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Effect of carborane groups and the structure of their surrounding organic residues on the reactivity of monomers and properties of polymers

N I Bekasova, N G Komarova
Nesmeyanov Institute of Organometal Compounds, Russian Academy of Sciences, Moscow

ABSTRACT. **The results of studies on carborane-containing polymers concerning the effect of carborane rings and the structure of the organic residues adjacent to carborane groups on the reactivity of monomers and the properties of the polymers obtained have been correlated.**

The bibliography includes 109 references.

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I. Introduction

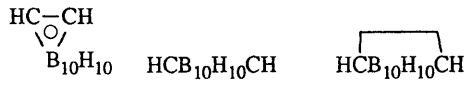
The first reports on the synthesis and properties of carborane-containing polymers were published in 1963.[1,2] Studies on the synthesis and research into the properties of carborane-containing polymers are undergoing rapid development at the present time. These polymers have attracted the attention of research workers because they have a whole series of interesting and valuable properties, such as a combination of high thermal stability and ready solubility. Many of these unusual polymers are capable of withstanding extremely severe conditions, under which normal organic polymers are almost completely degraded.

Carborane-containing polymers are obtained by both polycondensation and polymerisation. Polymers with different structures — polyethers, polycarboranylenes, polyamides, polyphenylenes, polyurethanes, polysiloxanes, polyazoles, and polyphosphazenes, etc. — have been reported.[3–14]

Some recently published reviews[15–18] are concerned with a correlation of the results on the synthesis and research into the properties of carborane-containing polymers.

The chemical structure of the monomer unit of a polymer is known to be one of the main factors governing its properties. Therefore, a study of the dependence of the properties of polymers on the structure of the initial components has both theoretical and practical value, since it makes it possible to carry out the directed synthesis of polymers with predetermined properties. The specific characteristics of icosahedral carborane groups are a negative inductive effect and steric hindrance, which have a considerable effect on the reactivity of monomers and the properties of the polymers obtained.

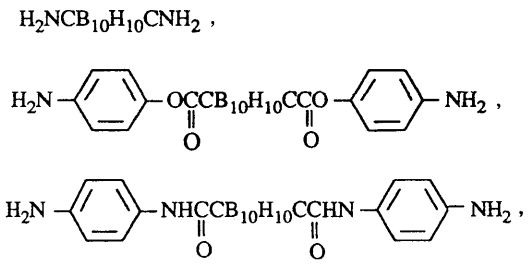
In this review an attempt is made to correlate the theoretical and experimental material on the synthesis and research into the properties of carborane-containing polymers in relation to the specific characteristics of carborane groups. The review covers polymers obtained from the isomeric carboranes which are usually depicted as follows:[19]



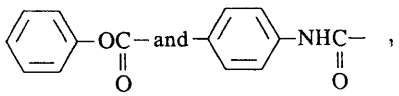
o-carborane *m*-carborane *p*-carborane .

II. Effect of carborane groups on the reactivity of monomers

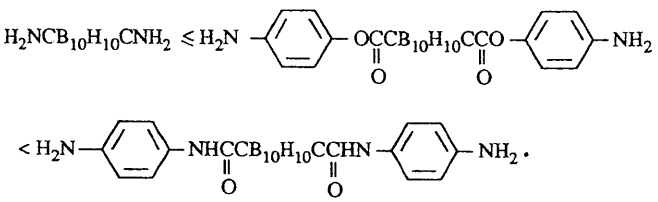
The presence of bulky carborane groups very frequently makes the synthesis of carborane-containing polymers difficult to carry out. However, the reason for the difficulty of synthesis does not arise solely from steric inhibition of polycondensation by the carborane groups (the effective van der Waals radius is equal to 4 Å) but also from the effect of the electron-withdrawing nature of these groups on functional groups in the monomers. Thus, for example, it was established from the kinetic data of acylation of aniline with *m*- and *p*-carboranedicarboxylic acid dichlorides in different solvents that *m*-carboranedicarboxylic acid dichloride is 2–3 times more active than the dichloride of *p*-carboranedicarboxylic acid.[20] This is probably due to the fact that the *p*-carborane group is a weaker electron acceptor than *m*-carborane. In a study of relative reactivity in the acylation of three *m*-carborane-containing diamines with the following structure:



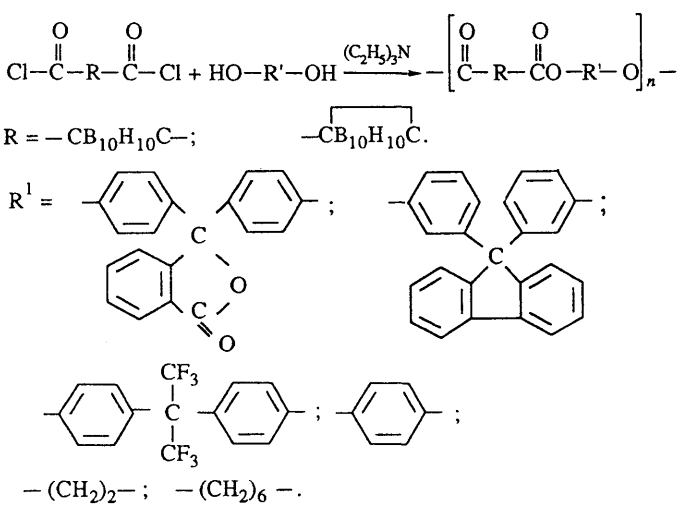
it was shown that introduction of the residues:



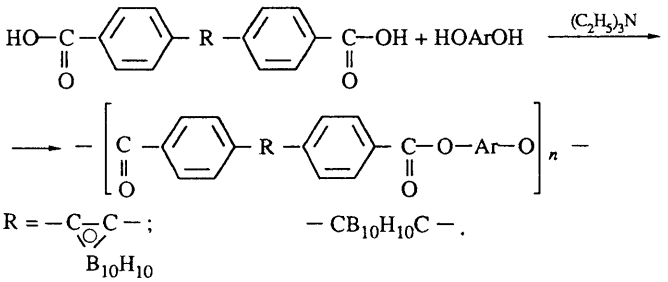
between the amino group and the *m*-carborane cage results in a marked increase in reactivity of the diamines in the following series:[21,22]



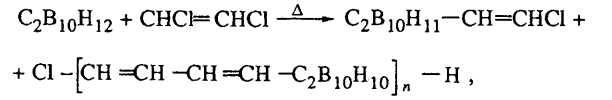
It was established, moreover, that polyesterification of *o*-carborane-containing diols occurs much more slowly than polyesterification of organic diols.[23] If an *o*-carborane group is present in both the diol and dicarboxylic acid, polyesterification occurs at such a low rate that low-molecular-weight compounds are formed.[24,25] However, with a correct choice of the initial reactants and also the synthesis conditions, which made it possible to reduce the steric inhibition of polycondensation and increase the rate of reaction, it proved possible to obtain high-molecular-weight polyesters. For example, if the polycondensation of dichlorides of *m*- and *p*-carboranecarboxylic acids with different diols is carried out in solution in the presence of a catalyst, polyesters with a molecular weight of 20 000 or more are formed:[26–28]



Starting from 1,2- and 1,7-bis(dicarboxyphenyl)carboranes and different dihydric phenols, high-temperature polycondensation in a solution of chlorinated biphenyl at 220 °C or acceptor-catalyst polycondensation in acetone solution gave *o*- and *m*-carborane-containing polyarylates with a molecular weight ranging from 22 000 to 132 000:[29,30]

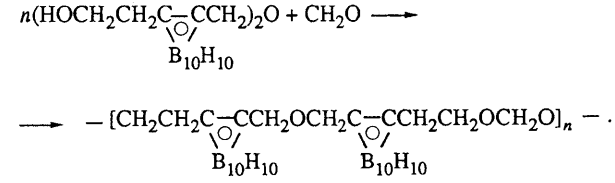


The variation in electron-withdrawing capacity of the groups in the series *o*- > *m*- > *p*-carboranes has an effect on their reactivity towards the addition of 1,2-dichloroethylene.[31] In a study of the kinetics and mechanism of high-temperature condensation of *o*-, *m*-, and *p*-carboranes with 1,2-dichloroethylene according to the reaction:



it was established that *o*- and *m*-carboranes exhibit almost the same reactivity in reactions with 1,2-dichloroethylene while *p*-carborane reacts 1.5 times more slowly than *o*-carborane.

The steric hindrance due to the bulky carborane groups has a very considerable effect on the formation of polyformals.[1] Thus, bis(hydroxymethyl-1-*o*-carboranylmethyl) ether does not react with formaldehyde. When bis(hydroxyethyl-1-*o*-carboranylmethyl) ether is reacted with formaldehyde, an oligomer with a molecular weight of 4400 is obtained:

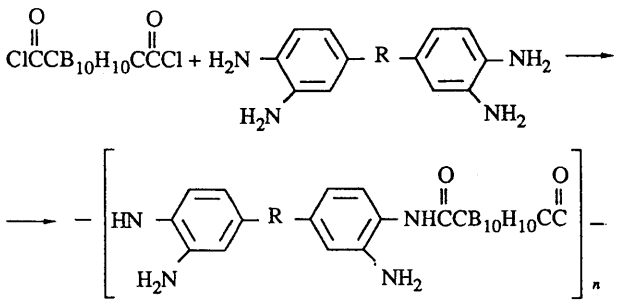


It has been suggested that in order to form polymers it is necessary for the distance between the carborane groups located sequentially to be not less than five carbon atoms at the very least.

The steric hindrance due to a carborane group has a considerable effect on the formation of high-molecular-weight poly(aminoamides).

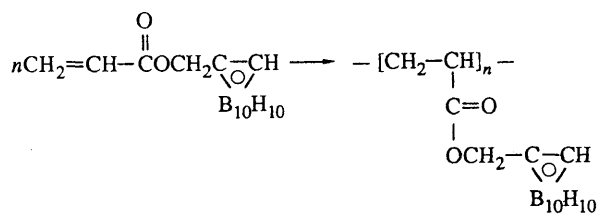
Normally polycondensation of aromatic acid dichlorides with different aromatic tetraamines results in the formation of cross-linked polymers, since the difference between the reactivities of the amino groups at the *ortho* position relative to each other does not change very much after one of them has reacted. When an aromatic acid dichloride is replaced by *m*- or *p*-carboranedicarboxylic acid dichloride, the difference in reactivity between the amino groups at the *ortho* position relative to each other increases after one of them has reacted as a consequence of the steric hindrance caused by the carborane residues. It was therefore possible under certain

conditions to obtain high-molecular-weight polyaminoamides according to the following scheme:[32–35]



R = —O—; —CH_2—; —SO_2—; —$C(CH_3)_2$—; bond.

A polymerisation process is used less frequently than polycondensation to obtain carborane-containing polymers. Not many studies devoted to the homopolymerisation of alkenylcarboranes have been published. The difficulty in conducting this type of synthesis is due to steric hindrance caused by the bulky carborane groups and also the electron-withdrawing nature of the groups, which is responsible for a decrease in electron density on the double bond and hence a decrease in its reactivity. The polymerisation of monomers in which the carborane group is situated some distance from the double bond occurs more readily. For example, 1-acrylyloxymethylene-*o*-carborane readily polymerises in bulk in the presence of 2% benzoyl peroxide at 60 °C:[36]



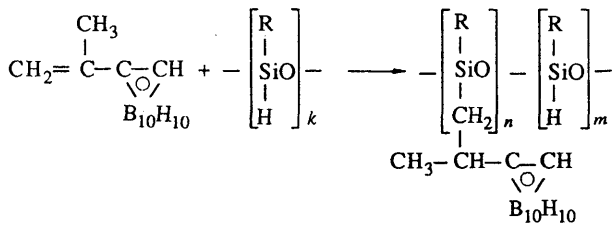
Since the homopolymerisation of carborane monomers occurs with difficulty, there is particular interest in the copolymerisation of carborane-containing compounds with vinyl monomers, making it possible to impart valuable new properties to known polymers through the introduction of carborane cages into their structure. This usually raises the temperature at which polymers start to decompose and increases the yield of carbon residue.

With the aim of modifying low-density polyethylene, the radical copolymerisation of ethylene with isopropenyl-*o*-carborane at a pressure of 1400 kg cm^{-2} and temperature of 160 °C was studied.[37] It was established from the IR spectroscopic data that the rate of copolymerisation and the molecular weight of the polymers decrease rapidly as the content of the *o*-carborane derivative in the reaction mixture increases from 1 to 40 mol%.

A study has been made of the effect of the structure of unsaturated *m*- and *p*-carborane-containing polyesters on their ability to undergo bulk, solution, and emulsion copolymerisation with styrene, acrylonitrile, and 1,1,2-trichloro-1,3-butadiene in the presence of radical and ionic initiators on exposure to γ-radiation or high pressure.[38,39] It was established that the introduction of electron-withdrawing *m*-carborane groups into unsaturated polyesters reduces their reactivity, as a result of which unsaturated polyester-*m*-carboranes in which there is one carborane cage for each unsaturated bond are incapable of undergoing thermochemical cross-linking and only form cross-links on exposure to γ-radiation and high pressure.

In contrast to *m*-carborane-containing polyesters, all polyesters of *p*-carboranedicarboxylic acid undergo copolymerisation with styrene, which evidently may be due to the weaker electron-withdrawing properties of the *p*-carborane cage, having virtually no effect on the reactivity of unsaturated bonds.

Information in the literature about the preparation of carborane-siloxane polymers by polymerisation and copolymerisation methods is sparse. Migration copolymerisation of isopropenyl-*o*-carborane with polyalkylhydroxysiloxanes gave polysiloxanes containing *o*-carborane cages in the side chain.[40,41]



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

Studies showed that without a catalyst there is virtually no reaction below 200 °C and even at higher temperatures the rates of copolymerisation remained low, which may be due to the electron-deficient nature of the carborane cage, which deactivates the adjacent unsaturated bond, and to steric hindrance.

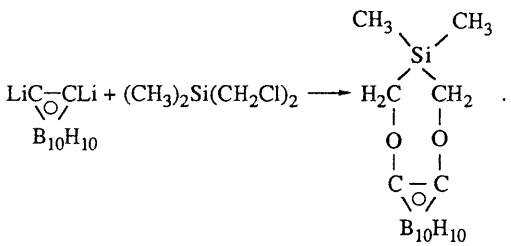
III. Effect of carborane groups on the properties of carborane-containing polymers

In 1963 Grafstein and Dvorak,[42] while attempting to carry out the thermal dehydrodimerisation and dehydropolymerisation of *o*-carborane, found that at 465–500 °C *o*-carborane is isomerised to *m*-carborane, while in 1964 Papetti and Heying,[43] on heating *o*-carborane at 617 °C, obtained a third isomer—*p*-carborane. In neither case were dehydropolymers detected. There are considerable differences in the chemical and phyiscal properties of derivatives of these isomers, which can be classified according to the different configuration of the carbon atoms in the *o*-, *m*-, and *p*-carborane skeleton, resulting in a decrease in electron-withdrawing properties in the series *o*- > *m*- > *p*-isomer,[44,45] and an increase in thermal stability: *o*- < *m*- < *p*-carborane isomer.[46] Moreover, in the series *o*- > *m*- > *p*-carborane isomer, there is a decrease in acidity of the hydrogen atom in the CH group,[47] ease of electrophilic, radical, and exchange halogenation of the B—H bond,[48,49] rate of nucleophilic substitution of the halogen atoms in halogen derivatives of the carborane by other atoms and groups compared to halogen derivatives of benzene and ferrocene.[50] The electron affinity of the carborane system decreases in the same series of isomers as does the ease of cleavage of a C_{carb}—C bond in carborane-containing aldehydes, ketones, acids, and alcohols by nucleophilic reagents. Therefore *o*-carborane derivatives are reduced much more easily than the other carborane isomers, and in the same series the stability towards bases[49,55] and oxidising agents[56] increases, and the volatility of the compounds and in the majority of cases the melting point[19] also increase.

This series of variation in the physicochemical propeties of *o*-, *m*-, and *p*-carboranes and their derivatives is related to the more uniform distribution of electron density in the *p*-carborane cage (all ten boron atoms are equivalent) compared to the *o*- and *m*-carborane cages.

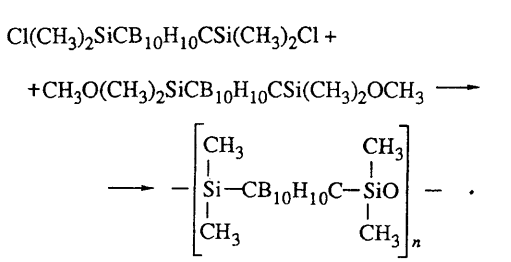
Isomerism of the carborane cage has a considerable effect on the preparation and properties of polymers based on different isomeric derivatives of carboranes.

It follows from a review of the considerable number of studies on the synthesis and research into the properties of carborane-containing polymers that the *m*- and *p*-carborane isomers have a greater tendency to form polymers than the *o*-isomer, since during the development of methods for the synthesis of polymers with *o*-carborane cages in the chain, research workers have frequently encountered steric problems. One of these is typically the tendency of C,C′-difunctional *o*-carborane derivatives to form *exo*-polyhedral rings. This evidently occurs as a result of the adjacent configuration of the carbon atoms in the *o*-carborane cage. The bond between them, with a length equal to that of a single covalent C–C bond (1.64–1.67 Å), is longer than the single covalent C–C bond of alkanes (1.54 Å), thus assisting the formation of *exo*-rings.[57–59] Therefore, the first attempts to synthesise silicon-*o*-carborane-containing polymers with a linear structure were unsuccesful because of the considerable tendency of the initial *o*-carborane-siloxane derivatives to form stable cyclic systems. For example, reaction of *o*-carboranedilithium with dimethyldichloromethylsilane gave a cyclic product instead of the expected polymer:[60]



The lack of success in attempts to synthesise silyl-*o*-carboane with a linear structure stimulated research workers to consider *m*-carborane systems, in which the nonadjacent configuration of the carbon atoms excludes the possibility of exocyclic structures being formed.

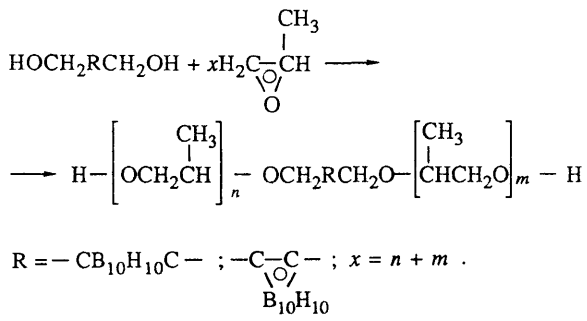
Thus, polycondensation of *m*-carborane-containing chlorosilanes and alkoxysilanes in the presence of a catalyst—ferrous chloride—gave elastomeric *m*-carborane-containing polysiloxanes,[19,61–65] the synthesis of which from the practical point of view may be regarded as an important advance in the development of heat-resistant carborane elastomers.



These polymers (trade name "Dexsil") consist of dialkyl- or diaryl-siloxane units linked by *m*-carborane groups and, in addition to the method already indicated, they are obtained by polycondensation of *m*-carborane-containing disilanol with an active silane such as bis(*N*,*N*-dimethylcarbamato)dimethylsilane or bis(ureidosilanes) or bis(*N*,*N*-dimethylamino)dimethylsilane[11,16,63,64] or directly from *m*-carborane.[65]

There have been reports on the synthesis of "Dexsil" polysiloxanes containing *p*-carborane groups.[66,67] These polymers are elastic materials but more rigid at low temperatures than the corresponding *m*-carborane-containing polysiloxanes.

In the migration copolymerisation of 1,2-bis(hydroxymethyl)-*o*-carborane with epoxypropyltriethoxysilane[68] and 1,2- or 1,7-bis-(hydroxymethyl)-*m*-carborane with propylene oxide[69,70] it was shown that the rate of reaction of propylene oxide with 1,2-bis(hydroxy-methyl)-*o*-carborane is higher than with 1,7-bis(hydroxymethyl)-*m*-carborane.

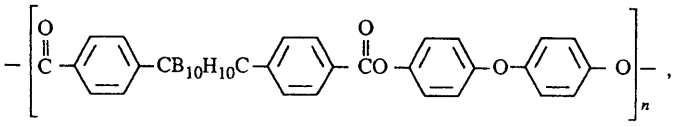


The more pronounced electron-withdrawing nature of the *o*-carborane cage evidently gives rise to a greater proton mobility of the hydrogen atoms of the hydroxyl group and hence assists a higher rate of reaction.

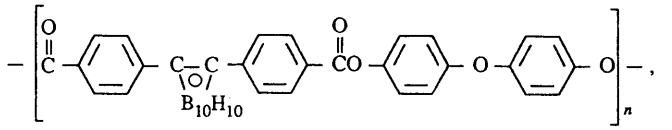
Korshak et al.[4] described the preparation of *o*-, *m*-, and *p*-carborane-containing esters of cellulose by acylating the latter with *o*-, *m*-, and *p*-carboranecarboxylic acid chlorides in toluene in the presence of pyridine at 110 °C. It was established that under these conditions the carborane cage decomposes in *o*- and *m*-carborane-carboxylic acid chlorides to the anion of dicarbaundecaborane while only a small degree of acylation of cellulose occurs (about 2 wt.% boron is introduced). *p*-Carboranecarboxylic acid chloride reacts with cellulose to form a *p*-carborane-containing cellulose ester with about 40 wt.% boron content and which does not dissolve in either organic solvents or in a cuprammonium complex or in cadoxene (a complex between ethylenediamine and cadmium hydroxide). On heating in an inert medium under isothermal conditions at 300 °C for 2 h the "char" residues of *o*-, *m*-, and *p*-carborane-containing cellulose at 48, 39, and 38% of the initial weight respectively. The "char" residue of the initial cellulose under these conditions does not exceed 22 wt.%.

The effect of the isomerism of the carborane cage on the molecular mobility of macromolecules has been demonstrated in two studies.[71,72] It was established that the vibrations of the *o*-carborane cage in polyarylates are more difficult compared to the *m*-isomer because of the greater conjugation of the *o*-carborane residue with the automatic rings and also because of steric effects. This characteristic affects the relaxation processes in carborane-containing

polyesters, and the results of studies on these using different methods suggest that there is an increase in rigidity of the macrochain and an increase in softening point on changing from *m*- to *o*-carborane-containing polyesters, as for example:



$T_{soft} = 240-260$ °C



$T_{soft} = 260-280$ °C.

An essentially ionic form of electrical conductivity is characteristic of carborane-containing polyesters, and the electrical conductivity of *o*-carborane-containing polyesters is higher than those values for the corresponding polyesters with *m*-carborane residues by a factor of 10^1-10^2.[73] All of the polyesters synthesised from bis(hydroxymethyl)-*m*-carborane have a softening point that is lower than that of the corresponding polyesters obtained from bis(hydroxymethyl)-*o*-carborane.[74]

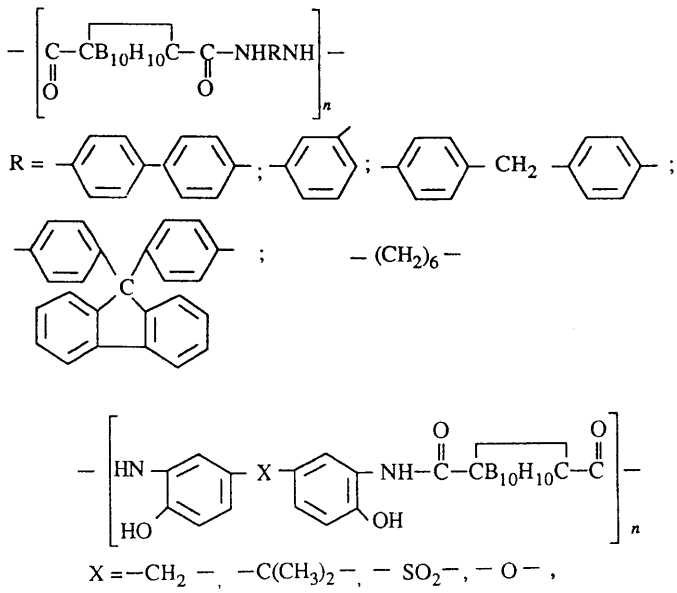
In a study of the properties of solutions of polyarylates obtained by acceptor-catalytic and high-temperature polycondensation from 1,2- and 1,7-(4-carboxyphenyl)carboranes and dihydric phenols such as 4,4′-dihydroxydiphenyl oxide, 4,4′-dihydroxydipyhenyl-2,2-propane, 9,9-bis(4-hydroxyphenyl)fluorene, and 9,9-bis(4-hydroxyphenyl)-10-anthrone, it was established that with similar molecular weight values, polyarylates with 1,7-diphenyl-*m*-carborane residues in the chain have a considerably higher intrinsic viscosity than polymers with 1,2-diphenyl-*o*-carborane residues.[75] The authors were able to conclude from this that polyarylates based on 1,2-bis-(4-carboxy-phenyl)-*o*-carborane are in the form of more compact macromolecular bundles in solution, which can be attributed to both steric factors and to a greater effect from the dipole moment for polyarylates with *o*-carborane groups.

It was established that polyarylates obtained by reaction of *p*-carboranedicarboxylic acid dichlorides with different bisphenols have a softening point that is 40–100 °C higher than that of the corresponding polyarylates of *m*-carboranedicarboxylic acid. However, the "char" residue of *p*-carborane-containing polyarylates at 800 °C is less by 10–20 wt.% than the "char" residue of *m*-carborane-containing polyarylates at the same temperature.[26-28]

In a study of the thermal stability of polyarylates with 1,2- and 1,7-diphenylcarborane residues in the chain in air and in an inert atmosphere under both dynamic and isothermal conditions, it was established thermogravimetrically that carborane-containing polyarylates have a decomposition temperature that is 20–60 °C higher than that of conventional polyarylates.[76] The authors note that all the *o*- and *m*-carborane-containing polyarylates are characterised by a high "char" residue (50–90% of the initial weight of the polymer) when they are heated in air to 900 °C, whereas conventional polyarylates (such as polyarylate D-9) are completely combusted at 650–700 °C. In an inert atmosphere the weight of polyarylates of 1,2- and 1,7-bis(4-carboxylphenyl)-carboranes starts to change at the same temperatures as in air, but their "char" residue after thermal degradation is even higher than on heating in air. On the basis on this the authors assumed that the "char" residue formed on heating *o*-and *m*-carborane-containing polyarylates results not only from oxidation but is generally typical of the thermal degradation of polyarylates of this structure.[76,77]

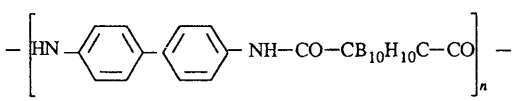
The majority of the *o*- and *m*-carborane-containing polyamides that have been reported are amorphous polymers that are readily soluble in organic solvents, whereas *p*-carborane-containing polyamides have a crystalline structure and an inferior solubility in organic solvents. This is due to the more ordered structure of *p*-carborane-containing polyamides as well as the nonpolar nature of the *p*-carborane cage.[76]

In contrast to infusible *m*-carborane-containing polyamides and poly(hydroxyamides), *p*-carborane-containing polyamides and poly(hydroxyamides) with the following structure:

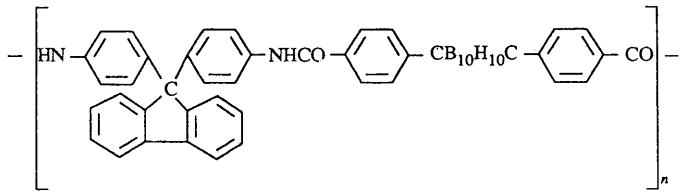


soften at 250–460 °C and 220–270 °C respectively.

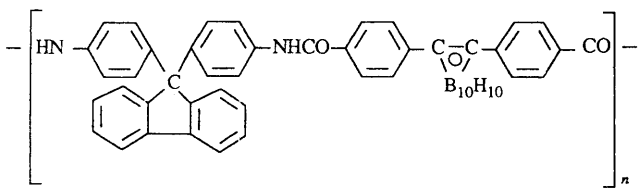
In a review article by Korshak et al.[79] detailed consideration is given to questions concerning the degradation of *o*-, *m*-, and *p*-carborane-containing polyamides with the following structure (under vacuum, in an atmosphere of oxygen, and water vapour at 200–800 °C):



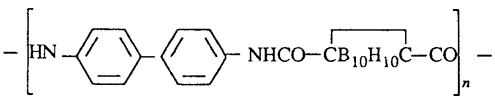
(I)



(II)



(III)



(IV)

It was demonstrated in the review that isomerism of the carborane cage has a considerable effect on the stability of polyamides. It transpired that the *p*-carborane-containing polyamide (IV) has inferior thermal stability compared to polyamides containing *m*- and *o*-carborane residues. Moreover, while the main degradation route in *o*- and *m*-carborane-containing polyamides is decomposition of the *o*- and *m*-carborane residues with evolution of hydrogen, whereby the amide groups become stable towards homolytic and heterolytic cleavage reactions, in *p*-carborane-containing polyamides cleavage of the NH—CO bond mainly occurs, and the principal gaseous degradation product is carbon dioxide.

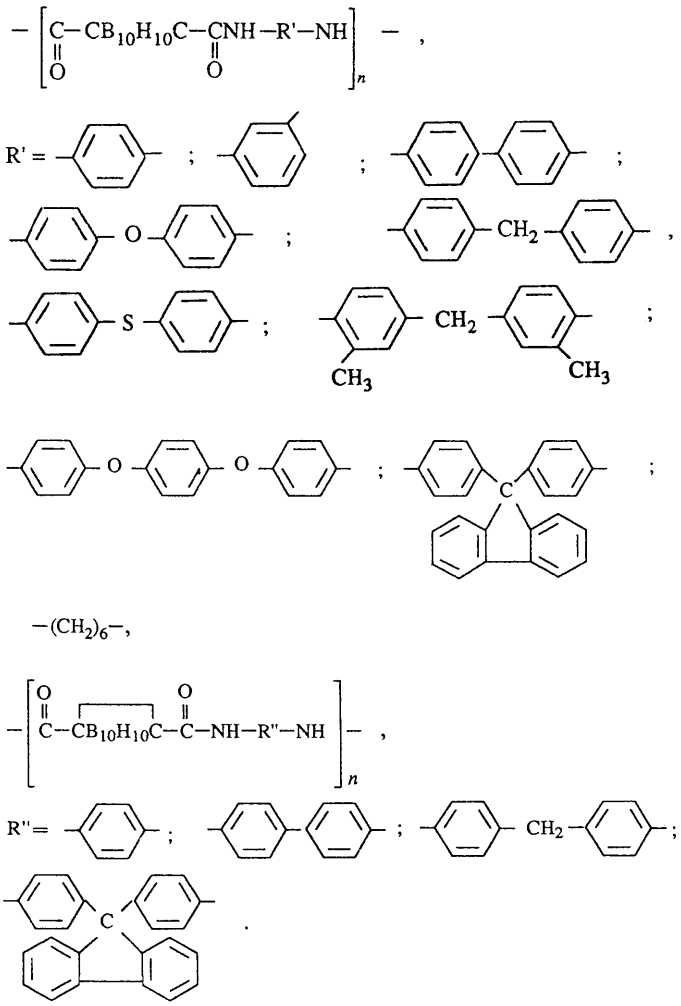
On degration in an atmosphere of saturated water vapour *o*- and *m*-carborane residues undergo more substantial decomposition, as is suggested by the increase in quantities of hydrogen and methane in the hydrolysis products, compared to degradation under vacuum. The degradation of the *p*-carborane-containing polyamide is similar to that of aromatic polyamides, i.e., the presence of excess moisture gives rise to more substantial hydrolysis of the amide groups.

During thermooxidative degradation a decisive factor is the oxidative stability of the carborane cage and, as is suggested by the experimental findings, this is virtually the same for all the isomers.

However, on comparing the degree and rate of degradation of polyamides containing *p*-carborane (IV) and *m*-carborane (I) residues in an atmosphere of oxygen, it should be noted that decomposition of *m*-carborane residues occurs to a much greater extent. Hence the degree of stability of the carborane isomers towards oxygen is not the only factor that governs the oxidation of carborane-containing polyamides, and, like thermal degradation, the electron-withdrawing properties of the carborane cage play a significant role. Although the oxidative stabilities of the *m*- and *p*-isomers of carborane are similar in magnitude, decomposition of the carborane cage and stabilisation of the amide groups occur to a greater extent in the thermal oxidation of the *m*-carborane-containing polyamide (I).

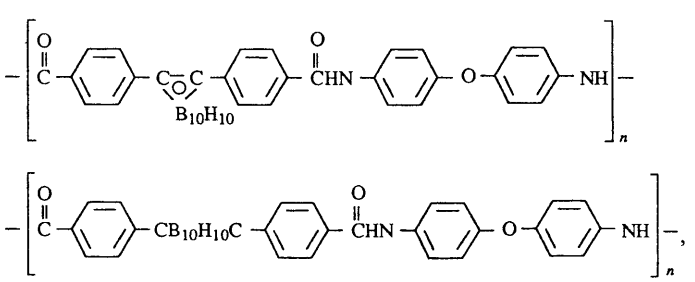
The antifrictional properties of *m*-carborane-containing polyamide (I) and its *p*- analogue (IV) have been studied over the temperature range 250—450 °C.[80] From the results obtained by Korshak et al.[80] concluded that the hydrogen which is formed in considerable quantities during decomposition of *m*-carborane-containing polyamides produces a reducing medium between the frictional surfaces, resulting in inhibition of the oxidative processes that occur at high temperatures. This is to a considerable degree responsible for the improvement in lubricating properties of antifrictional plastics based on *m*-carborane-containing polyamides compared to *p*-carborane-containing polyamides (in which the evolution of hydrogen occurs to a lesser degree over the studied temperature range) and in comparison with polyamides that do not contain carborane residues (which evolve virtually no hydrogen at these temperatures).

Isomerism of the carborane cage has an effect on the chemical stability of known carborane-containing polyamides. Thus, *m*- and *p*-carborane-containing polyamides with the following structure are stable towards boiling water and 40% sulphuric acid:



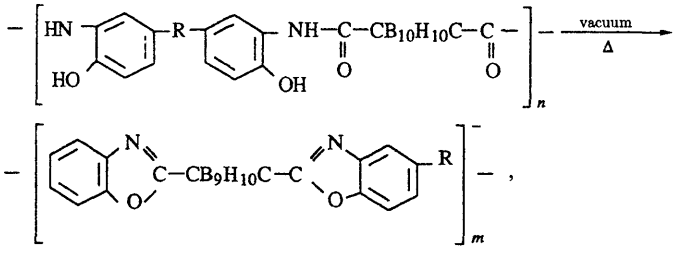
However, on heating in a 40% aqueous alkali solution only alkaline hydrolysis of the macromolecules occurs in *p*-carborane-containing polyamides while in polyamides with *m*-carborane residues decomposition of the *m*-carborane groups occurs together with alkaline hydrolysis.

The molecular mobility properties of carborane-containing polyamides with the following structure:



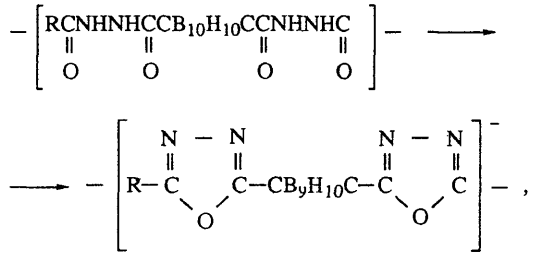
and an investigation of the effect of their structure on electrophysical properties were the subject of a study by Voishchev et al.[81] It was shown that replacement of the *o*-carborane cage by a *m*-carborane cage resulted in a decrease in rigidity of the macromolecules.

The isomerism of carboranes has a considerable effect on the formation of polyheterocycles.[12,15,82–88] Thus, according to the data of differential IR spectroscopy, the cyclohydration of *m*-carborane-containing poly(hydroxyamides) is always accompanied by partial conversion of the *m*-carborane groups to dicarbaundecarborate residues:



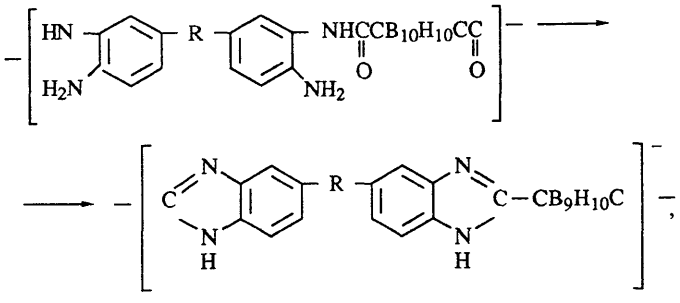
R = — CH_2—, —O—, — SO_2 —, — $C(CH_3)_2$ —.

The conversion of *m*-carborane groups to dicarbaundecarborate residues also occurs to a greater or lesser extent in the formation of *m*-carborane-containing poly(oxadiazoles):



R = arylene, alkylene;

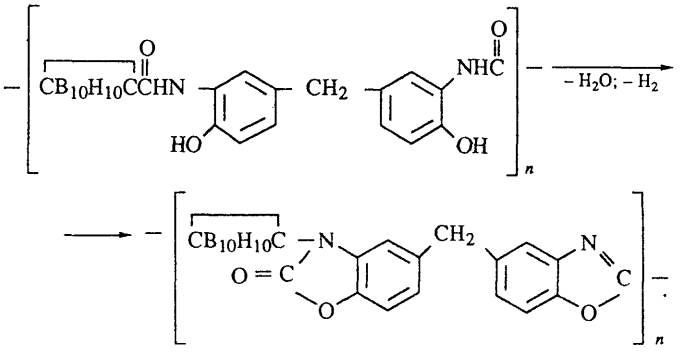
and poly(benzimidazoles):



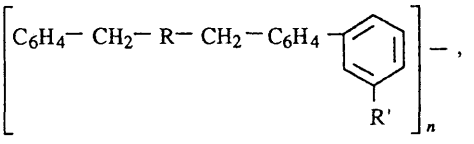
R = — O—, — CH_2—, — SO_2 —,

and, according to the authors, apparently takes place via the amide bond.

Since *p*-carborane residues are the most stable of the carborane isomers towards a basic compound, the conversion of *p*-carborane-containing poly(aminoamides) and polyhydrazides to the corresponding polyheterocycles occurs smoothly, without decomposition of the *p*-carborane residues. However, in this case Korshak et al.[88] recorded the conversion of a hydroxyamide structure to a benzoxazole group, which had not been observed previously in polymers:[89]



It follows from the examples given above that the properties of the polymers depend on which of the carborane isomers is present in them. However, in some cases isomerism of carborane has virtually no effect on the properties of the polymers. Thus, in a study of the properties of *o*-, *m*-, and *p*-carborane-containing polyphenylenes with the following structure:

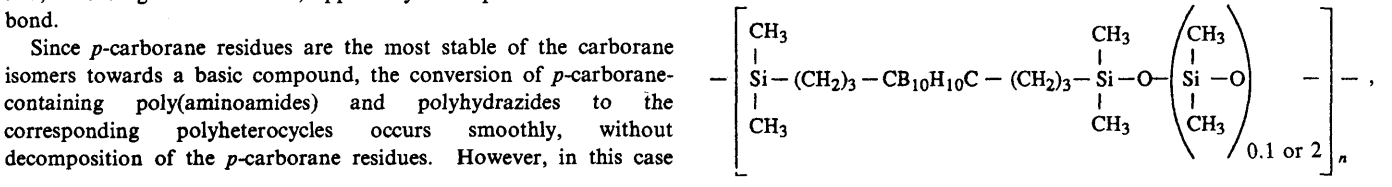


where R = *o*-, *m*-, or *p*-carboranylene and R′ = phenyl, benzyl-*o*-, benzyl-*m*-, or benzyl-*p*-carbonyl, it was established that the solubility of the oligophenylenes synthesised and the thermal stability of the polyphenylenes hardly depend at all on which of the carborane isomers are used to prepare them.[90–93]

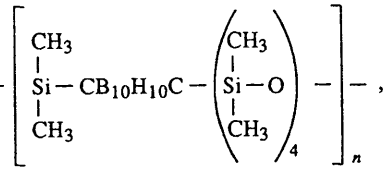
IV. Effect of the configuration of carborane groups in a macromolecule and the structure of the residues directly bonded to them on the properties of carborane-containing polymers

The properties of carborane-containing polymers are dependent on the configuration of the carborane groups in the side chain or main chain of macromolecules and also on the structure of the residues that are adjacent to the carborane groups.

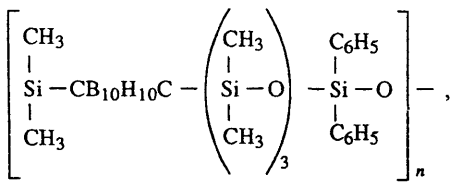
It was established that there is some correlation between the structure of *m*-carborane-containing siloxanes and their properties.[19,94] For example, the thermal stability and oxidative stability decrease with an increase in siloxane groups not bonded to the carborane. Thus, polymers of the type:



are susceptible to thermal oxidation even at 240 °C (in an atmosphere of nitrogen they are stable up to 350 °C).[95] At the same time a characteristic feature of all Dexsil polymers (in which the Si atom is bonded directly to the *m*-carborane residue) is their high thermal stability and resistance to oxidative attack at 300–500 °C.[94,96] This effect is attributed to the result of the inductive stabilisation of the silyl groups through the neighbouring electron-withdrawing *m*-carboranyl groups. Partial replacement of the methyl groups in Dexsil polymers by phenyl groups results in an increase in oxidative stability of the polymers. For example, Dexsil-400:



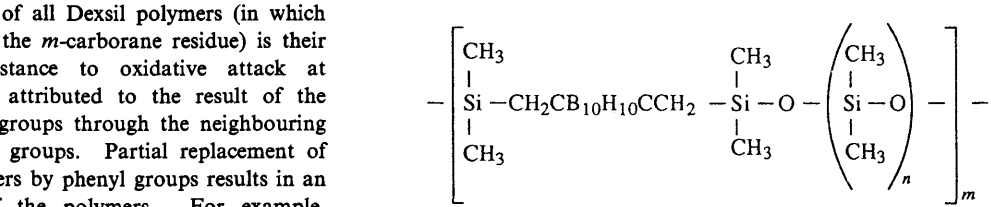
is oxidised at 325 °C, while a polymer with the structure:



is only oxidised at 370 °C.[94]

The presence of trifluoropropyl groups in the Dexsil skeleton imparts the greatest stability to the polymers and stability towards solvents. It was shown that with an increase in the number of siloxane units located between two carborane groups in Dexsil polymers, the softening point of the polymers decreases but the stability towards thermooxidative degradation changes only slightly and remains high (310–340 °C).[96] A feature that distinguishes the thermal degradation of poly(*m*-carboranylene-siloxanes) from that of conventional polysiloxanes is the small content of cyclic oligosiloxanes in the decomposition products.[97] Szekely and Blazgo[97] assume that the large size of the *m*-carborane group inhibits the formation of a helical macromolecular shape and hence decyclopolymerisation of *m*-carborane-containing polysiloxanes is made difficult. It has also been noted that, in contrast to conventional polysiloxanes, Dexsil polymers readily undergo cleavage of the $Si-C_{carb}$ bond by the action of nucleophilic and electrophilic reagents.

It was shown by Kalinin et al.[98] that the presence of methylene bridges between the carborane cage and silicon atom reduces the electron-withdrawing effect of the carborane cage on the silicon atoms, as a result of which the $Si-CH_2-C_{carb}$ system of bonds becomes less polar and hence more stable towards nucleophilic and electrophilic reagents. This is in contrast to the $Si-C_{carb}$ bond, which under identical conditions readily undergoes cleavage with elimination of *m*-carborane. Therefore, the synthesis of poly(*m*-carboranylene-organosiloxanes) was carried out in order to increase the chemical stability of *m*-carborane-containing polysiloxanes.[99] The molecular weight of the resulting polysiloxanes was equal to 171 000–400 000.



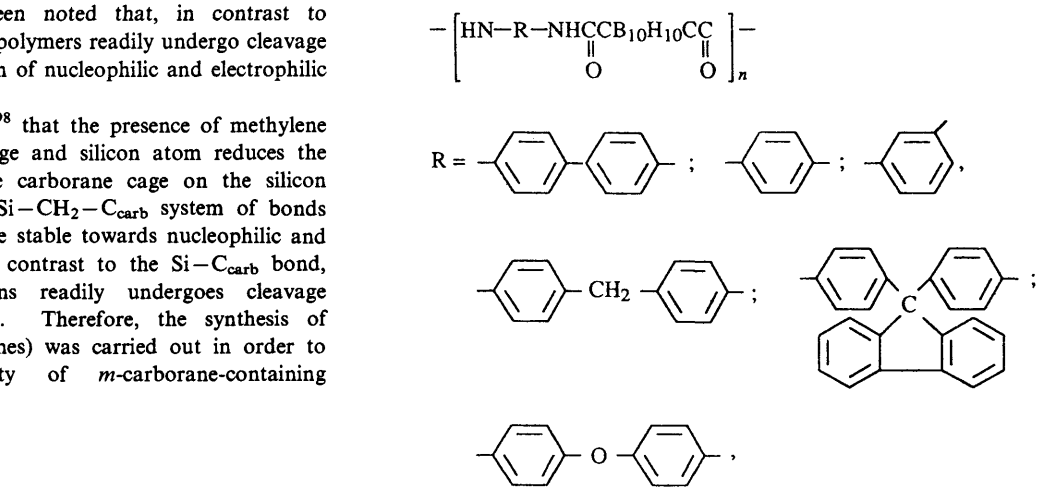
n = 2, 3, 5, 10, 80.

It was established that in terms of thermal stability polyorganosiloxanes with 1,7-bis(dimethylsilylmethyl)-*m*-carborane units are not inferior to similar polymers with 1,7-bis(dimethylsilyl)-*m*-carborane units and they have greater chemical stability than the latter. By changing the length of the organosiloxane block between carborane groups it is possible to vary the physicomechanical properties of the polymers over a wide range.

The properties of carborane-containing polyesters are very markedly dependent on the chemical structure of the organic residues located between the carborane groups. Aliphatic *m*- and *o*-carborane-containing polyesters obtained by reaction between carborane-containing diols and aliphatic dicarboxylic acids are generally low-molecular-weight viscous liquids or brittle materials with softening points at about 100 °C.[3,23,24,100] They are polydisperse[101] and soluble in aromatic hydrocarbons, chlorohydrocarbons, and acetone, and insoluble in aliphatic hydrocarbons, alcohols, and water; and they have an amorphous structure. Replacement of the methylene groups in aliphatic polyesters by CF_2 groups causes a lowering in softening point of these polymers.[3,23,24,100]

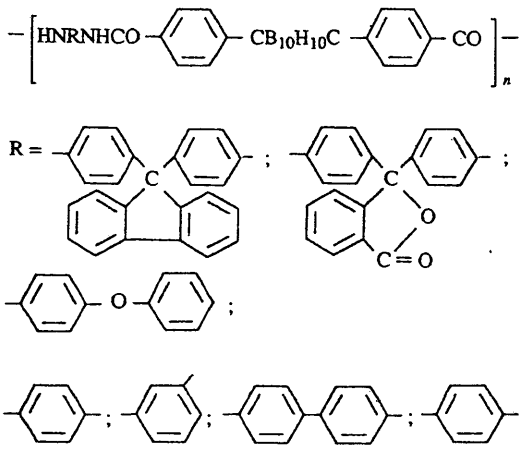
Polyesters synthesised by polycondensation of bis(hydroxymethyl)-*o*-carborane or bis(hydroxymethyl)-*m*-carborane with aromatic dicarboxylic acid dichlorides have greater thermal stability and are less soluble than polyesters obtained from the same diols and aliphatic dicarboxylic acids.[74,101,102] For example, the polyester derived from terephthaloyl dichloride and bis(hydroxymethyl)-*o*-carborane has a softening point of 204 °C,[74] while the softening points of polyesters derived from bis(hydroxymethyl)-*o*-carborane and aliphatic dicarboxylic acids do not exceed 100 °C.[3,23,24,100]

All aromatic *m*-carborane-containing polyamides with the following structure:



in which the NH—CO bond is adjacent to the carborane group are infusible products.

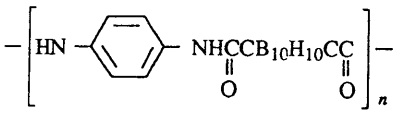
Polyamides with the structure:



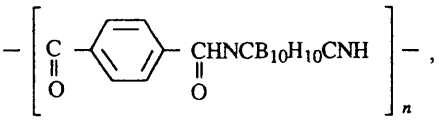
in which the NH—CO bond is separated from the *m*-carborane group by phenylene residues soften over a temperature range of 280—390 °C.

In a study of the thermal degradation of these polyamides over a temperature range of 200—300 °C it was established that the introduction of phenylene residues between the *m*-carborane cage and the NH—CO bond increases the temperature at which degradation of the *m*-carborane groups starts by approximately 100 °C. At the same time the stability of the NH—CO bond towards heterolytic and homolytic cleavage reactions decreases.[103]

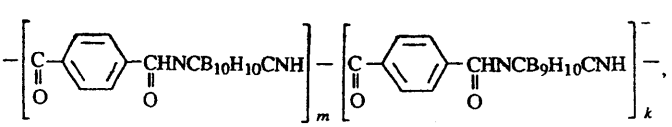
The thermal stability of *m*-carborane-containing polyamides depends to a considerable extent on the manner in which the NH—CO bond is joined to the *m*-carborane group. Thus, a polyamide with the structure:



with a molecular weight of 42000 is stable on heating in air to 230 °C, according to the data of thermogravimetric analysis and IR spectroscopy, while in a polyamide with the structure:

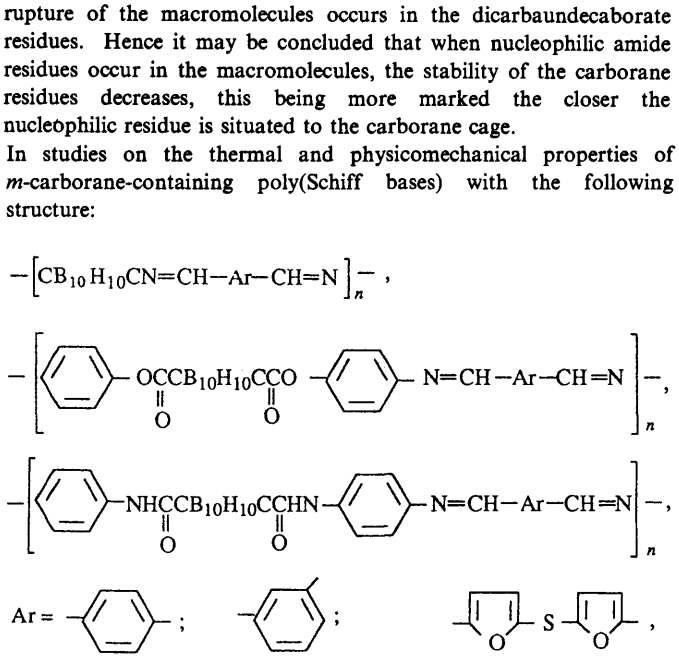


the *m*-carborane residue proved very unstable. Even at 20 °C while this polyamide was being formed, the *m*-carborane groups were partially converted to dicarbaundecaborate groups, according to the IR spectroscopic data. At the same time heterounit polyamides with the following structure were formed:

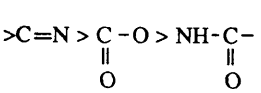


which slowly decomposed on standing. Since carbon dioxide or monoxide are not formed during the degradation of this polymer at room temperature, Korshak et al.[103] maintain that in this case rupture of the macromolecules occurs in the dicarbaundecaborate residues. Hence it may be concluded that when nucleophilic amide residues occur in the macromolecules, the stability of the carborane residues decreases, this being more marked the closer the nucleophilic residue is situated to the carborane cage.

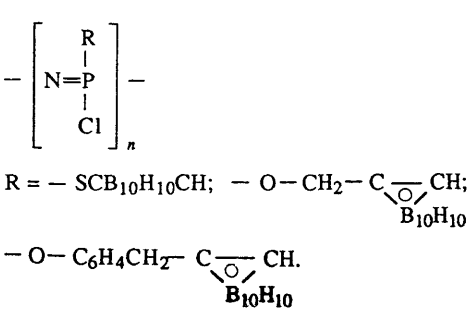
In studies on the thermal and physicomechanical properties of *m*-carborane-containing poly(Schiff bases) with the following structure:



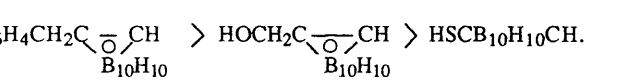
it was established that the chemical and thermal stability in air of these polymers depends on the structure of the organic residues that are adjacent to the *m*-carborane cage and it decreases in the following series:[104,105]



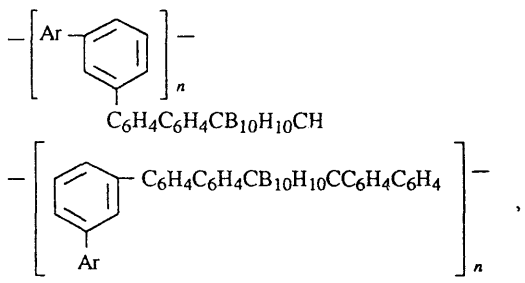
Polymer-like conversions of polydichlorophosphazene with different carborane-containing nucleophiles are used to synthesise the following carborane-containing polyphosphazenes:



Korshak et al. demonstrated that the carborane reagents studied can be arranged in the following series with respect to their favourable effect on the thermal and hydrolytic stability of polyphosphazenes:



Polyphenylenes with the following structure:



containing *o*-, *m*-, and *p*-carborane residues solely in the side chain or solely in the main chain of the macromolecules have been prepared and studied.[90,107–109] Korshak et al. note that the introduction of carborane residues into the side chain of polyphenylenes results in an improvement in their thermal stability but this effect is weaker than in polyphenylenes containing carborane groups in the main macromolecular chain.

Thus, it may be concluded from the above that the properties of carborane-containing monomers and polymers are affected not only by isomerism of the carborane but also by the configuration and structure of the organic residues adjacent to a carborane group.

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