above 500°C and resistance to oxidation up to 350°C. Thus, as was to be expected, these polymers were rather more thermostable than polycarboranesiloxanes with the carborane groups framing the main siloxane chain [51,52], which were stable in air up to 400–450°C.

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Summarising, we may predict that the peculiar chemical, physicochemical, and mechanical properties of polycarboranes (high thermal stability, strength, dielectric properties, adhesion to glass, metals, wood, etc.) will deservedly induce research workers to take an interest in these compounds, with the result that many new carborane polymers will be discovered which may find application in various branches of technology.

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POLYAZOLES

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I. INTRODUCTION

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

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

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

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

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

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

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