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Latest Advances in the Field of Carbaborane-containing Polymers

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The results of studies of carbaborane-containing polymers with different structures, carried out in the last six years, are surveyed. The methods of synthesis of carbaborane-containing polymers, their physicochemical properties, and their practical applications are considered.
The bibliography includes 128 references.

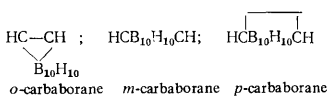
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I. INTRODUCTION

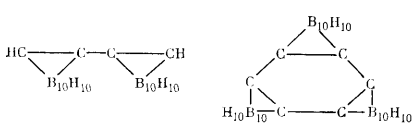
Carbaborane-containing polymers have already been known for approximately twenty years. Many of these unusual and very interesting polymers are capable of withstanding extremely severe conditions under which the organic polymers decompose almost completely.

The latest review on the synthesis and properties of carbaborane-containing polymers, included in the book "Advances in the Synthesis of Organoelemental Polymers"[1], contains data published between 1966 and 1976 inclusive. The chemistry of carbaborane-containing polymers is nowadays continuing to develop vigorously. The aim of the present review is to survey data which have been published from 1977 to 1982; the review also includes articles published in 1977 but not included in the earlier review[1]. In order to make it easier to become acquainted with the new advances in the study of carbaborane-containing polymers of different structure, the data surveyed are arranged in the same sequence as in Korshak's book[1]. Three isomeric forms of carbaborane have come to be represented in the following manner[1]:



II. POLYCARBABORANYLENES

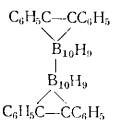
There are no examples in the literature of the specific synthesis of polycarbaboranylenes (i.e. polymers in which the carbaborane fragments are connected directly to one another via a C—C, B—C, or B—B bond). However, the condensation of carbaboranes with evolution of H_2 and the formation of oligomers has been described in some studies. Thus, when *o*-carbaborane was exposed to γ-radiation at 31 °C, the formation of dimers and trimers with a C—C bond and having the following structure was observed[2]:



A cyclic *o*-carbaborane trimer has also been detected in the γ-radiolysis of 1-phenyl-*o*-carbaborane (at 31 °C), which is accompanied by the evolution of benzene[3]. Under analogous conditions, partial isomerisation of *o*-carbaborane to *m*-carbaborane and of *m*-carborane to *o*-carbaborane, accompanied by the formation of dimeric and polymeric products (yield ~ 24%), was observed[4]. The authors believe that the polymers have a complex composition: both the polymers obtained on exposure of *o*-carbaborane to γ-radiation and the polymers derived from *m*-carbaborane contain isomeric *o*- and *m*-carbaborane fragments.

The formation of polycarbaboranylenes with an assumed B—B bond was also noted on heating *o*-, *m*-, or *p*-carbaborane *in vacuo* at temperatures above 600 °C.[5]

It is known that, when carbaboranes are heated in air at ~250 °C, they are oxidised with formation of B—OH and B—O—B bonds[6]. The formation of a dimer with a B—B bond, observed[7] on heating diphenyl-*o*-carbaborane in air in the temperature range 260—330 °C, is therefore extremely unusual. The structure of the dimer



was confirmed by gas—liquid chromatographic, mass-spectrometric, and ebullioscopic data.

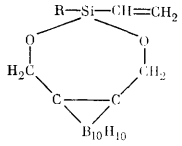
III. CARBOCHAIN POLYMERS

The synthesis and study of carbochain polymers and copolymers containing carbaborane groups in the side chain continues to attract the attention of investigators. Few studies devoted to the homopolymerisation of alkenylcarbaboranes have been published. Steric hindrance due to the bulky carbaborane groups is manifested[1] in the homopolymerisation of 1-alkenyl-*o*-carbaboranes. In addition, the electron density in the double bond diminishes due to the highly electron-accepting *o*-carbaborane fragments. For this reason, 1-alkenyl-*o*-carbaboranes polymerise less effectively the closer is the double bond to the carbaborane group. The hypothesis that the free-radical oligomerisation of 1-alkenyl-*o*-carbaboranes can lead to the formation of two different oligomers has been confirmed with the aid of a

quantum-chemical calculation of the charge distribution in 1-alkenyl-*o*-carbaboranes[8]. One of the oligomers consists of a polyethylene chain with the *o*-carbaboranyl group in the side chain, while the second oligomer contains the *o*-carbaborane fragment in the main chain.

The capacity of 4-(1-*o*-carbaboranyl)styrene for homopolymerisation under various conditions has been investigated[9]. Polymers with the highest molecular weight [$M \cong 60\,000$, softening temperature (soft.temp.) 280–340 °C] have been synthesised by the thermopolymerisation of 4-(1-*o*-carbaboranyl)styrene at 160–200 °C. In the presence of radical initiators (for example, t-butyl peroxide) polymers with $M \cong 12\,000$ and a softening temperature of 320–340 °C are formed. The homopolymerisation of 4-(1-*o*-carbaboranyl)-styrene via an anionic mechanism in the presence of C_4H_9Li takes place slowly, while the polymerisation via a cationic mechanism in the presence of $BF_3.O(C_2H_5)_2$ does not occur at all. From the infrared spectra of the polymers obtained, one can assume that the homopolymerisation of 4-(1-*o*-carbaboranyl)styrene proceeds in all cases mainly via the vinyl group. Thermogravimetric analysis of these polymers has shown that the weight loss by their specimens is ~20% at 400–430 °C.

The study of the homopolymerisation of *o*-carbaborane-containing exocyclic vinylsilanes with various substituents R at the silicon atom has been described[10]:



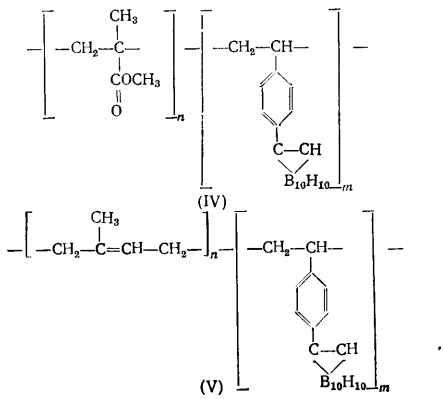
R = CH_3 (I); OCH_3 (II); Cl (III).

It has been established that the homopolymerisation of compound (I) in bulk (a mixture of benzoyl and t-butyl peroxides was used as the initiator) proceeds via the vinyl group with formation of a dimer. The homopolymerisation of compounds (II) and (III) via the vinyl group is accompanied by the partial substitution of the $SiOCH_3$ and SiCl groups by SiOH and the partial dissociation of one of the SiO bonds; this results in the formation of a mixture of dimers, trimers, and cross-linked oligomers. The latter are obtained on interaction of the SiOH groups with $SiOCH_3$ and SiCl. The formation of oligomers alone, and not polymers, has been explained[10] by the steric hindrance generated by the seven-membered exocyclic groups. All the homopolymers are colourless viscous liquids.

The copolymerisation of compounds (I), (II), and (III) with methyl acrylate takes place more readily. It has been carried out under the same conditions as the homopolymerisation[10]. The content of the initial vinylsilanes in the reaction mixture varies from 1 to 20 mole %. Solid glass-like substances with M ranging from 400 000 to 800 000 were obtained in all cases. Compound (II) proved to be the most reactive of the monomers; after the introduction of compounds (I), (II), and (III) into the reaction mixture in an amount of 20 mole %, the contents of their unit in the copolymers were 9, 12, and 3 mole % respectively.

The copolymerisation of 1-vinyl-*o*-carbaborane with styrene (in proportions of 1 : 3) under the influence of γ-rays has been investigated[11]. It was established that the copolymer consists of 11 or 12 units and that there are approximately 9 styrene units for each two 1-vinyl-*o*-carbaborane units. The copolymer softens at 85 °C and melts fully at 105 °C. Its structure was investigated with the aid of NMR and flash pyrolysis methods. However, the authors[11] were unable to determine the location of the *o*-carbaborane fragment (in the main or side chain).

New copolymers having the following structure have been synthesised on the basis of 4-(1-*o*-carbaboranyl)styrene and methyl acrylate[12]:



(IV)

(V)

The copolymers were obtained in 80–90% yield in bulk on heating the monomers to 80 °C in the presence of radical type initiators (t-butyl peroxide and azobisisobutyronitrile). The molecular weight of the copolymers (IV) increases from 3460 to 7130 as the ratio of 4-(1-*o*-carbaboranyl)styrene and methyl methacrylate is altered from 1 : 1 to 1 : 4, while the molecular weight of the copolymers (V) increases from 3550 to 278 000 as the ratio of 4-(1-*o*-carbaboranyl)styrene and isoprene is altered from 1 : 1 to 1 : 10. The influence of the heterounit structure (i.e. the ratio of the numbers of units n and m) on the glass point and on the onset of intense loss of weight has been analysed[12]. It has been shown that the thermal characteristics of the copolymers (IV) vary additively with the extent of their heterounit structure, while for the copolymers (V) the relation is non-additive.

Copolymers containing hydroxy- or carboxy-groups have been synthesiseed by the copolymerisation of 1-vinyl-*o*-carbaborane, 1-isopropenyl-*o*-carbaborane, or 1-acryloyloxymethyl-*o*-carbaborane with isoprene, butadiene, or chloroprene in solution in dioxane at 65 °C for 72 h in the presence of 4,4'-azobis(4-cyano-1-pentanol).[13] The authors note that the large difference between the polarities of the selected co-monomers ensures ease of copolymerisation. In all cases an increase of the content of unsaturated *o*-carbaborane derivatives in the reaction mixture from 5 to 50 wt.% entails a decrease of the yield and molecular weight of the copolymers. For example, the yield of the copolymer of acryloyloxymethyl-*o*-carbaborane with chloroprene decreases from 85 to 70% and its molecular weight decreases from 7400 to 4300.

The copolymers, which can be used as plasticisers and catalysts of the combustion of solid rocket fuels, have been obtained by the aqueous emulsion copolymerisation of methacryloyloxymethyl-*o*-carbaborane with butadiene in the presence of azobisisobutyronitrile, dodecanethiol, and benzylacetyldimethylammonium chloride at 50 °C with vigorous stirring[14]. Depending on the ratio of the comonomers, the copolymers contain 10–80 mole % of butadiene units and 90–20 mole % of methacryloyloxymethyl-*o*-carbaborane.

In order to modify low-density polyethylene, a study has been made of the radical copolymerisation of ethylene with 1-isopropenyl-*o*-carbaborane in an autoclave at a pressure of 1400 kg cm^{-2} and a temperature of 160 °C.[15] It has been established by infrared spectroscopy that the copolymerisation involves mainly the double bonds and that its rate and the molecular weight of the copolymers decrease rapidly with increase of the content of the *o*-carbaborane derivatives in the reaction mixture from 1 to 40 mole %. All the copolymers

obtained in this way are solid plastics soluble in aromatic hydrocarbons and capable of being pressed at 130–170 °C to form transparent elastic films. The specimens containing 2–3 mole % of 1-isopropenyl-*o*-carbaborane had a tensile strength and a relative elongation on extension of not less then 100 kg cm^{-2} and 300% respectively. With increase of the content of 1-isopropenyl-*o*-carbaborane in the copolymer, the density of the latter also increases (to 1 g cm^{-3}) and its thermo-oxidative stability improves. The effect of γ-radiation on copolymers containing 0.28–0.30 mole % of 1-isopropenyl-*o*-carbaborane has been investigated[16]. Measurements of the properties related to the strength of the copolymers have shown that their radiation stability is close to that of polyethylene. The resistance of the copolymers to oxidation diminishes after γ-irradiation.

The interaction of a chloromethylated polystyrene–divinylbenzene copolymer with lithio-*o*-carbaborane has been described[17]; on the basis of the results of elemental analysis for boron, the authors assume that the chlorine atoms in at least three-quarters of the chloromethyl groups have been substituted by the *o*-carbaboranyl groups.

Data on the use of polymers and copolymers based on various alkenylcarbaboranes in adhesives for the improvement of their thermal stability[18,19] and for the preparation of anion-exchange resins[20] are presented in the patent literature.

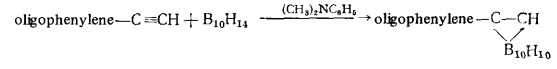
The copolymers of the diallyl esters of *m*- or *p*-carbaboranedicarboxylic acids and methyl methacrylate have been recommended as materials suitable for use in an atmosphere of oxygen at elevated temperatures[21].

IV. POLYMERS OF THE POLYPHENYLENE TYPE

A large number of publications devoted to the synthesis and investigation of polymers of the polyphenylene type, containing carbaborane fragments in both side and main chains, have appeared in recent years. Thus, after radiolysis, 1-phenyl-*o*-carbaborane was found to undergo oligomerisation as a result of the abstraction of hydrogen from the benzene ring with formation of dimers, trimers, and tetramers[3].

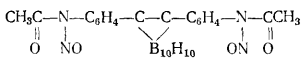
The polycondensation of 1,2-diphenyl-*o*-carbaborane in the presence of Lewis acids and oxidising agents yielded an oligomer with $M = 1300$, soluble in benzene and chloroform and not melting up to 350 °C.[22] According to thermogravimetric data, the mass of the specimen of the oligophenylene obtained does not change up to 500 °C; at 900 °C the weight loss is 11.6%.

Oligophenyl-*o*-carbaboranes, which are amorphous pale-brown powders readily soluble in the usual organic solvents, have been synthesised by the reaction of oligophenylene containing terminal triple bonds with decaborane in accordance with the following scheme[23]:

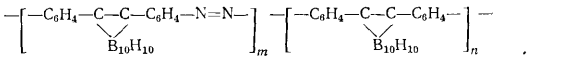


Infrared spectroscopic data and the results of elemental analysis have shown that the replacement of the ethynyl linkages in the oligophenylene by *o*-carbaborane fragments takes place almost quantitatively. The absence of residual ethynyl groups from the oligophenyl-*o*-carbaborane is responsible for its complete inability (in contrast to the usual oligophenylene) to pass to an infusible and insoluble state on heating to 300 °C. The oligophenylene-*o*-carbaboranes are characterised by a higher thermal stability (both in an inert atmosphere and in air) than the initial oligophenylenes. The yield of the carbon residue is 84.5% for oligophenylene-*o*-carbaborane at 900 °C according to thermogravimetric data, while the yield for the usual oligophenylene under analogous conditions is 68%.

The recombination of the phenyl and azophenylene decomposition products of 1,2-bis(*N*-nitrosoacetamidophenyl)-*o*-carbaborane



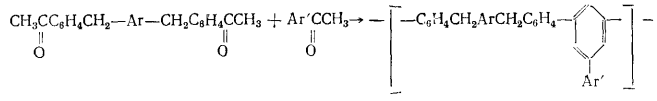
resulted in a quantitative yield of a *o*-carbaborane-containing polyazophenylene having the following structure[24–26]:



This polymer is a pale-brown powder soluble in chloroform, benzene, dimethylformamide, and tetrahydrofuran. Its structure has been confirmed by elemental analysis and infrared and ultraviolet spectroscopy. On isothermal heating at 400 °C in an atmosphere of helium, the mass of the polymer specimen initially decreases rapidly by ~10% and then remains almost unchanged for 3 h. According to the results of dynamic thermogravimetric analysis in air, polyazophenylene with *o*-carbaborane fragments is stable up to 350 °C and above this temperature there is an appreciable increase in the mass of the polymer specimens (up to 30% at 600 °C) owing to the oxidation of B–H groups and the formation of the B–O–B groups.

The ability of the *o*-carbaborane fragments of polyazophenylene to combine vigorously with O_2 at high temperatures with formation of inactive products can be used, according to the authors[25,26], for the inhibition of the thermo-oxidative degradation of thermostable polymers. Indeed, the copolymers of styrene with the decomposition products of 1,2-bis(*N*-nitrosoacetamidophenyl)-*o*-carbaborane, containing between 4 and 38 wt.% of polyazophenylene fragments, exhibit a high thermo-oxidative stability at 400–450 °C.[24]

Polyphenylenes, the first stage of the synthesis of which can be represented schematically by the reaction



(where Ar = *o*-, *m*-, or *p*-carbaboranylene and Ar′ = phenyl or benzyl-*o*-, -*m*-, and -*p*-carbaboranyl) have been obtained by Korshak and co-workers[27–29] by the joint polycyclocondensation of 4,4′-diacetyldibenzyl-*o*-, -*m*-, and -*p*-carbaboranes and various aromatic monoacetyl derivatives (in benzene at 20 °C in the presence of gaseous HCl as the catalyst) with subsequent heat treatment. Instead of acetyl derivatives, their ethylketals can be used in the reaction.

Korshak and co-workers[27–29] noted that the polycyclocondensation of the above compounds does not proceed unambiguously and is accompanied by the formation of dypnone as well as linear and cyclic polyvinylene fragments. The oligophenylenes obtained in this way, containing *o*-, *m*-, or *p*-carbaborane groups in the main molecular chain and in certain cases also in the side chain, are readily soluble in many organic solvents and in chloroform the oligomer concentration can be more than 20%.

All the carbaborane-containing oligophenylenes have low molecular weights ($\bar{M}_n = 1100–4600$), but their fractionation yielded a fraction with $\bar{M}_w = 115\,000$.[27,28] According to the results of thermomechanical studies, the softening temperature of the oligophenylenes synthesised is in the range 150 to

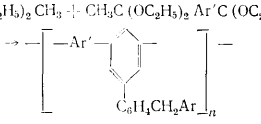
220 °C; at 400–500 °C in an inert atmosphere in the course of 4 h or during pressing with heating up to 400–450 °C at a pressure of 1000 kg cm^{-2}, they are converted into infusible and insoluble three-dimensional polymers as a result of the interaction via the terminal acetyl and ketal groups. According to infrared spectroscopic data, there are no ketal, acetyl, or dypnone groups in the hardened polymers.

The results of thermogravimetric analysis showed that the mass of the heat-treated polymer specimens increases by up to 18% at 400 °C in air as a consequence of the oxidation of the carbaborane groups at the B–H bond. On further increase of temperature to 1000 °C, an appreciable change in the mass of the specimen is not observed. The high thermal stability of the polymers, which are not deformed up to 450 °C, has been noted[27,28]. Detailed study of the properties of the oligophenylenes obtained from derivatives of isomeric carbaboranes enabled the authors[27,28] to conclude that the solubility and thermal stability of the oligomers synthesised are almost independent of the carbaborane isomer from which they have been obtained.

Polyphenylenes with *o*-, *m*-, or *p*-carbaborane fragments in the main chain exhibit an improved adhesion to glass fibre, amounting to 250–350 kg cm^{-2}, and have been recommended for use as thermostable binders for glass plastics[29].

Korshak and co-workers[27,30] also obtained oligophenylenes containing carbaborane fragments in the side chain by the polycondensation of the ethylketals of 4-acetylbenzyl-*o*-, -*m*-, or -*p*-carbaboranes with various ethylketals of aromatic diacetyl derivatives in accordance with the scheme

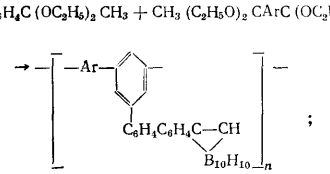
$$ArCH_2C_6H_4C(OC_2H_5)_2CH_3 + CH_3C(OC_2H_5)_2Ar'C(OC_2H_5)_2CH_3 \rightarrow$$



where Ar = *o*-, *m*-, or *p*-carbaboranyl and Ar′ = C_6H_4, $C_6H_4C_6H_4$, or $C_6H_4CH_2C_6H_4$. All the oligophenylenes synthesised in this way have low molecular weights (M = 1400–3200) and are readily soluble in organic solvents such as benzene, toluene, or dioxane and harden at 400–450 °C with formation of three-dimensional polymers. According to thermogravimetric data obtained in air, the mass of the specimens of the hardened polymers begins to decrease in the temperature range 550–600 °C.

The authors[27,30] noted that the introduction of carbaborane fragments into the polyphenylene side chain increases their thermal stability but this effect is smaller than in polyphenylenes containing carbaborane groups in the main macromolecular chain. In order to simplify the synthesis of polyphenylenes with *o*-carbaborane fragments, 4-acetylbenzoyl-*o*-carbaborane, whose synthesis is also technologically complex, has been replaced recently by the more readily available ethylketal of acetylbiphenylyl-*o*-carbaborane:[31,32]

$$HC(B_{10}H_{10})C{-}C_6H_4C_6H_4C(OC_2H_5)_2CH_3 + CH_3(C_2H_5O)_2CArC(OC_2H_5)_2CH_3 \rightarrow$$



Ar = C_6H_4, $C_6H_4C_6H_4$, $C_6H_4OC_6H_4$, $C_6H_4SC_6H_4$, $C_6H_4CH_2C_6H_4$.

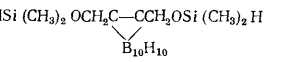
It has also been suggested that the replacement of the methylene bridge by a phenylene bridge on passing from 4-acetylbenzyl-*o*-carbaborane to acetylbiphenylyl-*o*-carbaborane increases the thermal stability of the final polymers.

The polycondensation of acetylbiphenylyl-*o*-carbaborane with the ethylketals of various aromatic acetyl derivatives has been carried out at temperatures between −20° and 150 °C in benzene or dichlorobenzene, toluene-*p*-sulphonic acid being used as the catalyst instead of gaseous HCl at 100 °C and above[31,32]. Infrared spectroscopic data for the oligophenylenes obtained showed that the macromolecules contain the dypnone fragments

and in an amount greater than in oligophenylenes without *o*-carbaborane fragments.

The oligophenylenes synthesised from acetylbiphenylyl-*o*-carbaborane were less soluble than oligphenylenes based on 4-acetylbenzyl-*o*-carbaborane: they dissolved fully only in chloroform and *o*-dichlorobenzene and were insoluble in benzene, toluene, and dioxane. However, their thermal stability did indeed prove to be higher than those of oligophenylenes based on 4-acetylbenzyl-*o*-carbaborane.

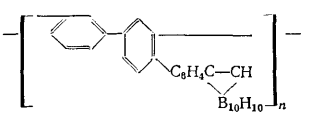
In order to optimise the structure formation process in polyphenylenes with terminal acetyl groups, a study has been made[33] of their interaction with the following di(hydroxymethyl)-*o*-carbaborane derivative:



It was established that at 200–300 °C the acetyl groups of polyphenylene interact with the above compound to form cross-linked monomers whose thermal stability is analogous to that of polyphenylene heat-treated at 450 °C without additives.

The use of *o*-carbaborane-containing polyphenylenes as binders for thermostable glass plastics[33] and for the manufacture of constructional materials[34] has been described.

In addition, *o*-carbaborane-containing oligophenylenes having the structure

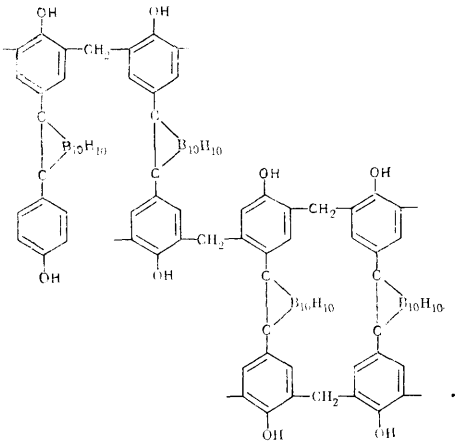


have been considered[35] as the ligands for the synthesis of π-arenechromium carbonyl complexes.

V. PHENOL-FORMALDEHYDE POLYMERS

Studies on the synthesis and properties of carbaborane-containing phenolformaldehyde polymers have continued in recent years. Mixed phenol-formaldehyde polymers of the resol type, based on 1,2-di(4-hydroxyphenyl)-*o*-carbaborane and phenol, whose molar ratio was varied from 1 : 3 to 1 : 21, have been synthesised and thoroughly investigated[36–39]. In contrast to resol, which is based solely on 1,2-di(4-hydroxyphenol)-*o*-carbaborane and hardens at 200–220 °C, mixed *o*-carbaborane-containing resols exhibit an enhanced fluidity (the softening temperatures are in the range 60–110 °C) and harden under the conditions usual for phenol-formaldehyde resols. With decrease of the content of the *o*-carbaborane fragments in the resol, its softening temperature diminishes from 110° to 60 °C, the mass of the coke residue falls from 61% to 18% on heating in air to 900 °C, and the molecular weight increases from 650 to 800.

From data obtained by NMR and infrared spectroscopy, the following structure has been proposed[39] for the resol based on 1,2-di(4-hydroxyphenol)-*o*-carborane hardened at 250 °C for 1 h:



The chemical reactions occurring in resols and resites based on 1,2-di(4-hydroxyphenyl)-*o*-carbaborane on heating in the range 50–450 °C in air and *in vacuo* have been investigated[37]. It was established that at 50–200 °C structure formation in the *o*-carbaborane-containing resol proceeds via the mechanism usual for resols and the *o*-carbaborane groups do not undergo significant transformations, the degree of reaction depending on the heating conditions (in air or *in vacuo*).

From the results of elemental analysis and infrared spectroscopic data as well as studies of the thermo-oxidative degradation of a number of model compounds, it has been suggested[37] that the large carbon residue from the *o*-carbaborane-containing resites is caused either by the oxidation of the B–H group in the *o*-carbaborane nuclei or by the interaction of the *o*-carbaborane fragments with atmospheric moisture and the phenolic hydroxyls and the inhibition of the thermo-oxidation of the organic fragments of the resites in the presence of *o*-carbaborane groups or the products of their thermal or thermo-oxidative reactions.

In order to elucidate the nature of the high thermal stability of the *o*-carbaborane-containing resites, their EPR spectra were investigated[38,40] and a study was made of their structural transformations by X-ray diffraction after heat treatment in the temperature range 200–1200 °C.[41] The results confirmed that both the oxidation of the B–H group of the *o*-carbaborane fragment and other processes associated with the consumption of these groups are most characteristic of *o*-carbaborane-containing resites at temperatures above 400 °C. An appreciable amount of hydrogen is evolved and the three-dimensional polymer network is compacted as a result of the formation of strong B–B, B–O–B and possibly B–C linkages. By virtue of the presence of the thermally stable macronetwork system, the resulting radicals are therefore unable to emerge from the "cage" and undergo secondary recombination processes. It has been suggested[40] that the hydrogen split off from the B–H bond can interact with the radicals, inhibiting further polymer decomposition processes.

Adhesives whose main strength characteristics are not reduced after prolonged (500 h) ageing at 500 °C have been prepared on the basis of *o*-carbaborane-containing resol resins[42]. There are tentative data concerning the synthesis of phenol-formaldehyde resins based on phenolphthalein *N*-[4-(*o*-carbaboranyl)phenyl]imide, which have been recommended as thermostable binders[43], and concerning the use of di[*N*,*N*'-di(hydroxymethyl)aminophenyl]-*o*-carbaborane for the hardening of phenol-formaldehyde oligomers[44].

VI. HETEROCHAIN POLYMERS

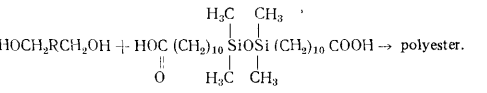
1. Polyesters

The number of studies on the synthesis of carbaborane-containing polyesters has diminished while the number of publications devoted to the investigation of the properties of the previously synthesised polyesters with carbaborane fragments remains comparatively large.

Korshak and co-workers described the synthesis of unsaturated carbaborane-containing polyesters[45]. Polyesters having different structures were synthesised, their boron content varying from 1 to 33 wt.%, which corresponds to the variation of the ratio of the number of carbaborane fragments to the number of unsaturation centres from 1 : 36 to 1 : 1. The starting compounds were *m*- and *p*-carbaboranedicarboxylic acids or their dichlorides, maleic anhydride, and various saturated and unsaturated aliphatic glycols such as ethylene glycol, hexamethylene glycol, but-2-enediol, but-2-ynediol, triethylene glycol, and tetraethylene glycol. All the carbaborane-containing unsaturated substances obtained proved to be oligomers having molecular weights ranging from 1400 to 6300 and readily soluble in organic solvents. Most of them readily copolymerise with styrene and form cross-linked polymers whose decomposition temperatures were in the range 275–400 °C. It has been established[45] that the thermal stability of the polymers synthesised depends mainly on the structure of the initial glycol and that the variation of the amount of boron in the polymer from 1 to 19 wt.% does not have a significant influence.

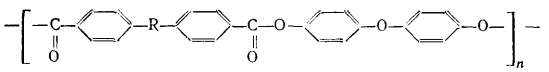
Thermostable adhesive compositions with a shear strength of 330 kg cm^{-2} at 25 °C and 50–60 kg cm^{-2} at 250 °C have been obtained from unsaturated polyester-*m*-carbaboranes containing 2–3 wt.% of boron[45]. In addition, the same polyesters containing 5–11 wt.% of boron were used to obtain an optical adhesive thermally stable up to 250 °C and ensuring the formation of a transparent adhesive seam with a transmittance coefficient up to 92% in the wavelength range 0.4–1 μm.[46]

The reaction of 1,2- or 1,7-di(hydroxymethyl)carbaborane with 1,3-di(10-carboxydecanyltetramethyldisiloxane yielded *o*- and *m*-carbaboranesiloxane polyesters[47]:

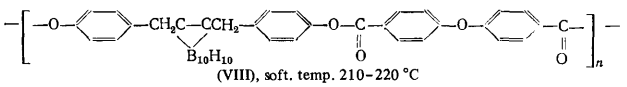


where R = *o*-carbaboranylene or *m*-carbaboranylene. The study of the kinetics of this polycondensation reaction showed that the introduction of the carbaborane fragments into the macromolecular chain greatly reduces the rate of formation of the polymers and the rate of reaction of the dibasic acid with 1,7-di(hydroxymethyl)-*m*-carbaborane is higher than that of the reaction with 1,2-di(hydroxymethyl)-*o*-carbaborane. It has been suggested[47] that the thermal stability of the carbaboranesiloxane polyesters is not inferior to that of the carbaborane-containing polyarylates, but, in contrast to the latter, they have lower softening temperatures. They are soluble in many solvents.

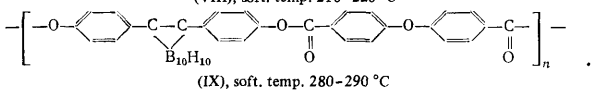
A number of studies[48–56] have been devoted to the carbaborane-containing polyesters with the following structure described previously:



R = *o*-carbaboranylene [compound (VI), soft. temp. 260–280 °C] or *m*-carbaboranylene [compound (VII), soft. temp. 240–260 °C]



(VIII), soft. temp. 210–220 °C



(IX), soft. temp. 280–290 °C

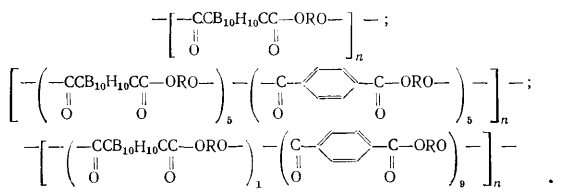
The kinetics of sorption and structural transformations in the tetrahydrofuran-polymers (VI)–(IX) systems have been investigated and it has been shown that the sorption of tetrahydrofuran vapour entails an improvement of the amorphous structure of the polymer, while in the case of polymers tending to crystallise there is a transition from the amorphous to a partly crystalline state[49]. The authors note that during the sorption of tetrahydrofuran vapour only the polymer (IX) crystallises. The latter phenomenon agrees well with the result of a study (by the dipole moment method) of the structures of low-molecular-weight compounds which serve as models of the polymers investigated[50]. It was established that the polymer (IX) can be represented by only one conformer, while a set of conformers is characteristic of other polymers.

In addition it has been shown that the vibrations of the *o*-carbaborane nucleus are hindered compared with the *m*-isomer both owing to the much more effective conjugation of the *o*-carbaborane fragment with the aromatic rings and due to steric effects. This feature is reflected in the relaxation processes in the carbaborane-containing polymers, the results of the study of which by various methods indicate an increase of the rigidity of the macrochain and an increase of the softening temperature on passing from *m*- to *o*-carbaborane-containing polyesters[51,52].

Ionic electrical conduction is mainly characteristic of carbaborane-containing polyesters, the conductivity of *o*-carbaborane-containing polyesters being higher by 1–2 orders of magnitude than the corresponding values for polyesters with *m*-carbaborane fragments[53].

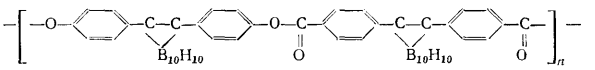
The structural-chemical transformations of *o*- and *m*-carbaborane-containing polyarylates on isothermal heating (225 to 325 °C) *in vacuo* in the presence of oxygen have been investigated[55]. It has been established that at a temperature as low as 225 °C processes involving the rupture of the ester linkage take place in the polymers with simultaneous changes in the carbaborane fragments (decrease of the number of B–H bonds and the appearance of the B–O–B linkages) and the formation of cross-linked structures. It has been shown that in the presence of oxygen the latter are formed owing to the interaction of the carbaborane fragments with oxygen, while *in vacuo* they result from the interaction with the oxygen-containing groups in the macromolecules.

In order to elucidate the influence of the quantitative content of *m*-carbaborane fragments on the thermal stability of polyarylates, a comparative study has been made of the thermal stabilities of polymers having the following structures[57]:



It has been established that the temperature of the onset of the decomposition of the test polymers (evolution of gaseous degradation products) *in vacuo* decreases from 375° to 320 °C as their content of *m*-carbaborane fragments increases. The different transformations of the *m*-carbaborane groups with evolution of hydrogen begin in all the polyesters at a temperature lower by 20–25 °C than the degradation of the main chain with formation of CO and CO_2. It is noteworthy that the weight loss by the polyester specimens at 700 °C diminishes from 34.7 to 19.5 wt.% with increase of their content of *m*-carbaborane fragments.

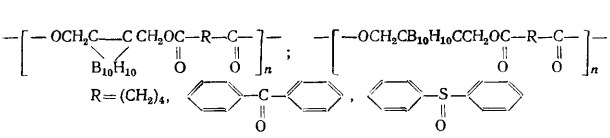
The structure of the involatile residues from the polyarylate having the structure



after its vacuum heat treatment in the temperature range 300–1200 °C has been studied by X-ray diffraction[56]. It was found that heating to 300 °C hardly induces any changes in the crystalline polymer specimen; under analogous conditions, an amorphous specimen becomes crystalline. An increase of the temperature to 400 °C leads to the complete disruption of the crystalline structure of the polyarylate and its conversion into the amorphous form. After heating at 500 °C, considerable chemical transformation occur in the polymer and an appreciable amount of H_3BO_3 is formed, indicating the interaction of the *o*-carbaborane groups and the products of their thermal transformations with the oxygen bound chemically in the polymer. At 600 °C the structure of the polyarylate with *o*-carbaborane fragments is fully disrupted and a dense network structure with strong B–B and B–O bonds is produced. Treatment at 700 °C leads to the appearance of a small number of graphite blocks; subsequent heat treatment of the polymer up to 1000 °C is hardly reflected in the structure and the mass of the specimens changes by only 5–8% under these conditions.

From their investigation, the authors[56] concluded that the main difference between the *o*-carbaborane-containing polyarylates and their normal analogues consists in the displacement of the temperature of the extensive decomposition and the rearrangement of the initial structure into the region of high temperatures and also in a specific interaction of the *o*-carbaborane fragments or the products of their thermal transformations with the chemically bound oxygen.

However, in the case of thermally less stable structures, for example, polyesters with aliphatic fragments having the structure



the presence of carbaborane groups does not affect the mechanism of the degradation of the polymers in the temperature range 300–420 °C.[58] The polyesters of aromatic dicarboxylic acids are stable on heating to 350 °C and those of

adipic acid are stable up to 250 °C. The thermal degradation of these polymers in the above temperature range proceeds without change in the carbaborane fragments via the mechanism usual for organic polymers.

There exist data concerning the use of *o*-carbaborane-containing polyarylates as binders for the formation of thermoplastic and thermostable self-lubricating materials[59] and for the preparation of negative photoresistors[60]. Furthermore, the VK-28 epoxide adhesive, which hardens at 150–200 °C and forms adhesive junctions between steel specimens having a shear resistance of 100–140 kg cm^{-2} at 20 °C and 80–90 kg cm^{-2} at 250 °C, has been devised on the basis of carbaborane polyethers[42,61].

2. Polyurethanes and Polyureas

The synthesis of *m*-carbaborane-containing unsaturated polyurethanes, formed by the interaction of unsaturated oligoesters with *m*-carbaboranylene di-isocyanate in accordance with the scheme[62]

$$H-(-ORO-COCH=CHCO-)_n-ORO H + OCNCB_{10}H_{10}CNCO \rightarrow$$
$$\rightarrow -[-(-ORO-COCH=CHCO-)_n-ORO-CONHCB_{10}H_{10}CNHCO-]_m$$
$$n = 2, 5, 6;\ R = -(-CH_2-)_2-,\ -(-CH_2-)_6-$$

has been described. The reaction is almost quantitative and does not involve the formation of volatile products. The polymers obtained are colourless rubber-like substances which are readily soluble in chloroform, tetrahydrofuran, acetone, benzene, and styrene and are insoluble in alcohol, ether, and hexane. They exhibit an effective adhesion to metallic surfaces and are capable of being hardened by styrene at 80 °C. According to thermogravimetric data obtained in air, the weight loss by the hardened polyurethane specimens is 5% at 340–350 °C (for a heating rate of 4.5 K min^{-1}). An adhesive composition, which hardens at room temperature after 6 h or at 85 °C after 2 h is effective at temperatures ranging from −60° to +150 °C, and can be used to join articles made of metals, plastics, ceramics, and glass, has been obtained on the basis of the *m*-carbaborane-containing polyurethanes synthesised[63]. In addition, the VK-20 hot-hardening adhesive, which is a polyurethane composition modified by a carbaborane-containing compound, has been described[42,64]. The adhesive junctions based on it are effective for 500 h at 350–400 °C and briefly at 800 °C. The VK-20 M adhesive, whose composition is analogous to that of the VK-20 adhesive, contains a catalyst which makes it possible to harden it at room temperature[42].

o-Carbaborane-containing polyureas have been obtained by the interaction of 1,2-di(*B*-amino-*o*-carbaboranyl)ethane with di-isocyanate in tetrahydrofuran at 18–25 °C in accordance with the scheme[65]

$$HC-C-CH_2CH_2-C-CH + OCN-R-NCO \rightarrow$$
$$B_{10}H_9NH_2 \qquad B_{10}H_9NH_2$$
$$\rightarrow -\left[\begin{array}{c} HC-C-CH_2CH_2-C-CH \\ -HNB_{10}H_9 \qquad\qquad B_{10}H_9NHCNH-R-NHC- \\ \qquad\qquad\qquad\qquad\qquad\quad \| \qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\quad O \qquad\quad O \end{array}\right]_n - ;$$
$$R = CH_3C_6H_3,\ C_6H_4CH_2C_6H_4$$

These polymers soften at 195–200 °C, begin to decompose at 240–250 °C, and their coke residues after heat treatment in air at 800 °C amount to 90–92%.

3. Polyamides

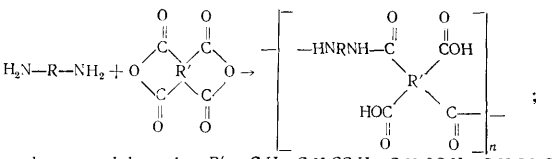
In the publications of the last decade comparatively little attention has been devoted to the synthesis of new carbaborane-containing polyamides[66–68], but a whole series of studies have been undertaken to investigate various properties of polyamides described previously[69–83].

A diamine in which the amino-groups were attached to a boron atom of the carbaborane nucleus and not to a carbon atom was first used for the synthesis of carbaborane-containing polyamides[66]:

$$HC-C-CH_2CH_2-C-CH$$
$$H_2NB_{10}H_9 \qquad B_{10}H_9NH_2 .$$

Polyamides stable on heating in air to 320–330 °C were obtained by the polycondensation of this diamine with aromatic dicarboxylic acid dichlorides.

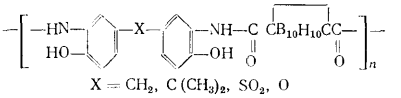
The synthesis and properties of polyamidoacids, obtained by the reaction of *m*- or *p*-carbaboranylenediamines with tetracarboxylic acid dianhydrides, has been reported[67]:



R = *m*-carbaboranylene or *p*-carbaboranylene; R′ — C_6H_2, $C_6H_3CC_6H_3$, $C_6H_3OC_6H_3$, $C_6H_3SO_2C_6H_3$.

All the *m*- and *p*-carbaborane-containing polyamidoacids are light coloured powders with $\eta_{int} = 0.1–0.5$ dl g^{-1}, which are readily soluble in the majority of organic solvents. *p*-Carbaborane-containing polyamidoacids hardly undergo a change in their viscosity characteristics on storage in the dry stage and in solution (in *N*-methylpyrrolidinone). Polyamidoacids with *m*-carbaborane fragments gradually decompose; their viscosity characteristics (the value of η_{int}) decrease from 0.35 to 0.20 dl g^{-1} after storage for a month.

A study has been published[68] in which *p*-carbaborane-containing polyhydroxyamides having the structure

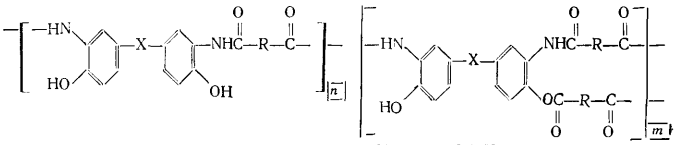


X = CH_2, $C(CH_3)_2$, SO_2, O

were obtained by analogy with the *m*-carbaborane-containing polyhydroxyamides described previously[1]. The structure of the *p*-carbaborane-containing polymers has been confirmed by elemental analysis and by comparing their infrared spectra with those of a model compound—the 1,12-di(*o*-hydroxyphenylamide) of *p*-carbaboranedicarboxylic acid. In contrast to the infusible *m*-carbaborane-containing polyhydroxyamides, the *p*-carbaborane-containing polyhydroxyamides soften in the range 220–270 °C and their molecular weights are 9000 to 10 000. As regards chemical stability, polyhydroxyamides with *p*-carbaborane fragments are analogous to the corresponding *m*-derivatives.

It has been noted[69] that, depending on the conditions in the formation of *m*- and *p*-carbaborane-containing polyhydroxyamides (depending on the ratio of the starting materials, the nature of the solvent, and other factors determining the course of the polycondensation process), their

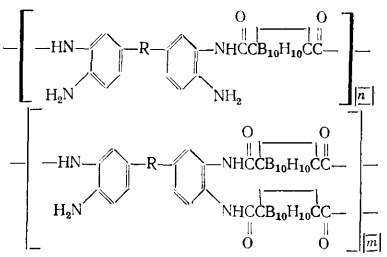
macromolecules can incorporate both linear and branches units:



R = *m*-carbaboranylene or *p*-carbaboranylene; X = CH_2, C $(CH_3)_2$, SO_2, O .

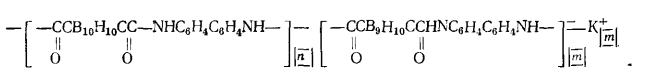
Their ratio $n : m$ varies from 1 : 0 to 0 : 1. The degree of heterounit structure in these polymers has been estimated quantitatively with the aid of infrared spectroscopy[69].

The relation between certain properties of *p*-carbaborane containing polyaminoamides and the structure of their macromolecules has been investigated[70]:



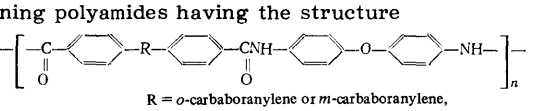
It was established that, as the degree of heterounit structure of the polyamides ($n : m$) varies from 0.9 : 1 to 1 : 9, the degree of their 'swellability' in tetrahydrofuran increases from 55% to infinity (i.e. the polymers become soluble) and the interchain distance in the polymer diminishes from 5.8 to 5.4 Å.

In the study of the chemical stabilities of the *m*-carbaborane-containing polyamides obtained previously it was observed that the *m*-carbaborane fragments are cleaved to the dicarbaundecaborate anion by dimethylformamide on heating to 100 °C or by alcoholic alkali in solution in tetrahydrofuran to form polyamides having the following structure[71]:



The dicarbaundecaborate fragments in these polyamides were determined quantitatively by ^{1}H NMR [72] and it was shown that the heterounit polyamide in which the numbers of the *m*-carbaborane and dicarbaundecaborate fragments are approximately equal ($n \cong m$) differs in a number of features from the polyamide containing only *m*-carbaborane groups ($m = 0$). Thus, in contrast to the latter, the heterounit polyamide does not dissolve in tetrahydrofuran, but is readily soluble in dimethyl sulphoxide and methanol, and transparent films of the polymer can be obtained from these solutions. The presence of dicarbaundecaborate fragments in the macromolecule greatly reduces the chemical and thermal stabilities of the polymer. Thus the viscosity of the heterounit polyamide decreases from 1.20 to 0.7 dl g^{-1} in boiling water after 3 h, while under the influence of dry HCl it diminishes from 1.20 to 0.3 dl g^{-1} in 1 h. The initial *m*-carbaborane-containing polyamide remains unchanged in both cases. The temperature of the onset of evolution of hydrogen from the heterounit polyamide is 80 °C, while that for the *m*-carbaborane-containing polymer is 200 °C.[71]

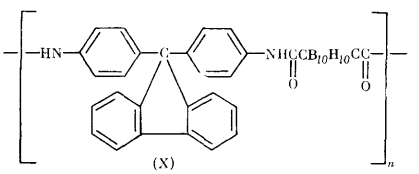
The electrophysical properties of *o*- and *m*-carbaborane-containing polyamides having the structure



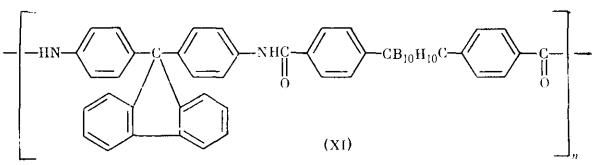
R = *o*-carbaboranylene or *m*-carbaboranylene,

have been investigated. It was shown that the replacement of the *o*-carbaborane fragment in the polyamides, as in the carbaborane-containing polyarylates, by the *m*-carbaborane fragment diminishes the rigidity of the macrochains[73].

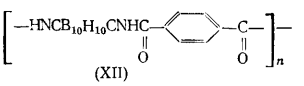
The study of the structural transformations of polyamides having the structures



(X)



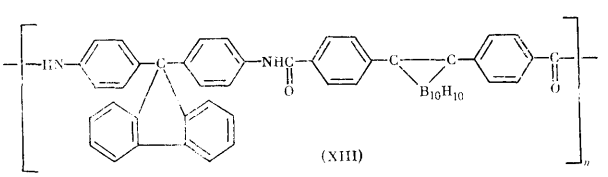
(XI)



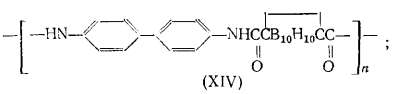
(XII)

at 100–350 °C *in vacuo* in an atmosphere of oxygen and water vapour established that in the above temperature range their macromolecules undergo simultaneously cross-linking and cleavage[74]. The branching and cross-linking processes predominate in the polyamide (XI), while chain dissociation as a consequence of the cleavage of the *m*-carbaborane fragments predominates in the polyamides (X) and (XII).

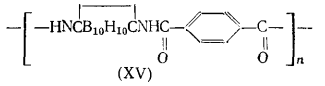
Questions concerning the degradation of the *m*-carbaborane-containing polyamides (X)–(XII) as well as polyamides with *o*- and *p*-carbaborane fragments having the structure



(XIII)



(XIV)



(XV)

in vacuo and in an atmosphere of oxygen and water vapour at 200–800 °C have been considered in detail in a review by Korshak et al.[6] The study of carbaborane-containing polyamides of this kind revealed the influence on the thermal stability of the polymers not only of the isomerism of the carbaborane group but also of the chemical nature of their substituents, in particular the influence on the stability of the carbaborane nucleus by nucleophilic and electrophilic groups such as the carbonyl, phenyl, and amide groups.

Korshak et al.[6] established that the isomerism of carbaborane influences significantly the stability of polyamides *in vacuo*. Whereas the breakdown of the *o*- and *m*-carbaborane fragments is the main degradation reaction in the polyamides (X)–(XIII), the amide groups becoming resistant to homolytic and heterolytic decomposition reactions, in the *p*-carbaborane-containing polyamides the NH–CO linkages are broken.

The isomeric *m*- and *p*-carbaborane-containing polyhydroxyamides have also significantly different thermal stabilities[68].

The antifriction properties of the *p*-carbaborane-containing polyamide (XIV) and its *m*-isomeric analogue have been investigated in the temperature range 250–450 °C.[75] On the basis of the results, the authors concluded that the hydrogen formed in large amounts on decomposition of *m*-carbaborane-containing polyamides creates a reducing medium between the surfaces involved in friction, which leads to the inhibition of the oxidative processes occurring at high temperatures. This is to a large extent responsible for the improvement of the lubricating properties of the antifriction plastics based on *m*-carbaborane-containing polyamides compared with the *p*-carbaborane-containing polyamides (a smaller amount of hydrogen is evolved from the latter in the experimental temperature range) and compared with polyamides without carbaborane fragments (these hardly evolve hydrogen at the above temperatures).

A series of studies in which the polyamides of *m*-carbaboranedicarboxylic acid were used as stabilisers against the thermal and thermo-oxidative degradation of aromatic cardo-polyamides[76–80] and polyphenylquinoxalines[81] have been published. It was established that, both *in vacuo* and in oxygen, the polyamides of *m*-carbaboranedicarboxylic acid are effective stabilisers of cardo-polyamides, which is reflected both in a considerable decrease of the rate of evolution of carbon oxides and in a decrease of the weight loss by the polymer specimens at 300–450 °C.[76,79] The authors suggest that the high thermal stability of specimens of aromatic cardo-polyamides to which 0.5 wt.% of the polyamide of *m*-carbaborane-dicarboxylic acid has been added is due to the appreciable weakening of the degradative processes and the formation during heat treatment of cross-linked structures containing the thermally stable B–N, B–C, and B–O bonds[82,83].

4. Poly-Schiff Bases

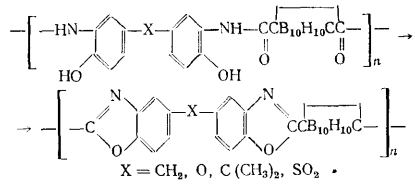
Only tentative data have been published about *m*- and *p*-carbaborane-containing poly-Schiff bases[84,85]. These polymers were first obtained by French investigators by the interaction of *m*- or *p*-carbaboranedialdehydes with various aromatic diamines in halogenated hydrocarbons, phenols, dioxan, and tetrahydrofuran in the presence of acceptors of the water involved, namely sodium and magnesium sulphates, calcium chloride, or molecular sieves. Polymers having the structure

$$H_2{-}[{-}NArN{=}CH{-}R{-}CH{=}]_n{=}O$$

(R = *m*-carbaboranylene or *p*-carbaboranylene; n = 5–1000), which are readily soluble and thermally stable, were obtained. They have been recommended for the manufacture of films, adhesives, and surface coatings.

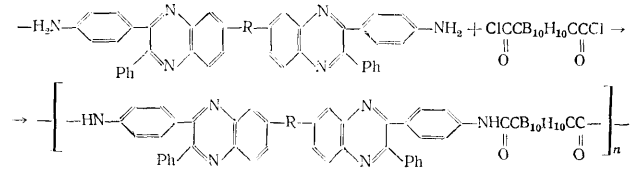
5. Polyheterocycles

Recently Korshak and co-workers synthesised carbaborane-containing polybenzoxazoles and polyphenylquinoxalines which had not been described previously[86–88]. *p*-Carbaborane-containing polybenzoxazoles were obtained by the thermal or chemical (in polyphosphoric acid) cyclocondensation of the corresponding poly-*o*-hydroxyamides in accordance with the scheme[86,87]

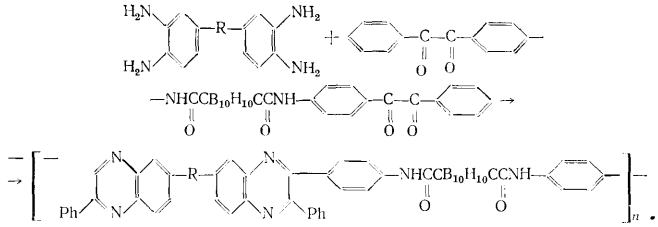


The structure of the polybenzoxazoles obtained was confirmed by elemental analysis and by comparing the infrared spectra of the polymers and model compounds. All the *p*-carbaborane-containing polybenzoxazoles are yellowish or pale-brown powders, which are amorphous (according to X-ray diffraction data) and soluble in amide solvents and in a tetrachlorethane–phenol mixture. The intrinsic viscosities of these polymers are 0.4–1.1 dl g^{-1}, their softening temperatures are in the range 290–360 °C, their decomposition temperatures are 400–550 °C, and their coke residue in air at 900 °C amounts to 80–98%. Polybenzoxazoles with *p*-carbaborane fragments are hydrolysed by hot water (η_{int}^{25} diminishes from 1.1 to 0.4 dl g^{-1} after boiling the polymer in water for 24 h).

m-Carbaborane-containing polyphenylquinoxalines have been synthesised in two ways[88]: 1) by the polycondensation of bis(aminophenylquinoxalines) with *m*-carbaboranedicarboxylic acid chloride in tetrahydrofuran at room temperature using triethylamine as the acceptor of the hydrogen chloride evolved:



2) by the interaction of aromatic tetramines with *m*-carbaborane-containing bis(α-diketone) at room temperature in *m*-cresol or in chlorinated hydrocarbons with added proton donors:

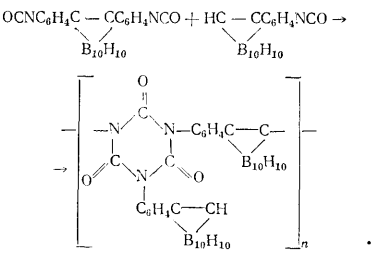


The use of mixtures of *m*-carbaboranedicarboxylic acid chloride with the chlorides of other dicarboxylic acids in various proportions in the first method of synthesis or of mixtures of bis(α-diketones) in the second method makes it possible to vary the content of the *m*-carbaborane fragments in the polymers and the properties of the latter in the required way. The *m*-carbaborane-containing polyphenylquinoxalines synthesised are fibrous or powdered products

with intrinsic viscosities in the range 0.8–2.2 dl g^{-1}. Depending on the quantitative content of the *m*-carbaborane groups in their macromolecules, the polymers soften in the temperature range 280–310 °C or begin to decompose, without softening, at ~400 °C. The carbon residue from the polymers after heat treatment in air at 800 °C amounts to 32–57%, while in an inert atmosphere it amounts to 70–80%. The solubilities of certain *m*-carbaborane-containing polyphenylquinoxalines in chloroform and tetrahydrofuran make it possible to obtain films with effective physicomechanical parameters from their 10% solutions.

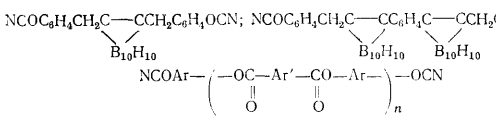
It is believed[88] that *m*-carbaborane-containing polyphenylquinoxalines are of undoubted interest for practical applications as heat-resistant and thermostable film materials, coatings, binders, fibres, etc.

There are reports in the patent literature concerning the synthesis of *o*- and *m*-carbaborane-containing polyisocyanurates, polycyanurate, and polymelamines[89–92]. *o*-Carbaborane-containing polyisocyanurates have been obtained by the polycyclotrimerisation of 1,2-di(isocyanatophenyl)-*o*-carbaborane with 1-isocyanatophenyl-*o*-carbaborane in a polar organic solvent (butyl acetate or dimethylformamide) or without solvent at 150–170 °C:[89]



Mixtures of various mono- and di-isocyanates have also been used instead of the *o*-carbaborane-containing monoisocyanates. Depending on the ratio of the starting materials, fusible soluble or infusible and insoluble polymers with enhanced thermal and thermal-oxidative stabilities were obtained.

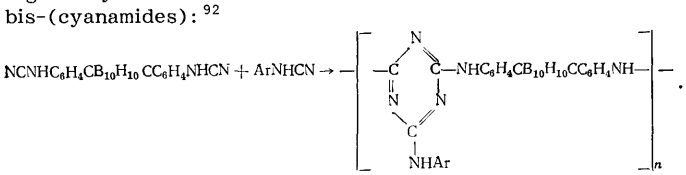
Polycyanurates with *o*- and *m*-carbaborane fragments have been obtained either by the polycyclotrimerisation of the *o*- and *m*-carbaborane derivatives[90,91]



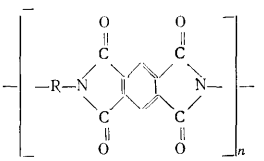
Ar = *o*-carbaboranylene, Ar′ = *o*- or *m*-carbaboranylene, and n = 1–20,

or by their copolymerisation with the monocyanate C_6H_5OCN. The temperature of the onset of decomposition of these polymers is 310–380 °C in air and 380–390 °C in an inert atmosphere, their specific impact strength reaches 30 kg cm^{-2}, their Brinell hardness is 1600 kg cm^{-2}, and their bending strength is 1500 kg cm^{-2}. The authors[90,91] suggested that the degradation of polycyanurates begins with the hydrolytic cleavage of the ester linkage and is accompanied by the subsequent decomposition of the triazine ring via both heterolytic and homolytic mechanisms.

The corresponding polymelamines have been synthesised by the polycyclotrimerisation of the *m*-carbaborane-containing bis(cyanamides) or their mixture with aromatic mono- and bis-(cyanamides):[92]



The thermal and chemical cyclodegradation of *m*- and *p*-carbaborane-containing polyamidoacids, which results in the formation of the polyimides having the following structure have been described[67]:



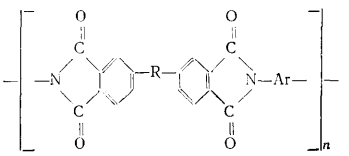
R = *m*-carbaboranylene or *p*-carbaboranylene.

It has been established that the formation of *m*-carbaborane-containing polyimides is accompanied by the conversion of the *m*-carbaborane fragments into dicarbaundecaborate fragments, while the conversion of polyamidoacids with *p*-carbaborane groups into a polyimide takes place without the cleavage of the *p*-carbaborane nucleus.

All the polyimides obtained in this way are soluble in amide solvents and the intrinsic viscosities η_{int} = 0.15–0.40 dl g^{-1} have been obtained for them. The polyimides with *m*-carbaborane fragments do not soften and begin to be oxidised in air at 250 °C, while those with *p*-carbaborane fragments soften at 400–450 °C with decomposition. The carbon residues from these polymers after heating in air up to 800 °C amount to 79–100%.

The study of the thermal degradation of these polymers in the temperature range 100–600 °C established that the introduction of *m*-carbaborane fragments into the polyimide macromolecule reduces the rate of the homolytic and heterolytic decompositions of the rings to a greater extent than the introduction of *p*-carbaborane groups[93].

The electrophysical properties and molecular mobilities of *o*- and *m*-carbaborane-containing polyimides having the following structure have been studied in detail[94,95]:



R = *m*-carbaboranylene or *o*-carbaboranylene.

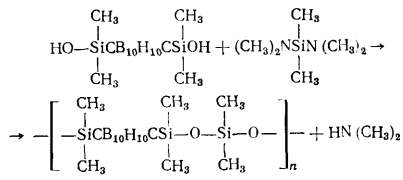
The study of the pyrolysis of these polyimides at 1000 °C in an inert medium and in air established that the diphenyl-*o*-carbaborane or diphenyl-*m*-carbaborane fragments with the adjoining imide rings are subjected to homolytic decompositions to the greatest extent and their primary decomposition products can be H_2 (from carbaborane fragments), carbon monoxide (from the imide ring), benzene, and mono- and di-phenyl-*o*- or -*m*-carbaboranes[96]. The yield of carbon from the *o*- and *m*-carbaborane-containing polyimides in an inert atmosphere is 93–95% on heating to 900 °C.

6. Polysiloxanes and Polysilazanes

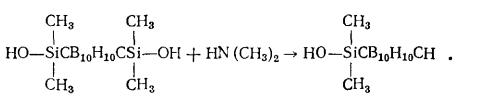
The studies in the field of new methods of synthesis of *m*-carbaborane-containing polysiloxanes of the type of Dexsil and the studies of their properties continue to develop vigorously. The difficulties in the synthesis and vulcanisation of these polymers, in which improved thermal stability is combined with elasticity, hinder their practical application[97].

In the methods of synthesis of Dexsils used previously[1] the difficulties were associated with the employment of iron(II) chloride as the catalyst of the condensation of *m*-carbaborane-containing chlorosilane and alkoxysilane, which induced premature structure formation and prevented the formation of

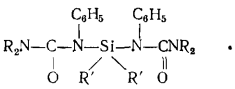
linear polymers. A new method of synthesis of linear Dexsils with a molecular weight of ~18 000, based on the condensation of an *m*-carbaborane-conaining disilanol with a reactive silane, for example bis(*N*,*N*-dimethylamino)dimethylsilane or bis(*N*,*N*-dimethylcarbamato)dimethylsilane, under mild conditions has been described[97]:



The formation of Dexsils with higher molecular weights by both procedures is prevented by the occurrence of the side reaction



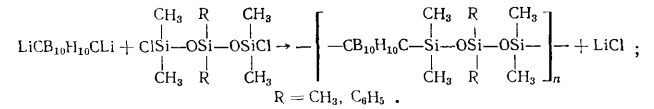
Dexsils with molecular weights > 25 000 have been synthesised using stable bisureidosilanes as the reactive silanes[97–99]:



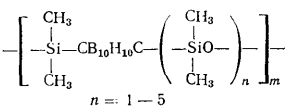
With increase of the molecular weight of Dexsils to 283 000, there is a sharp improvement of their elastomeric properties. Thus polymers with molecular weights of 50 000, 150 000, and 283 000 have tensile strengths of 7.0, 7.2, and 23 kg cm^{-2} and relative elongations of 5, 60, and 700% respectively.

A new method of synthesis of Dexsils[97–99] facilitates its modification. For example, by employing a certain amount of bis(ureido)diphenylsilane or bis(ureido)methylphenylsilane in the bis(ureido)silane mixture during the synthesis, one can introduce phenyl groups into Dexsils in order to improve their thermo-oxidative stability[98]. Trifluoropropyl groups are introduced similary into Dexsils in order to improve their resistance to the action of solvents[100].

American investigators proposed another very convenient method of synthesis of Dexsils directly from *m*-carbaborane[101]:



However, the molecular weights of the polymers thus obtained are low. Studies on the influence of the length of the siloxane fragment on the thermal characteristics of poly-*m*-carbaboranylenesiloxanes having the structure



are being continued[102,103]. Their results confirm the earlier conclusion that, with increase of the length of *n* of the siloxane fragment from 1 to 5, the glass points of the polymer gradually diminish from 25° to −88° and the weight losses by the polymer specimens after heat treatment at 800 °C in argon increase greatly.

The thermal, thermo-oxidative, and hydrolytic stabilities of high-molecular-weight poly-*m*-carbaboranylenesiloxanes have been studied in detail[103–105]. It was established[104] that the main transformations are undergone by the polymers in the temperature ranges 240–310 °C and 450–550 °C. A virtually complete loss of solubility of the polymer without change in the mass of its specimens is characteristic of the first temperature range, while only a change in the mass of the specimens, amounting to 3–6% in argon and 1–3% in air, is characteristic of the second range.

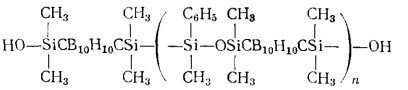
It has been shown that the thermal degradation of poly-*m*-carbaboranylenesiloxanes involves two competing processes: the degradation of the main chain, which results in the formation of oligomeric products, and the dissociation of the Si–C and C–H bonds accompanied by the evolution of CH_4 and H_2 and leading to structure formation[103]. The replacement of one or several methyl groups by phenyl groups activates the structure formation processes and diminishes the weight losses by the polymer specimens. The thermo-oxidative stability of poly-*m*-carbaboranylenesiloxanes greatly increases in the presence of Fe_2O_3.[106]

A characteristic feature of the thermal degradation of poly-*m*-carbaboranylenesiloxanes is an insignificant content of cyclic oligosiloxanes in the decomposition products[105]. It has been suggested[105] that the large bulk of the *m*-carbaborane groups prevents the formation of a helical form of the macromolecule and hinders thereby the decyclopolymerisation of the *m*-carbaborane-containing polysiloxanes. It has also been noted that the introduction of *m*-carbaborane fragments into the main chain of siloxane polymers reduces their hydrolytic stability as a result of of the appearance of the hydrolytically weak $Si-C_{carbaborane}$ linkage in these substances[104].

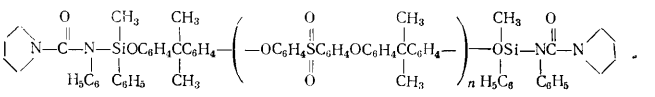
A method for the quantitative determination of the degree of branching of poly-*m*-carbaboranylenemethylphenylsiloxane, obtained in the presence of catalytic amounts of $FeCl_2$, has been proposed[107].

Poly-*m*-carbaboranylenesiloxanes tend to crystallise, which greatly impairs their elastomeric properties[108]. In order to diminish the crystallinity of these polymers, it has been suggested[108] that some of the *m*-carbaborane fragments be replaced by *p*-carbaborane fragments or that dimethylsiloxane units be replaced by diphenylsiloxane units. It was established that the introduction of 30 mole % of *p*-carbaborane or 33 mole % of diphenylsiloxane fragments into poly-*m*-carbaboranylenesiloxanes is sufficient for the formation of a fully amorphous polymer.

A new thermoplastic elastomeric block copolymer with $M \cong 10^6$ has been obtained by the reaction of poly-*m*-carbaboranylenesiloxane having terminal OH groups (molecular weights 45 560), i.e.

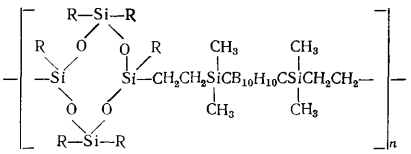


with the polysulphone (molecular weight 6020) [109]



It was shown that this block copolymer has two glass points (−27° and 165 °C), which correspond to the elastic (poly-*m*-carbaboranylenesiloxane) and rigid (polysulphone) blocks. According to thermogravimetric data, the block copolymer is stable up to 400 °C and is usable in the range from −40 °C to >300 °C. Polyimides, polyesters, poly(phenylene sulphides), and polybenzimidazoles can also be used for the preparation of the block copolymers instead of the polysulphone[110].

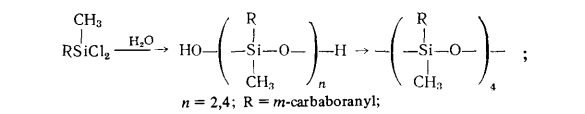
There exist patent data concerning the synthesis of linear *m*-carbaboranylenesiloxane oligomers having the following structure[111]:



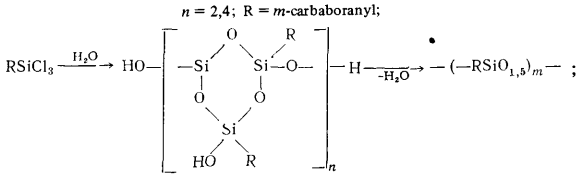
R = alkyl or aryl and n = 3-5.

These are formed when equimolar amounts of divinylorganocyclosiloxane and di(hydroxymethyl)-*m*-carbaborane interact at 50–200 °C in the presence of a hydrosilylation catalyst. When trivinylorganocyclosiloxane is used, branched oligomers are obtained[112]. All the oligomers synthesised in this way are transparent viscous liquids with $M \cong 2000$, which are readily soluble in aromatic hydrocarbons, ethers, and esters. The authors[112] recommend their use as thermostable rubbers and hermetic seals. The temperature of the onset of the thermo-oxidative degradation of the oligomers in air is ~400 °C. Infrared spectroscopic data have shown that the oligomers are synthesised solely as a result of the hydride addition reaction with retention of the structures of the initial compounds in the oligomers.

Oligomers with silanol groups have been obtained by the hydrolytic polycondensation of *m*-carbaboranylmethylorganochlorosilanes. Compounds with cyclic or cyclic-three-dimensional structures are formed from these substances at 250 °C:[113]



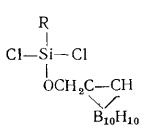
n = 2,4; R = *m*-carbaboranyl;



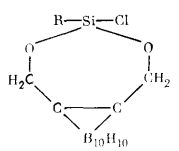
n = 2,3; m = 18, 24 .

The hardening of phenol-organosilicon oligomers by *N*,*N*-di(hydroxymethyl)aminophenol-*o*-carbaborane has been studied[114] and it has been found that the polymers hardened in this way exhibit a high thermal stability and heat resistance, while materials based on them possess improved dielectric properties.

Oligomeric organosilazanes containing *o*-carbaborane-fragments in the main or side chains in their molecules were synthesised for the first time by the ammonolysis of *o*-carbaboranylmethoxy(organo)dichlorosilanes



or *o*-carbaboranylenedimethoxy(organo)chlorosilanes



R = CH_3, C_6H_5, $CH{=}CH_2$

or by the co-ammonolysis of their mixture with organochlorosilanes having the formula R_mSiCl_{3-m}.[115,116] The *o*-carbaborane-containing oligo-organosiloxanes obtained have been recommended as hardening and modifying agents for polyphenylenes[117].

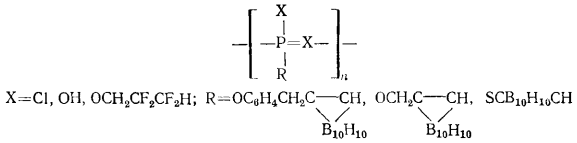
The practical value of poly-*m*-carbaboranylenesiloxanes, in which a high thermal stability (up to 500 °C) is combined with effective fire resistance (oxygen index 62), has been noted in a review[118]. These polymers have found extensive applications as the liquid phases in gas chromatography for the separation of organosilicon and organic substances[119] and for the analysis of polycyclic aromatic hydrocarbons at 20–450 °C.[120]

Adhesive compositions, capable of being used for a long time (up to 2000 h) at 600 °C and of withstanding brief exposures to a temperature of 1200 °C, have been created on the basis of *m*-carbaborane-containing polysiloxanes[42,121]. These adhesives are designed for the glueing of semiconducting materials to metals and silicate glasses in electrovacuum devices.

Poly-*m*-carbaboranylenesiloxanes are used as coatings for conducting wires and other articles capable of withstanding a temperature of ~300 °C [118,122] and also as lubricating materials in constructions subjected to irradiation at high temperatures[123].

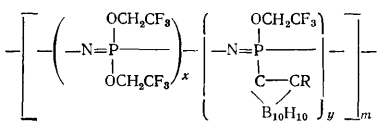
7. Polyphosphazenes

In order to improve the thermal stability of polyphosphazenes, Korshak and co-workers attempted to introduce *o*- and *m*-carbaboranyl groups into these polymers; as a result, *o*- and *m*-carbaborane-containing polyphosphazenes



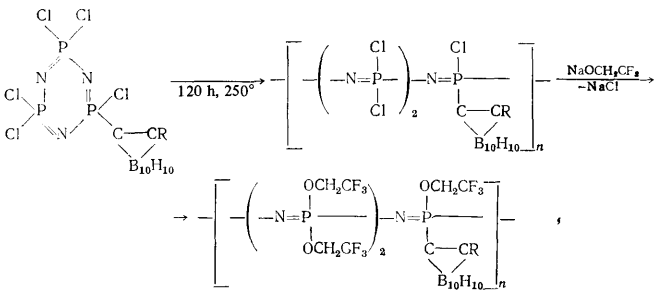
were obtained for the first time and characterised[124,125]. It was shown that, when polydichlorophosphazenes react with monolithio-derivatives of the corresponding *o*-carbaboranes or with monomercapto-*m*-carbaborane in solution in tetrahydrofuran, the maximum degree of substitution of chlorine by *o*- or *m*-carbaboranyl groups does not exceed 50%. The polymers obtained are white or pale-yellow powders with intrinsic viscosities ranging from 0.15 to 3.00 dl g^{-1}. Their chemical and thermal stabilities are determined by the character of the groups surrounding the main polymer chain. The softening temperatures of these polymers are therefore in the range 90–270 °C and the carbon residue after heat treatment in helium at 900 °C is 26–100%.

Somewhat later Allcock and co-workers[126–128] described *o*-carbaborane-containing polyphosphazenes having the structure

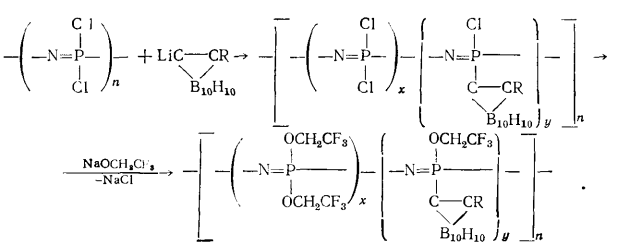


R = CH_3, C_6H_5 .

These polymers were obtained by two methods: either by the polymerisation of the corresponding mono-*o*-carbaboranylpentachlorocyclotriphosphazene in sealed tubes with subsequent substitution of chlorine atoms by CF_3CH_2O groups:



or by the interaction of polydichlorophosphazene (molecular weight 10^4–10^6) with monolithio-*o*-carbaborane:



The molecular weights of some of the *o*-carbaborane-containing polyphosphazenes obtained in this way reached 10^5 and the carbon residue in an inert atmosphere at 1000 °C was 56.5%. The authors[128] recommend *o*-carbaborane-containing polyphosphazenes for use as thermostable thermally insulating materials.

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Thus the literature data published in recent years permit the conclusion that carbaborane-containing polymers continue to attract the attention of investigators. The study of the properties of polymers with carbaborane fragments, their modification, and the search for new, simpler methods of synthesis of polymers showing the greatest promise in practical applications are of special interest.

As regards the prospects for the further development of the chemistry of carbaborane-containing polymers, one can suppose that, in view of the high cost of the starting materials, the amount of these polymers manufactured will not be great; nevertheless, in view of their unique properties, they will probably become in future some of the most important of polymeric materials.

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