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Polymers Based on Unsaturated Derivatives of Carbaboranes

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The literature data on the polymerisation and copolymerisation of unsaturated derivatives of carbaboranes and silicon- and carbaborane-containing compounds as well as the physicochemical properties of the polymers obtained are surveyed. Special attention has been devoted to the synthesis of polymers with dicarbaundecaborate fragments and metallocarbaborane complexes based on them.
The bibliography includes 118 references.

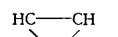
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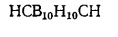
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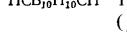
I. INTRODUCTION

One of the interesting advances in the modern chemistry of organoelemental compounds is the discovery in 1962–1963 of carbaborane(12)† $C_2B_{10}H_{12}$ and its derivatives—a new class of electron-deficient polyhedral systems.[1-3] The great synthetic possibilities due to the high reactivity of the B–H and C–H bonds in the carbaborane nucleus and the unusual thermal behaviour of carbaboranes[4,5] have attracted the attention of investigators to these boron compounds for more than 20 years.

Carbaborane(12) has three isomeric forms which have come to be represented schematically in the following manner:[6]


1,2-dicarba-*closo*-dodecaborane(12) (*o*-carbaborane)


1,7-dicarba-*closo*-dodecaborane(12) (*m*-carbaborane)


1,12-dicarba-*closo*-dodecaborane(12) (*p*-carbaborane)

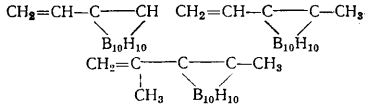
A large series of compounds have been synthesised on the basis of carbaboranes,[6-11] many of which are used to obtain various classes of polymers containing carbaborane units in the main or side chain. Carbaborane-containing polymers are obtained both by polymerisation and polycondensation methods. The advances in the synthesis of these polymers have been examined in a series of monograph and reviews,[12-18] but the latter have been devoted mainly to polymers of the polycondensation type. Hitherto there have been virtually no reviews on the polymerisation and copolymerisation of unsaturated carbaborane-containing monomers and to the study of the properties of carbochain polymers based on them. Nevertheless, appreciable progress has been noted in this field in recent years. The copolymerisation of carbaborane-containing compounds with vinyl monomers, which makes it possible to impart new valuable properties to known polymers by introducing carbaborane nuclei into their structure which as a rule increases the temperature of the onset of the decomposition of the polymers and the yield of the coke residue, has aroused special interest.

Since 1984, information has appeared in the literature on the polymerisation of new types of monomers—unsaturated derivatives of dicarbaundecaborates. A special section of the review has therefore been devoted to polymers with dicarbaundecaborate fragments and to polymeric metallocarbaborane complexes based on them.

II. CARBOCHAIN POLYMERS BASED ON UNSATURATED DERIVATIVES OF CARBABORANE(12)

The problem of the synthesis of polymerisation carbaborane-containing polymers reduces to a study of the reactivity of the monomer, which is also usual for other compounds, and the allowance for specific properties of icosahedral carbaboranes such as the presence of steric hindrance due to bulky groups and the electron-accepting character of the carbaborane nucleus, which reduces the electron density in the double bonds of alkenylcarbaboranes.[13] In addition, one should note the sensitivity of the carbaborane groups to the action of the nucleophiles.[19] For this reason, the attempts to carry out the radical and ionic polymerisation of alkenylcarbaboranes were unsuccessful for a long time or led only to the formation of oligomers.

The first carbaborane-containing carbochain polymers were synthesised by polymerising monomers containing the vinyl group linked directly to the carbon atom of the *o*-carbaborane nucleus:



The polymerisation was carried out in solution or in bulk in the presence of phenyl-lithium at 33–200 °C. This yielded polymers with a molecular weight of $(1.4-7.1) \times 10^4$, which have been proposed as a component of the solid fuel for rocket engines.[20]

Subsequently, polyvinyl-*o*-carbaborane with a molecular weight (MW) ranging from 5×10^4 to 14×10^4 was obtained at room temperature in solution in ethyl ether in the presence of phenyl-lithium.[21] The polymers were white amorphous substances with a softening temperature of 250–280 °C (depending on the MW), soluble in benzene and ether, and insoluble in aliphatic hydrocarbons. The radiation-induced polymerisation of vinyl- and isopropenyl-*o*-carbaboranes in the melt at 100–140 °C [22] also leads to the formation of soluble polymers with MW up to 2.5×10^4.

† Dicarbadodecaborane(12) (Ed. of Translation)

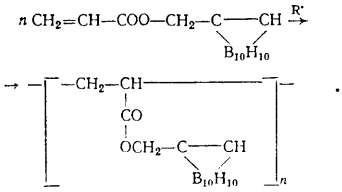
The polyvinyl-*o*-carbaborane synthesised by polymerising vinyl-*o*-carbaborane at 31 °C under the influence of γ-radiation[23–25] differs in its properties from those described above. It does not soften up to 430 °C, is readily soluble in alcohols, acetone, and dimethyl sulphoxide, and is less soluble in hexane and benzene. It has been found that the yield of the polymer increases linearly with increase in the radiation dose, reaching 50% for a dose of 3.5×10^{21} eV g^{-1} h^{-1}. The rate of polymerisation is proportional to the intensity of radiation raised to the power 0.76, the maximum degree of polymerisation being 11–12. The set of IR and ^1H and ^{11}B NMR spectroscopic data justified the hypothesis that the polymerisation of vinyl-*o*-carbaborane under the influence of γ-radiation is of the "head to tail" type.

All the attempts to obtain a polymer from isopropenyl-*o*-carbaborane by radical polymerisation were unsuccessful.[21,26] The polymerisation of this monomer in the presence of t-butyl peroxide, the amount of which was 50 wt.%, yielded only a trimer, and a product with a MW of 1790, a softening temperature of 165 °C, and a melting point of 270 °C was obtained only when $AlCl_3$ (~5%) was used. Dimers and trimers with a main hydrocarbon chain, carbaborane side groups, and terminal vinyl groups have also been obtained by the radiation-induced polymerisation of isopropenyl-*o*-carbaborane.[23]

A solid vitreous substance with a molecular weight of (1.0 to 7.5) $\times 10^4$ is formed from 1-allyl-*o*-carbaborane in the presence of $AlCl_3$.[21] The products of the radiolysis of 1-allyl-*o*-carbaboranes by ^{60}Co γ-rays[27] were fractionated by gel chromatography and investigated by the IR, NMR, and chromatomass-spectrometric methods. It was found that the main products comprised seven dimers with the same molecular weight of 366, differing in the positions of two double bonds in the molecule, and saturated oligomers with a degree of polymerisation of 5, independent of the radiation dose and dose rate. According to the reaction mechanism proposed, the abstraction of a hydrogen atom from the allylcarbaborane results in the formation of radicals of the allyl type whose recombination yields unsaturated dimers. The addition of a hydrogen atom to the carbaborane monomer affords radicals of the propyl type, which propagate the radical chain process with chain transfer leading to the formation of unsaturated oligomers. The chain termination in the dimer and oligomer formation processes takes place via a bimolecular mechanism.

The influence of the physical state on the radiolysis of solid alkenyl-*o*-carbaboranes, for example, 1-allyl-*o*-carbaborane,[28] has been demonstrated. 1-Allyl-*o*-carbaborane can exist in three mesomeric phases: in the temperature range from −3° to −16 °C (phase 1), from 16° to −36 °C (phase 2), and below −36 °C (phase 3). The average degree of polymerisation of the oligomers obtained by the radiolysis of the allylcarbaborane is 5 and is independent of temperature in the range from −50° to +50 °C. The results obtained have been discussed from the standpoint of the influence of the structure of the crystal lattice and diffusion-controlled processes. The authors note that the nature of the solid state, i.e. the crystallinity, plays an important role in radiolytic reactions. The dipole moments of vinyl-, isopropenyl-, and allyl-*o*-carbaboranes have been measured.[29] The quantum-chemical calculation of the charge distribution in these compounds and of the dipole moments μ with the experimental (taken from the literature) bond lengths and valence angles have been carried out by the INDO (incomplete neglect of the differential overlap of atomic orbitals) method. The calculated absolute values of μ were found to be about twice as high as the experimental values taken from the literature. However, the orientation of μ and the charge distribution, indicating the transfer of negative charge to the substituent, confirmed qualitatively, in the authors' view, the hypothesis that the free-radical oligomerisation of 1-alkenyl-*o*-carbaboranes can result in the formation of radicals, leading to the incorporation of the carbaborane fragment in the main chain. However, the carbochain polymer with carbaborane groups in the main chain is formed preferentially, which has been demonstrated convincingly by the EPR method.

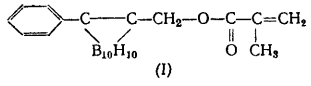
The polymerisation of monomers whose double bond is remote from the carbaborane nucleus, which promotes a decrease in the steric influence of the carbaborane group and the formation of polymers with large molecular weights, proceeds more readily. For example, 1-acryloyloxymethylene-*o*-carbaborane polymerises readily in bulk in the presence of 2% of benzoyl peroxide at 60 °C:[26]



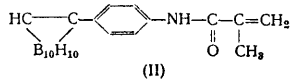
The polymer is a solid and brittle substance soluble solely in boiling terphenyl. It softens and becomes rubber-like at 165 °C. The poor solubility of this polymer is associated, according to the authors,[30] with the cross-links formed as a result of the interaction of the unsubstituted CH group of the *o*-carbaborane with the acrylic group of the growing chain. Under analogous conditions, 2-methacryloyloxymethyl-1-methyl-*o*-carbaborane affords a polymer which is readily soluble in chloroform.

A homopolymer of 1-methacryloyloxymethylene-*o*-carbaborane (MOC) with a MW of 5000 has been obtained by carrying out the reaction in benzene in the presence of 2% of azobisisobutyronitrile (ATBN).[22] Later, analysis of the structure of the MOC molecule, taking into account the remoteness of the carbaborane nucleus from the double bond, justified the assumption[31,32] that the radical polymerisation of this compound can yield products with higher molecular weights. A study of the kinetics of the radical polymerisation of MOC in benzene revealed the characteristic features of this reaction and demonstrated the influence of the concentration of the monomer in solution on the molecular weight characteristics as well as the possibility of obtaining polymers with molecular weights of (1.5–40) $\times 10^4$. The gel effect, which is so characteristic of the polymerisation of methacrylic acid esters, is absent. The orders of the polymerisation reaction with respect to the monomer and the initiator (1.28 and 0.44 respectively) and the process activation energy (17.5 kcal mol^{-1}) were determined. The polymer, with a MW of 40×10^4, begins to decompose vigorously in air at 270 °C without passing to a viscofluid state.

The synthesis and radical polymerisation in bulk of methacryloyl derivatives of *o*-carbaborane, not described previously, have been reported:[33] 1-methacryloyloxymethylene-2-phenyl-*o*-carbaborane (I) and 1-[4-(methacryloylimino)phenyl]-*o*-carbaborane (II):



(I)

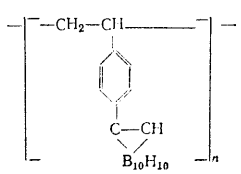


(II)

The homopolymers obtained from these monomers are colourless transparent blocks insoluble in organic solvents and characterised by a gel fraction content of up to 70%. According to the results of dynamic thermogravimetric analysis (DTGA) in air, the temperatures of the onset of decomposition of the polymers of compounds (I) and (II) are 215° and 190 °C. The formation of structured polymers may be associated, in the authors' view, with the presence in the compound synthesised of mobile hydrogen atoms both in the C—H group of the carbaborane and in the *para*-position in the benzene ring, on the one hand, and in the methylene group $-CH_2-$, which is influenced by two electron-accepting groups in the monomer (I) and by the amide hydrogen in the monomer (II), on the other.

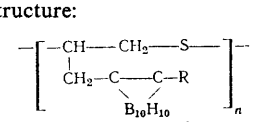
Communications explaining structure and formation in the course of the synthesis of carbaborane-containing polymers in the presence of peroxides by the involvement of free boron-centred radicals, leading to branching and to network structures have appeared recently.[34-36]

The capacity of 4-(1-*o*-carbaboranyl)styrene for polymerisation under various conditions has been investigatged.[37] Polymers with the highest molecular weight (up to 6×10^4) and a softening temperature of 280—240 °C have been obtained by thermal polymerisation at 160—200 °C. In the presence of radical initiators, polymers with a MW of $\sim 1.2 \times 10^4$ and a softening temperature of 320 to 340 °C are formed. Polymerisation via the anionic mechanism takes place slowly, while that involving the cationic mechanism does not occur at all. On the basis of the IR spectra of the polymers, the authors suggested that the polymerisation takes place in all cases via the vinyl group and that the polymer has the following structure:



The polymerisation of *p*-(*o*-carbaboranyl)phenylacetylene in solution in aromatic solvents in the presence of triphenylphosphine-nickel acetylacetonate has been investigated.[38] The use of this catalyst made it possible to obtain linear polyconjugated carbaborane-containing oligophenylacetylenes with MW of 1230—1320. A mechanism has been proposed for the formation of the active centre and the chain propagation. The oligomers synthesised are thermoplastics with a softening temperature of 80—115 °C.

The ionic polymerisation, with ring opening, of 3-[alkyl(aryl)-*o*-carbaboranyl]-1,2-epithiopropanes in bulk and in solution has been investigated[39] in order to obtain polymerisation polysulphides with enhanced solubility and thermal stability. Polymers with the highest molecular weight (2.5×10^5) were obtained via the anionic mechanism in solution using specially synthesised cyclic cadmium carbaboranylthiolates as initiators. Cationic polymerisation under the influence of BF_3 etherate takes place even at -20 °C, but it leads to polymers with a lower molecular weight (1.7×10^4). Polycarbaboranyl sulphides with the *o*-carbaborane group in the side chain are amorphous substances softening at 50—120 °C, which apparently have the following structure:



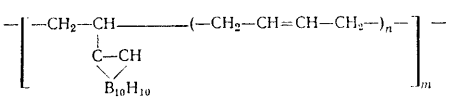
R=C_6H_5, $(CH_3)_2CH$;
n=60—970

According to DTGA data, the temperatures corresponding to a 5% weight loss by these polymers are 250—300 °C.

There are only a few literature data on the three-dimensional polymerisation of bifunctional unsaturated carbaborane-containing monomers. Carbochain cross-linked carbaborane polymers have been obtained by the radical polymerisation of unsaturated compounds with two allyl or acryloyl groups.[40,41] Thus the network polymer based on diallyl *m*-carbaboranedicarboxylate[40] with a glass point of 300 °C has been synthesised in bulk in the presence of a mixture of benzoyl peroxide and t-butyl peroxide as initiators. There is a good correspondence between the experimental and calculated glass points, which indicates the virtually complete conversion of the double bonds of the allyl groups. The polymerisation of di(acryloyloxymethylene)-*o*-carbaborane in the presence of peroxide initiators has been investigated by IR spectroscopy and differential thermal analysis.[41] It was shown tht the most effective initiator of the polymerisation leading to the formation of thermostable polymers is dicumenyl peroxide.

Thus, despite the difficulties encountered by investigators in the study of the homopolymerisation of carbaborane-containing compounds, definite advances have been achieved in this field in recent years and polymers with high molecular weight (MW up to 10^5) have been synthesised.

Unsaturated carbaborane-containing compounds are known to copolymerise readily with various vinyl polymers. Thus a rubber-like product having the following structure has been obtained by the copolymerisation of vinyl-*o*-carbaborane with butadiene:[21]



n = 5 or 7.

The copolymers of isopropenyl-*o*-carbaborane with butadiene have been synthesised by radical copolymerisation in bulk (the molecular weight did not exceed 1000)[42] and in emulsion.[43] The copolymer of acryloyloxymethylene-*o*-carbaborane with butadiene has been obtained in emulsion.[44] The radical copolymerisation of vinyl-*o*-carbaborane with allyl-*o*-carbaborane and 1-isopropenyl-*o*-carbaborane-2-carboxylic acid results in the formation of copolymers with MW of $(6-55) \times 10^3$.[21]

The synthesis of carbaborane-containing oligomers based on isoprene and vinyl- and isopropenyl-*o*-carbaboranes, with the copolymerisation initiated by hydrogen peroxide and cumenyl hydroperoxide in solution in alcohol, has been described.[45] The copolymerisation constants for the systems investigated were calculated by the integral Mayo—Lewis method and the low activity of alkenylcarbaboranes in copolymerisation with dienes was demonstrated. The oligomers obtained had molecular weights ranging from 2000 to 3340 and contained terminal hydroxy-groups. On the basis of the dependence of the degree of polymerisation on the concentration of monomers and the bifunctional nature of the oligomer, the authors suggested that chain termination takes place via a recombination reaction and that the reactions involving chain transfer from the alkenylcarbaborane group to the monomers and the solvent do not take place.

The copolymerisation of ispropenyl-*o*-carbaborane with methyl acrylate (MA) in the presence of AIBN produces a copolymer whose boron content depends on the concentration of isopropenyl-*o*-carbaborane in the initial mixture.[26,46] The copolymer, containing 22% of

boron, is a vitreous substance with a softening temperature of 45 to 80 °C, while the copolymer with 10% of boron softens at 45 – 50 °C. Copolymers with approximately the same boron content are formed in the copolymerisation of MA with vinyl-*o*-carbaborane.[46]

In contrast to MA, methyl methacrylate (MMA) hardly copolymerises with isopropenyl-*o*-carbaborane in solution in toluene in the presence of ATBN.[47] Vinyl-*o*-carbaborane does not copolymerise with MMA under these conditions either. The higher reactivity of vinyl- and isopropenyl-*o*-carbaboranes in copolymerisation with MA compared with MMA is due to the smaller steric hindrance and the higher activity of the macroradicals with terminal MA units.[46]

Both these carbaborane-containing monomers are relatively inactive in copolymeristion with styrene, which is indicated by the low boron content (not more than 4%) in the copolymers formed. Later it was possible to obtain[48] copolymers of the above monomers with *p*-chlorostyrene and *p*-methoxystyrene, in which the boron content reached 25 – 50% of the theoretical value.

Analogous results have been obtained in the copolymerisation 2-ferrocenyl-1-vinyl-*o*-carbaborane and 2-ferrocenyl-1-isopropenyl-*o*-carbaborane with styrene in MMA.[49] It was shown that both ferrocenyl-*o*-carbaboranes enter into the composition of the copolymers with MMA in an extremely limited amount and are much more active in copolymerisation with styrene. Furthermore, in all cases an increase in the content of the ferrocenyl-*o*-carbaboranes in the initial mixture reduces the molecular weight of the copolymers.

A copolymer of methacryloyloxymethylene-*o*-carbaborane with acryloylferrocene, having a MW of 3×10^4, and a copolymer of vinylferrocene, isopropenyl-*o*-carbaborane, and isoprene have also been synthesised.[50]

The radical copolymerisation of acryloyloxymethylene-*o*-carbaborane with fluorinated acrylates has been carried out in bulk and in emulsion.[26,51] Some of these copolymers are rubber-like substances with an MW of 2.3×10^3, soluble in acetone, ethyl methyl ketone, or diethyl ketone.

Copolymers with a boron content up to 24% have been obtained by the radical copolymerisation of 1-methacryloyloxymethylene-2-phenyl-*o*-carbaborane (I) and MMA in bulk in the presence of benzoyl peroxide.[52] It was found that the copolymers are enriched in MMA units for any initial monomer ratios. With increase in the fraction of the carbaborane compound (I), the softening temperature and the temperature of the onset of decomposition of the copolymers increase together with the yield of the coke residue. The copolymerisation under the same conditions of MMA with 1-[4-(methacryloylimino)phenyl]-*o*-carbaborane (II), the content of the latter in the reaction mixture not exceeding 5 mole % (limiting solubility),[52] results in the formation of copolymers with $\overline{M}_w$ = (9.1 to 10.8) $\times 10^4$ and polydispersity coefficients $\overline{M}_w/\overline{M}_n$ of 1.53 – 2.31.

In order to modify low-density polyethylene, the radical copolymerisation of ethylene with isopropenyl-*o*-carbaborane was carried out at a pressure of 1400 kg cm^{-1} and 160 °C in bulk and in solution.[53] It was shown that the rate of reaction and the molecular weight of the copolymers decrease with increase in the content of the carbaborane monomer in the reaction mixture. For a low overall degree of conversion of the monomers and a low content of isopropenyl-*o*-carbaborane in the initial mixture (up to 15 mole %), this relative activity proved to be higher than that of ethylene. The copolymers are plastic solids soluble in aromatic hydrocarbons and giving rise to elastic films on pressing at 130 – 170 °C. The influence of γ-radiation on copolymers containing 0.55 – 2.70 mole % of isopropenyl-*o*-carbaborane has been studied.[54] Measurements of the strength properties of the copolymers have shown that, for a low content of boron, their radiation stability is close to that of polyethylene. It has also been established that the resistance of the copolymers to thermo-oxidation diminishes after γ-irradiation.

The copolymerisation of vinyl-*o*-carbaborane with styrene in proportions of 1 : 3, initiated by γ-rays, has been investigated.[55] It was shown that the copolymer consists of 11 – 12 units and that there are approximately nine styrene units for two vinyl-*o*-carbaborane units. The structure of the copolymer was studied by NMR and flash pyrolysis; it softens up to 85 °C and melts at 105 °C.

Copolymers containing terminal hydroxy- or carboxy-groups have been synthesised by the copolymerisation of vinyl-*o*-carbaborane, isopropenyl-*o*-carbaborane, and acryloyloxymethylene-*o*-carbaborane with isoprene, butadiene, and chloroprene in solution at 65 °C in the presence of 4,4′-azobis(4-cyano-1-pentanol) or 4,4′-azobis(4-cyanovaleric) acid.[56] It has been noted that the large difference between the polarities of the comonomers ensures the ease of copolymerisation. The M_n of the copolymers are 2200 – 7400 and M_w/M_n = 1.38 to 1.85. In all cases, the yield and the molecular weight of the copolymers decrease with increase in the content of the unsaturated derivatives of *o*-carbaborane in the reaction mixture from 5 to 50 wt.%.

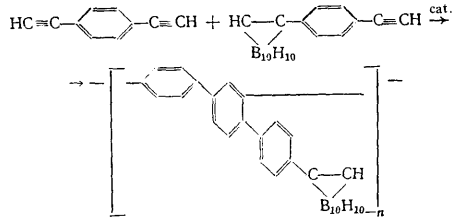
A copolymer of MMA and 4-(1-*o*-carbaboranyl)styrene with a MW of 3.08×10^4 and a softening temperature of 172 – 220 °C has been obtained.[37] While according to DTGA data a weight loss of 2% by PMMA is observed at 100 °C, the above copolymer loses 2% of its weight at 250 °C. Subsequently the authors[57,58] carried out the radical and thermal copolymerisation of 4-(1-*o*-carbaboranyl)styrene with MMA, isoprene, and acryloylferrocene. The copolymers synthesised with MW up to 2.8×10^4 were tested by the thermomechanical method and the stress relaxation method under scanning conditions. It was shown that, owing to the heterounit nature of the copolymers, their thermal characteristics (the glass point and the temperature of the onset of weight loss) vary both additively (copolymers with MMA) and non-additively (copolymers with isoprene). For the copolymers with acryloylferrocene,[58] a smooth increase in the glass point and the non-additive variation of the thermal stability are observed with increase in their content of carbaborane units.

In order to increase the thermo-oxidative stability of PMMA, network copolymers of MMA with bifunctional unsaturated isomeric derivatives of carbaboranes—the diallyl esters of *m*- and *p*-carbaboranedicarboxylic acids[59,60] and 1,2-di(methacryloyloxymethylene)-*o*-carbaborane [61,62]—were synthesised in bulk via a radical mechanism. Investigation of the thermo-oxidative degradation of all the copolymers obtained showed that the introduction from 0.1 to 0.5 mole % of *m*- and *o*-carbaborane fragments into the PMMA chain increases sharply the thermo-oxidative stability of the polymer, while the presence of *p*-carbaborane nuclei in the copolymer structure reduces such stability. It has been suggested that small amounts of *m*- and *o*-carbaborane act as inhibitors of radical-chain processes.

The thermal and mechanical relaxation properties of network copolymers of MMA and the diallyl ester of *m*-carbaboranedicarboxylic acid of different composition have been investigated and the network structure has been determined from the comparison of the experimental and calculated glass points.[40] It has been found that, at a high concentration of the carbaborane comonomer, the network consists of two components, one of which is the product of the interaction of MMA with part of the diallyl *m*-carbaboranedicarboxylate used in the reaction, while the second is a network based on the homopolymer of the carbaborane monomer. This results in the formation of specimens having two main transition

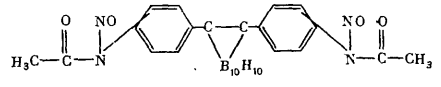
temperatures and two regions of relaxation processes of different intensity.

The joint polycyclotrimerisation of *p*-(*o*-carbaboranyl)phenylacetylene with *p*-diethynylbenzene in the presence of $NiCl_2.2PPh_3.2NaBH_4$ or $Al(iso\text{-}C_4H_9).TiCl_4$ in accordance with the scheme:[63]

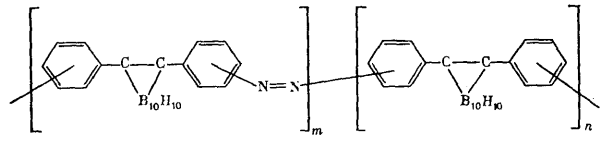


has been achieved. The interaction of equimolar amounts of the starting materials yielded co-oligophenylenecarbaboranes soluble in toluene and having a high boron content. With increase in the amount of *p*-(*o*-carbaboranyl)phenylacetylene in the initial mixture, the yield of the oligomer and its molecular weight decrease (from 78 to 20% and from 3350 to 1020 respectively). *o*-Carbaborane-containing oligophenylenes are characterised by high thermal and thermo-oxidative stabilities. Furthermore, they are regarded[64] as ligands for the synthesis of π-arene complexes of chromium carbonyl. The use of the "triphenylphosphine–nickel acetylacetonate" catalytic system in the copolymerisation of *p*-(*o*-carbaboranyl)phenylacetylene and *p*-diethynylbenzene made it possible to obtain thermoreactive carbaborane-containing polyarylacetylenes in yields up to 93% and with a higher molecular weight.

The recombination of the phenyl and azophenylene products of the decomposition of 1,2-di(*N*-nitrosoacetamidophenyl)-*o*-carbaborane (DC), i.e.



yielded *o*-carbaborane-containing polyazophenylene (PAPC) having the following structure:[65,66]



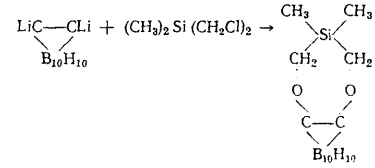
By combining the processes involving the recombination of the DC decomposition products with processes involving the radical polymerisation of various vinyl monomers, it is possible to obtain copolymers with carbaborane units. Thus copolymers containing between 4 and 38% of PAPC fragments have been synthesised by the emulsion copolymerisation of styrene with DC decomposition products. It was shown that the introduction of the carbaborane fragments into the macromolecules of polystyrene increases significantly the thermo-oxidative stability of the latter.

The influence of the nature of unsaturated *m*- and *p*-carbaborane-containing polyethers on their capacity for copolymerisation with vinyl compounds in bulk, solution, and emulsion in the presence of radical and ionic initiators under the influence of γ-radiation or high pressure has been examined.[67,68] The vinyl comonomers used were styrene, acrylonitrile, and 1,1,2-trichlorobuta-1,3-diene. It was found that the copolymers of carbaborane-containing unsaturated polyethers are characterised by a higher resistance to thermo-oxidation and by more effective adhesion parameters compared with the analogous copolymers in which there are no carbaborane groups.

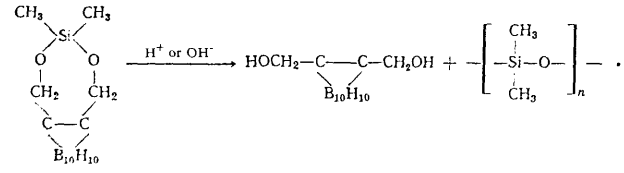
Polymers and copolymers based on alkenylcarbaboranes can be used in various fields: as plasticisers and combustion catalysts,[44] as materials with enhanced thermo-oxidative stability,[59] in adhesives in order to increase their thermal stability,[69,70] for the preparation of anion-exchange resins,[71] and for the modification of rubbers.[72,73]

III. SILICON-CARBORANE-CONTAINING POLYMERS

It is known[15] that the polymers in which hydrolytic and chemical stability is combined with high thermal stability include silicon-carbaborane-containing polymers. The first attempts to synthesise such compounds by polymerisation and polycondensation methods were unsuccessful, since the initial *o*-carbaborane-siloxane derivatives exhibited a high tendency towards the formation of stable cyclic systems. This occurred apparently as a consequence of the adjacent location of the carbon atoms in the *o*-carbaborane nucleus involved in an ordinary covalent C–C bond whose length (1.64–1.67 Å) greatly exceeded the length of the ordinary covalent C–C bond in olefins (1.54 Å), which in fact favoured the formation of exocyclic derivatives.[74–76] For example, a stable cyclic product has been obtained by the interaction of dilithio-*o*-carbaborane with di(chloromethyl)dimethylsilane:[77]

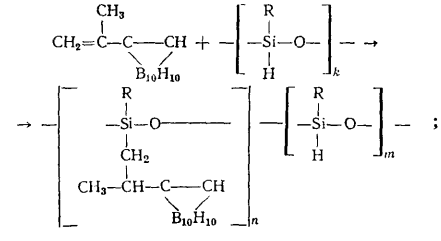


The reaction of 1,2-di(hydroxymethylene)-*o*-carbaborane with dichlorodimethylsilane also results in the formation of a seven-membered cyclic compound.[78] When an attempt is made to open this ring in order to obtain a linear polymer, hydrolysis leads to the reformation of the initial carbaboranediol and polydimethylsiloxane:



For this reason studies were continued on the synthesis of monosilyl-*o*-carbaborane monomers from which various polymers containing *o*-carbaborane groups in the side chain were synthesised by polycondensation reactions.

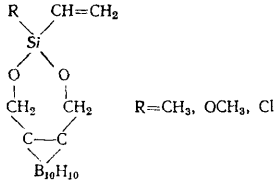
There are few available literature data on the synthesis of carbaborane-siloxane polymers. Polysiloxanes containing *o*-carbaborane nuclei in the side chain have been obtained by the migration copolymerisation of isopropenyl-*o*-carbaborane with the polyalkylhydrosiloxanes:[79,80]



R=CH_3, C_2H_5, C_6H_5; $k=n+m$.

Studies have shown that, in the absence of the catalyst below 200 °C, the reaction hardly occurs and that even at high temperatures the rates of copolymerisation remain low, which can be accounted for by the electron deficiency of the carbaborane nucleus, deactivating the neighbouring unsaturated bond, and by steric hindrance. With increase in the boron content in the polymer, the solubility of the latter in aromatic hydrocarbons and alcohols diminishes. According to DTGA data, the above polymers are stable in air up to 400 to 500 °C.

Carbochain silicon-carbaborane-containing polymers have been synthesised by the radical polymerisation in bulk of carbaborane-containing exocyclic vinylsilanes with various substituents at the silicon atom:[81,82]



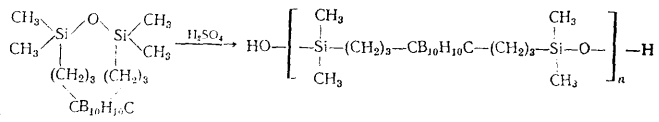
A mixture of benzoyl peroxide and t-butyl peroxide was used as the initiator. It was established that, in the polymerisation of the compounds with R = CH_3, only the dimer is formed, while in other cases insoluble homopolymers were obtained in yields up to 80%. The copolymerisation of the above vinylsilanes with MMA and styrene was achieved under the same conditions for different monomer ratios.[81-83] The copolymerisation with MMA yielded both linear soluble copolymers with a MW of $(4.0-6.9) \times 10^5$ and three-dimensional copolymers; linear copolymers with styrene have molecular weights up to 1.6×10^5. The formation of insoluble polymers and copolymers with MMA is determined by the fact that in certain cases homo- and co-polymerisation not only occurs via the vinyl group but is also accompanied by the partial ring opening and condensation of the resulting silanol groups SiOH.[82] The influence of the substituent at the silicon atom on the reactivity of the exocyclic compounds has been examined and it has been shown that the monomer with R = OCH_3 shows the greatest activity in the copolymerisation reaction. It has been noted that, with increase in the content of the silicon-carbaborane compound in the reaction mixture, its mole fraction in the copolymer also increases and the yield and the molecular weight of the copolymer diminish. Furthermore, the temperatures of the onset of weight loss by the copolymers and yield of the coke residue increase with increase in the mole fraction of the exocyclic derivative in the copolymer, while the softening temperatures decrease.

The migration copolymerisation reaction of epoxypropoxypropyltriethoxysilane with 1,2-di(hydroxymethylene)-*o*-carbaborane, which takes place with formation of a linear oligomer in the first stage, has been investigated.[80,84] In the second stage, the content of the epoxy-groups reaches a minimum, the ethoxy-groups undergo alcoholysis, and the product passes from the viscofluid state to the elastic state.

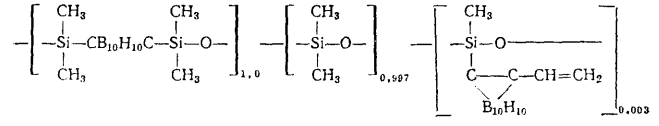
The study of the deformation thermal stability of siloxanecarbaborane oligoethers showed[84] that, in contrast to the majority of polymers, the product does not soften and does not melt with increase in temperature its volume increasing under these conditions at temperature above 360 °C. In view of the high thermal stability of the oligomers obtained, in which effective adhesion to glass and metal is combined with good dielectric properties, they can be used as thermoinsulating coatings.

The failure of the attempt to synthesise silyl-*o*-carbaborane compounds with a linear structure stimulated investigators to turn to *m*-carbaborane systems, in which the adjacent positions of the carbon atoms rule out the possibility of the formation of exocyclic structures. The stability at high temperatures is retained in these systems.

Thus an elastomeric *m*-carbaborane-containing polysiloxane with a molecular weight of 8500 has been obtained by the polymerisation of cyclic *m*-carboranylenesiloxane in the presence of acid catalysts:[85]



From the practical point of view, the synthesis of poly-*m*-carbaborane-siloxanes has been an important advance in the development of thermostable carbaborane elastomers.[6,86,87] These polymers (given the brand name "Decsil") consist of dialkyl- or diaryl-siloxane units linked by *m*-carbaborane groups and are obtained by the polycondensation of *m*-carbaborane-containing chlorosilanes and alkoxysilanes in the presence of $FeCl_3$ as catalyst. The high thermo-oxidative stability and the effective mechanical and elastic properties of the above polymers have served as a precondition for the development of a technology of the preparation of thermostable siloxane-carbaborane rubbers.[88-90] Polymers with the brand name "Decsil-201", in which some of the methyl groups have been substituted by vinyl derivatives of *o*-carbaborane, have been synthesised for this purpose:



This made it possible to carry out hardening via a free-radical mechanism.

There have been communications[91-93] about the synthesis by analogy with Decsils, of carbaborane-siloxane elastomers containing the carbaboranes $C_2B_5H_7$ and $C_2B_8H_{10}$ in the siloxane chain. In order to prevent their crystallisation and to improve their elasticity, these elastomers were modified by introducing 5–20% of vinyl-*o*-carbaborane into the main or side chain.[94,95] It was established that heating of such modified polymers in nitrogen to 350 °C and in air to 250 °C has no appreciable influence on the glass point and that even the solubility of the polymer in xylene is retained under these conditions. After heating in an atmosphere of nitrogen to 550 °C, the polymers are cross-linked.

Summarising the analysis of the literature data on the polymerisation and copolymerisation of silicon-carbaborane-containing monomers, one may conclude that the polymerisation methods of synthesis of silicon-carbaborane-containing polymers have been little investigated hitherto. This is also indicated by the reviews published in recent years,[17,18,96-98] which have been mainly devoted to questions of the preparation of carbaborane-siloxane polymers by polycondensation methods.

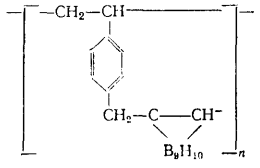
IV. POLYMERS CONTAINING DICARBAUNDECABORATE FRAGMENTS

Apart from polyhedral carbaboranes, i.e. carbaboranes with a closed structure (*closo*-carbaboranes), open carbaborane structures of

nido-carbaboranes are known. On interaction with nucleophiles such as alkali metal alkoxides[19] or amines,[99] *o*- and *m*-carbaboranes(12), are cleaved selectively with abstraction of the boron atom from the third position in the *o*- and *m*-carbaborane nuclei with formation of dicarbaundecaborates(13) anions. Such anions are acids and on treatment with NaH they split off a proton and afford the dicarbollide ion (Fig.1).[100]

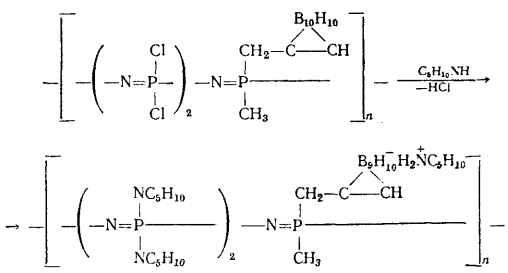
The negative charge on the dicarbaundecaborate anion leads to the appearance in the system of an electron-donating effect via inductive and resonance mechanisms, in contrast to the neutral *C*-carbaboranyl groups, which exhibit electron-accepting properties. Thus the electron-donating effect of the (3)-1,2-dicarbaundecaborate group is manifested in the pK_a values for the carboxylic acids of the (3)-1,2-dicarbaundecaborate group is manifested in the pK_a values for the carboxylic acids of the (3)-1,2-dicarbaundecaborate series (6.9–7.3 in 50% ethanol), which are very weak acids compared with carbaboranecarboxylic acids.[101]

Methods are known for the preparation of polymers with dicarbaundecaborate fragments[102–104] whose carbaborane nuclei are cleaved by alkalies or amines. However, these are multistage procedures and each stage takes 3–8 days. Thus, in studies by Hawthorne and co-workers,[102,103] polystyrene cross-linked with 1% of divinylbenzene was made to undergo successive reactions in accordance with the following scheme: (1) chloromethylation of polystyrene; (2) cleavage of *o*-carbaborane with alcoholic alkali to the dicarbaundecaborate anion; (3) preparation of the dicarbollide ion $(7,8\text{-}C_2B_9H_{11})^{2-}$; (4) reaction of the chloromethylated polystyrene with the dicarbollide ion leading to the formation of a polymer with dicarbaundecaborate groups:



Rudolph and co-workers[104] also obtained the above polymers from cross-linked polystyrene in accordance with the following scheme: (1) chloromethylation of polystyrene; (2) preparation of *o*-carbaboranyl-lithium with chloromethylated polystyrene; (4) cleavage with piperidine of the carbaborane linked to polystyrene to give the dicarbaundecaborate anion.

Later Allcock et al.[105] obtained *nido*-carbaboranylpolyphosphazenes by the interaction of carbaborane-containing polyphosphazenes with piperidine in solution in tetrahydrofuran:



Different reactions of *m*-carborane-containing polymers are very frequently accompanied by the cleavage of their *m*-carbaborane nucleus to the dicarbaundecaborate anion. This happens, for example, on heating *m*-carbaborane-containing polyamides in dimethylformamide and concentrated alkalies,[106] in their thermal and thermo-oxidative degradation,[107] in the cyclodehydration of *m*-carbaborane-containing polyaminoamides and polyhydroxamides,[108,109] and also in the formation of polyamides based on *m*-carbaboranyl-enediamine and the dichlorides of aromatic acids.[110] All these reactions result in the formation of heterounit polymers, whose properties depend on their content of dicarbaundecaborate groups.

Later Korshak, Bekasova, and co-workers[111–113] obtained heterounit *m*-carborane-containing polyamides by treatment with nucleophiles and demonstrated by ^{1}H NMR that the maximum attainable content of dicarbaundecaborate fragments, without degradation, in such polymers is about 50%. Polyamides differ from the starting materials in their solubility and chemical and therm-oxidative stability.

As already mentioned in the introduction, up to 1984 there was no information whatever in the literature about the preparation of polymers with dicarbaundecaborate fragments by the polymerisation or copolymerisation method. It is known that vinyl derivatives of *o*-carbaborane show a low reactivity in the radical polymerisation reaction. It was shown for the first time in a number of studies[114–117] in relation to 1-isopropenyl-*o*-carbaborane that the transition from neutral *closo*-carbaboranes to negatively charged *nido*-carbaborane structures facilitates the copolymerisation reaction of their unsaturated derivatives and it was established that the latter are capable of copolymerisation with vinyl monomers. The salts of 1-isopropenyl-(3)-1,2-dicarbaundecaborate (IDC) synthesised do not polymerise via radical and ionic mechanisms, but, in contrast to 1-isopropenyl-*o*-carbaborane,[47] enter into the copolymerisation reaction with MMA

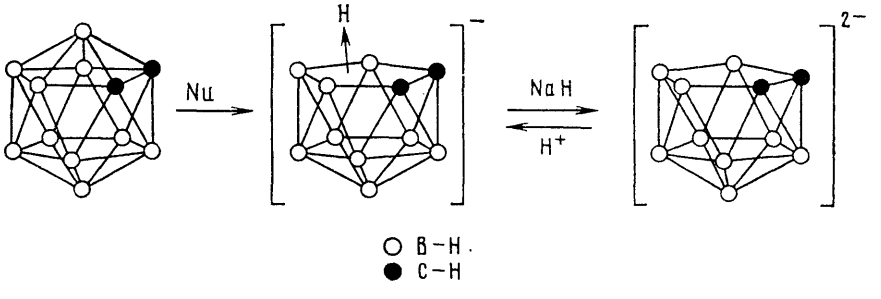
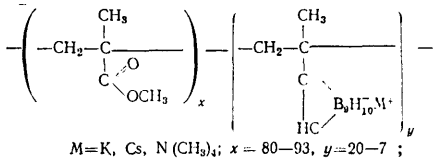
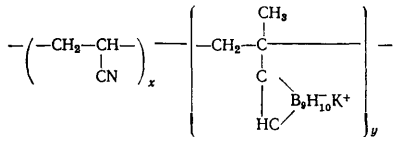


Figure 1. Scheme for the preparation of the dicarbaundecaborate(13) anion and the dicarbollide ion.[100]

and acrylonitrile, forming copolymers containing dicarbaundecaborate fragments:



M=K, Cs, $N(CH_3)_4$; $x = 80-93$, $y = 20-7$;



$x=50-99$, $y=50-1$.

The radical copolymerisation was carried out in solution at 60 to 80 °C in the presence of AIBN. The dependence of the yield, the intrinsic viscosity, and the composition of the copolymers on the reaction conditions was investigated[115,117] and the optimum parameters of the synthesis were determined. It was shown that the reactivity of the IDC salts in the copolymerisation with acrylonitrile is higher than in the copolymerisation with MMA: in the former case, it is possible to introduce up to 50 mole % of the dicarbaundecaborate units into the copolymer, while in the latter up to 20 mole % can be introduced. The molecular weights of the copolymers with acrylonitrile and MMA reach 5.0×10^4 and $(2.5-5.2) \times 10^4$ respectively. It was found that the yield and molecular weight of the copolymer diminish with increase in the mole fraction of the dicarbaundecaborate and also with increase in the ionic radius of the salt cation, which is caused in all probability by steric factors.

Copolymers of this kind are of interest also because they contain dicarbaundecaborate groups capable of behaving as ligands in transition metal complexes. For this reason, the copolymers of MMA with IDC salts have been used as polymer matrices in the synthesis of polymeric metallocarbaborane complexes (Fig.2).[114,116] A characteristic feature of the structure of these complexes is the fact that the dicarbollyl ligand of the metallocarbaborane is linked directly via a carbon atom to the main chain of the polymer matrix. The structure has been confirmed by elemental analysis, IR spectroscopy, and ^{31}P NMR. The catalytic activity of the synthesised phosphinocarbaborane complexes of rhodium in hydrogenation and isomerisation reactions of unsatuated hydrocarbons was investigated[114,118] and it was shown that these complexes are much more effective catalysts of the above reactions than the carbaboranerhodium complexes fixed on polystyrene which had been known previously.[102-104]

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Thus, the literature data presented show that the use of homo- and co-polymerisation methods for the synthesis of carbaborane-containing polymers makes it possible both to obtain new high-molecular-weight compounds and to modify the known polymers and to impart to the latter properties of practical importance. The study of the polymerisation of unsaturted derivatives of dicarbaundecaborates and of the properties of the polymers formed is of great interest.

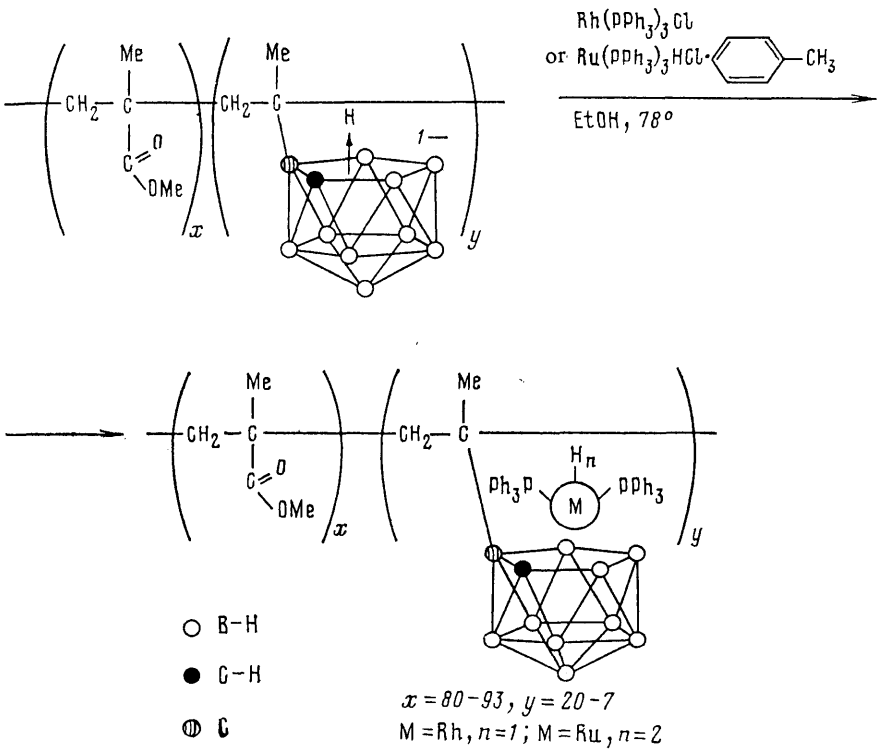


Figure 2. Scheme for the preparation of polymeric phosphinocarbaborane complexes of rhodium(I) and ruthenium(II).[114,116]

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