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Polymers with arylenedicarbadodecaborane fragments in the chain

S V Vinogradova, P M Valetskii, Yu A Kabachii

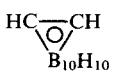
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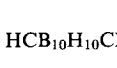
Abstract. The results of studies on polymers with arylene dicarbadodecaborane fragments in the chain are surveyed. The characteristic features of the formation of these polymers, their properties, and their unusual thermal behaviour are examined. The mechanism of the thermal transformations of polyarylenedicarbadodecaboranes is discussed. The probable usefulness of the radical arylation of dicarbadodecaboranes(12) is demonstrated. Certain aspects of the practical employment of dicarbadodecaborane-containing polymers are considered. The bibliography includes 135 references.

I. Introduction

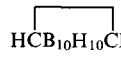
Communications appeared in 1962 – 1964 about the synthesis of new organoboron compounds having the empirical formula $C_2B_nH_{n+2}$ and, in particular, the compound $C_2B_{10}H_{12}$ – dicarba-*closo*-dodecaborane(12) (its trivial names are 'carborane' or 'barene'),[1-10] for which three isomeric forms are known:



1,2-Dicarba-*closo*-dodecaborane(12) (*o*-carborane)†



1,7-Dicarba-*closo*-dodecaborane(12) (*m*-carborane)



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

The first dicarbadodecaborane-containing polymers were also obtained almost at the same time.[10,11] A large number of various heterochain and carbochain polymers with 1,2-, 1,7-, and 1,12-dicarbadodecaborane fragments in the chain have been synthesised since that time and data on these polymers have been described in numerous review-type communications.[12-28]

The introduction of dicarbadecaborane-containing fragments into the polymer chain appeared attractive, since investigators hoped to obtain polymers with improved thermal characteristics, because dicarbadodecaboranes are thermally stable: 1,2-dicarbadodecaborane withstands heating under an inert atmosphere to 475 °C, after which it isomerises to the more stable 1,7-dicarbadodecaborane;[29] when 1,2-dicarbadodecaborane is heated at 700 °C, a mixture of 1,7- and 1,12-dicarbadodecaboranes is obtained;[30] prolonged heating of 1,7-dicarbadodecaborane at 615 °C afforded 1,12-dicarbadodecaborane.[31]

At the same time, in the first stages investigators encountered difficulties in the preparation of high-molecular-mass polymers from bifunctional dicarbadodecaborane derivatives [for example, 1,2- and 1,7-bis(hydroxymethyl)dicarbadodecaboranes, 1,2- and 1,7-bis(carboxymethyl)dicarbadodecaboranes, and their derivatives].[12,24-27,32] It was suggested[12,23,25,27] that this is due to the specific properties of dicarbadodecaborane, which constitutes a strongly electron-accepting group, and also the structural characteristics and the associated steric hindrance in the reactions involving the synthesis of the polymers. However, by virtue of the development and the determination of the principal characteristic features of the polymer formation reactions and in particular polycondensation, the difficulties in achieving high molecular masses in the synthesis of dicarbadodecaborane-containing polymers were overcome and true high-molecular-mass polymers were obtained.

Dicarbadodecaborane-containing monomers with functional groups directly attached to the dicarbadodecaborane nucleus [1,7- and 1,12-dicarbadodecaborane-dicarboxylic acid, 1,7- and 1,12-dicarbadodecaboranylenediamines, and 1,2- and 1,7-bis-(hydroxymethyl)dicarbadodecaboranes] have been widely used in the synthesis of dicarbadodecaborane polymers. Diverse heterochain polymers have been obtained from these starting materials: polyesters, polyamides, polybenzimidazoles, polyoxadiazoles, polybenzoxazoles, polyimides, and many others.[12,19-27,32-34] However, the search for methods of synthesis of polymeric systems with enhanced thermal characteristics led to the conclusion that the use of functional aromatic derivatives of dicarbadodecaborane is promising for the synthesis of dicarbadodecaborane-containing polymers. Since the end of the 1960s, the chemistry of dicarbadodecaborane-containing polymers began to develop successfully. The results of studies in this field are examined and surveyed in the present review.

† Unless otherwise stated, henceforth dicarba-*closo*-dodecaborane(12) will be abbreviated to dicarbadodecaborane (Translator).

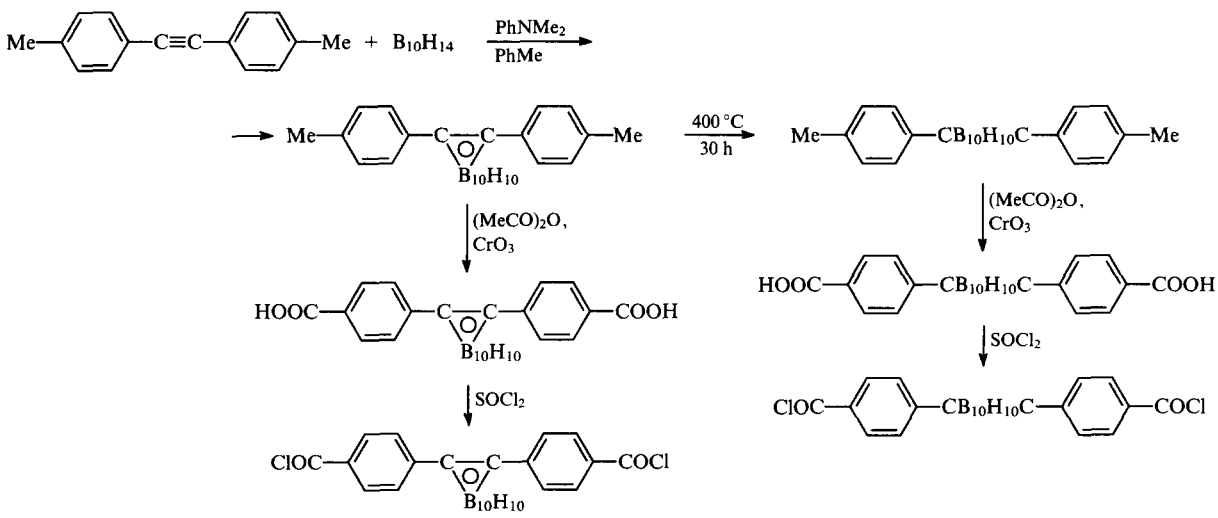
S V Vinogradova Heterochain Polymer Laboratory, Nesmeyanov Institute of Organoelement Compounds, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 61 78
P M Valetskii, Yu A Kabachii Polymer Synthesis Laboratory, Nesmeyanov Institute of Organoelement Compounds, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax. (7-095) 135 50 85

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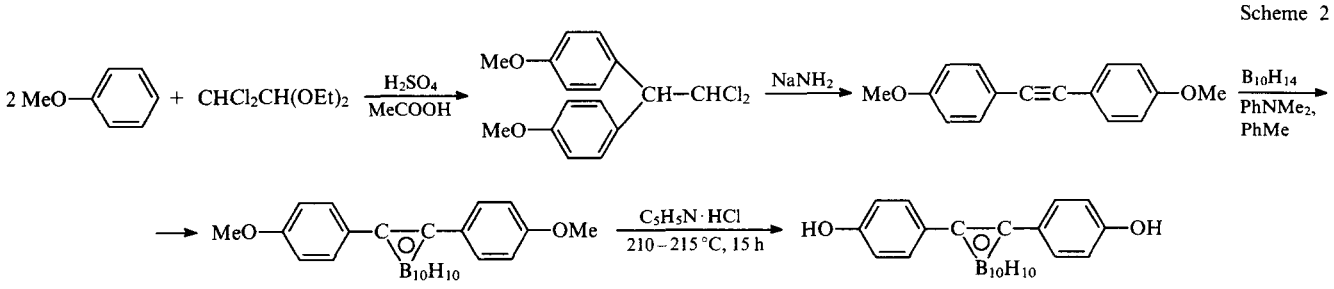
II. Synthesis of aromatic bifunctional derivatives of dicarbadodecaborane(12)

Synthesis of polymers with diarylenedicarbadodecaborane fragments in the macromolecule requires functional aromatic derivatives of dicarbadodecaborane with the corresponding structure. At the beginning of studies in this field, there was no information in the literature about the synthesis of di- and tetrafunctional aromatic derivatives of dicarbadodecaborane. Therefore, in the first stage of this research, much attention was devoted to the chemistry of these monomers. This led to the development of methods of synthesis of compounds such as 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes, their chlorides, and their dihydrazides, 1,2-bis(4-hydroxyphenyl)-dicarbadodecaborane, the dianhydrides of 1,2- and 1,7-bis-(3,4-dicarboxyphenyl)dicarbadodecaboranes, etc.[35-39] Schemes for the synthesis of some of them are presented below as examples.

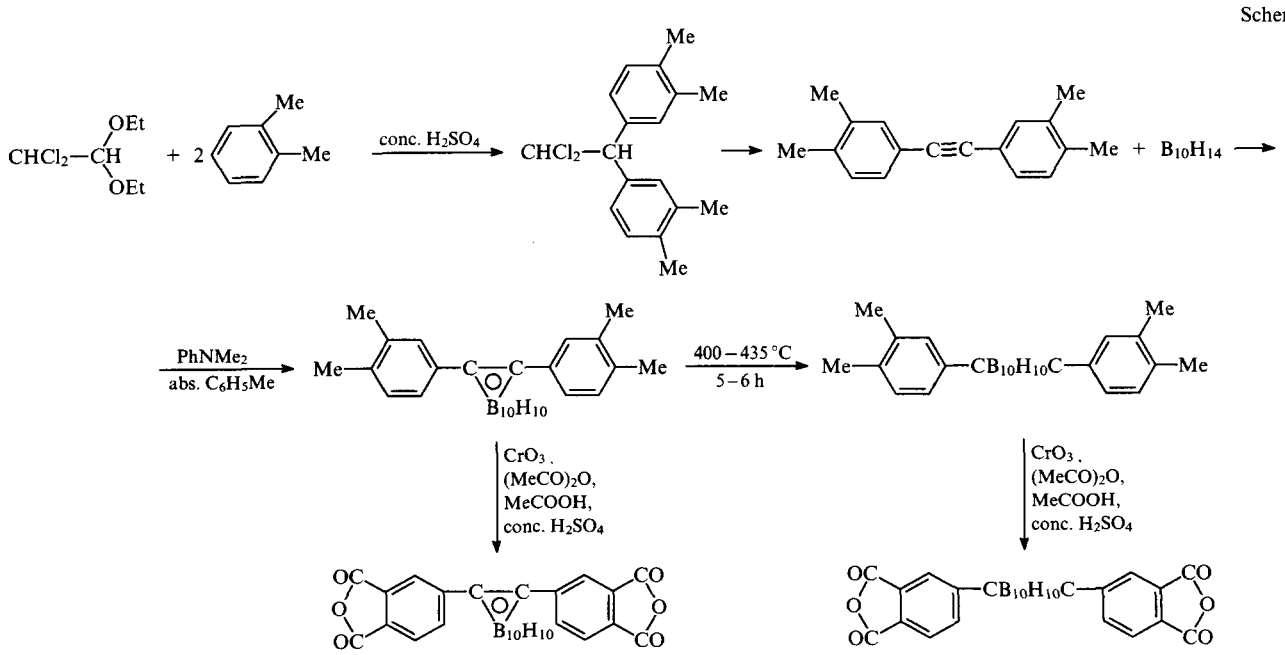
Scheme 1



Scheme 2



Scheme 3



Thus 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes were obtained by oxidising the corresponding ditolyl derivatives of 1,2- and 1,7-dicarbadodecaboranes with chromium trioxide.[35] Scheme 1 illustrates the synthesis of these dicarboxylic acids and their chlorides. 1,2-Bis-(4-hydroxyphenyl)-dicarbadodecaborane was synthesised in accordance with Scheme 2.[36]

The dianhydrides of 1,2- and 1,7-bis(3,4-dicarboxyphenyl)-dicarbadodecaborane were obtained in accordance with Scheme 3.[37,38] The tetramethyltolane required for this purpose was synthesised both by the reaction of asymmetric dichlorodisilylethanes with $NaNH_2$ in aromatic hydrocarbons and by the dehydrochlorination of the same compounds with the aid of KOH in dimethyl sulfoxide.

A fairly large set of the initial functional diarylenedicarbadodecaboranes made it possible to synthesise a wide variety of linear aromatic dicarbadodecaborane-containing heterochain polymers, including polymers with heterocycles in the chain: polyarylates, polyesterketones, polyamides, poly-1,3,4-oxadiazoles, polyimides, polyazophenylenedicarbadodecaboranes, as well as thermoreactive polymers of the type of polyphenylene, and phenol-formaldehyde and epoxide polymers.

III. Linear heterochain polymers with diarylenedicarbadodecaborane fragments in the chain

Polyarylates, polyesterketones, aromatic polyamides, poly-1,3,4-oxadiazoles, polyimides, and polyazophenylenedicarbadodecaboranes with diarylenedicarbadodecaborane fragments in the chain are considered in this section.

1. Polyarylates

The synthesis of dicarbadodecaborane-containing polyarylates with diarylene-dicarbadodecaborane fragments in the chain was achieved by the high-temperature or acceptor-catalytic [in the presence of triethylamine (Schemes 4–6)] polycondensation in three versions:

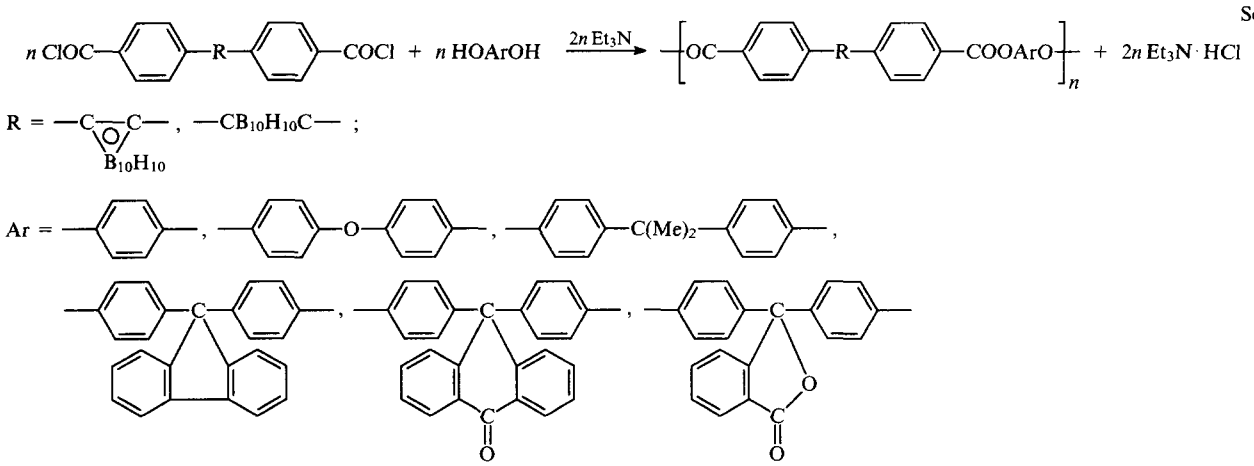
(1) by the reaction of the chlorides of 1,2- and 1,7-bis-(4-carboxyphenyl)dicarbadodecaboranes with various dihydric phenols;

(2) From 1,2-bis(4-hydroxphenyl)dicarbadodecaborane (phenolcarborane) and the chlorides of various aromatic dicarboxylic acids;

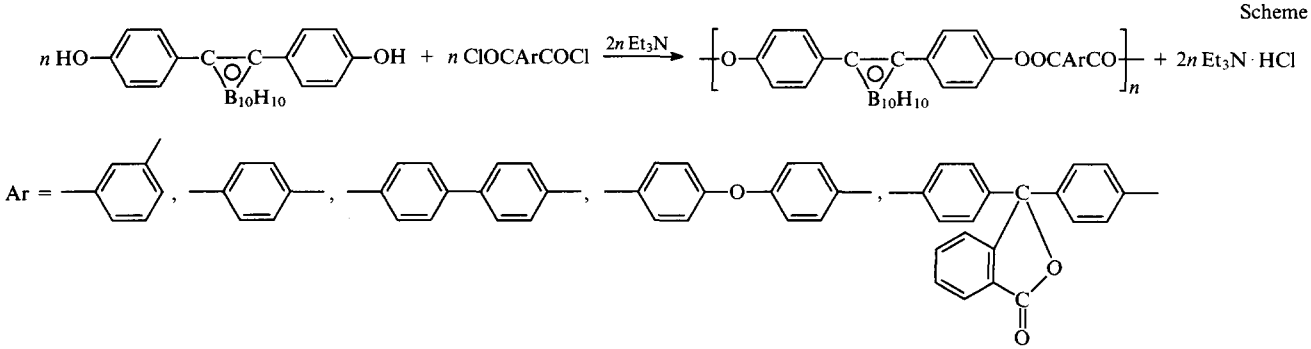
(3) By the reaction of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane with the chloride of 1,2-bis(4-carboxyphenyl)dicarbadodecaborane.

The characteristics of formation of these polymers and their properties have been examined in a series of studies.[21,25,40–60]

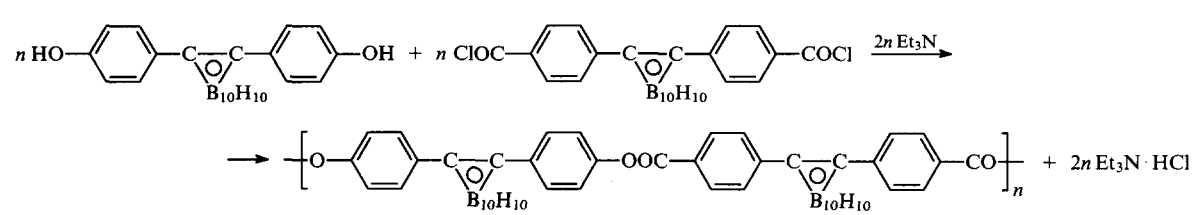
Scheme 4



Scheme 5



Scheme 6



In order to find ways of synthesising high-molecular-mass polyarylates derived from 1,2- and 1,7-bis(4-carboxyphenyl)-dicarbadodecaborane, a series of characteristics of the synthesis of these polymers under the conditions of acceptor-catalytic and high-temperature polycondensation in solution have been investigated in relation to the polycondensation of the chlorides of these acids with 9,9-bis(4-hydroxyphenyl)fluorene (phenol-fluorene). The influence of the nature of the solvent, the concentrations of the starting materials, the reaction temperature, the reaction time, and the method used to introduce the monomers on the molecular mass and yield of the polymers were studied. It was found that both procedures can be successfully employed to synthesise high-molecular-mass polymers (Table 1).

In the acceptor-catalytic polycondensation, polymers with a high molecular mass are obtained when the process is carried out in acetone at 45–50 °C for 1 h with a solid acid chloride introduced into a solution of the bisphenol and triethylamine.

The study of the polycondensation occurring on heating in high-boiling solvents showed that the molecular mass of the dicarbadodecaborane-containing polyarylates is influenced significantly both by the nature of the solvent and by the concentrations of the initial compounds. The most suitable solvent proved to be Sovol (chlorinated biphenyl) and α-chloronaphthalene. The optimum concentrations of the starting materials were 1–2 M. The polycondensation was carried out at 220 °C for 10–16 h. The yields of the dicarbadodecaborane-containing polyarylates [of 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes] were nearly quantitative both in the acceptor-catalytic and in the high-temperature polyesterification. Table 2 presents certain properties of the polyarylates derived from 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes.

The interesting influence of the bulky cardo-group on the structure of the dicarbadodecaborane-containing polyarylates under consideration is noteworthy.[40] Thus the polyarylates derived from 1,2-bis(4-carboxyphenyl)dicarbadodecaborane and dihydric phenols containing bulky groups of the cardo-type (phthalide, fluorene, and anthrone) possess a crystallinity with an average degree of order according to X-ray diffraction data.

Table 1. The reduced viscosities (η_{red}) and molecular masses (M_w) of polyarylates obtained from the acid chlorides of 1,2- (**A**) and 1,7-bis-(4-carboxyphenyl)dicarbadodecaboranes (**B**) and various dihydric phenols by acceptor-catalytic (1) and high-temperature (2) polycondensation.

Initial components in the synthesis of polyarylates		η_{red}/dl g^{-1}		$10^{-3} M_w$	
		1	2	1	2
dihydric phenol	acid chloride				
Hydroquinone	**A**	0.6	0.3	–	–
	B	0.6	0.9	–	–
Bis(4-hydroxyphenyl) ether	**A**	0.6	0.9	116	107
	B	2.0	1.9	94	132
2,2-Bis(4-hydroxy-phenyl)propane	**A**	0.9	–	110	–
	B	0.6	2.3	22	–
9,9-Bis(4-hydroxy-phenyl) fluorene	**A**	0.9	2.3	99	80
	B	1.3	1.2	50	27
9,9-Bis(4-hydroxy-phenyl)-10-anthrone (phenolanthrone)	**A**	0.9	0.5	66	52
	B	1.1	0.7	76	–
Phenolphthalein	**A**	1.2	–	–	–
	B	2.0	2.4	–	–

Note. η_{red} was obtained for a 0.5% solution of the polymer in tetrachloroethane at 25 °C; M_w was determined by light scattering in chloroform.

On the other hand, an amorphous or a weakly ordered structure is characteristic of dicarbadodecaborane-containing polyarylates based on dihydric phenols such as hydroquinone, di(4-hydroxyphenyl) ether, and 2,2-bis(4-hydroxyphenyl) propane.

The polyarylates obtained from the more symmetrical 1,7-isomer and dihydric phenols of the type of hydroquinone

Table 2. The properties of polyarylates obtained from the acid chlorides of 1,2- (**A**) and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes (**B**) and various dihydric phenols by acceptor-catalytic polyesterification.

Initial components in the synthesis of polyarylates		Softening temperature[a]/°C	Properties of film[b]		Temperature of onset of decrease in mass[c]/°C	Coke residue on heating (%)	
			σ/kgf cm^{-1}	ε(%)		up to 900 °C[d]	at 400 °C[d]
dihydric phenol	acid chloride						
Hydroquinone	**A**	320	Brittle film		380	88	94
	B	320	"		380	85	91
Bis(4-hydroxyphenyl) ether	**A**	290	500	23	390	85	90
	B	280	990	10	390	81	85
2,2-Bis(4-hydroxyphenyl) propane	**A**	290	570	4	400	62	96
	B	320	650	2	420	50	86
9,9-Bis(4-hydroxyphenyl) fluorene	**A**	350	680	4	420	60	95
	B	360	1050	5	400	58	90
9,9-Bis(4-hydroxyphenyl)-10-anthrone	**A**	350	470	–	410	70	96
	B	340	920	4	400	–	98
Phenolphthalein	**A**	350	570	2	400	78	98
	B	340	1100	7	400	80	98

[a] The temperature corresponding to the point of intersection of the tangents to the thermomechanical curve in the region of the onset of flow was adopted as the softening temperature; the load applied to the specimen was 0.8 kgf cm^{-2} and the heating rate was 70 K min^{-1}.
[b] σ is the tensile strength of a nonoriented film and ε is the relative elongation at break.
[c] Determined from the thermogravimetric curve at a heating rate of 4.5 K min^{-1} in air.
[d] Determined under isothermal conditions in air in the course of 3 h.

or 2,2-bis(4-hydroxyphenyl)propane have a more ordered structure than those derived from the 1,2-bis(4-carboxyphenyl)-dicarbadodecaborane.[42] According to X-ray diffraction data, the former polyarylates have a fairly high degree of order. The polyarylates derived from 1,7-bis(4-carboxyphenyl)dicarbadodecaborane and dihydric phenols with a cardo-group differ little as regards the degree of order from the analogous polymers based on the 1,2-dicarbadodecaborane-containing monomer. On passing to the polyarylates based on the 1,7-isomer, only a slight tendency towards the formation of an amorphous structure may be noted.[42]

The softening temperatures of the polyarylates based on the 1,2- and 1,7-isomers of bis(4-carboxyphenyl)dicarbadodecaborane and dihydric phenols having the same structure are similar for the same phase state. The highest softening temperatures (340–360 °C) are characteristic of the polyarylates derived from dihydric cardophenols.

The polyarylates derived from both isomers of bis(4-carboxylphenyl)dicarbadodecaborane dissolve in many organic solvents, including aromatic hydrocarbons.[42] The study of the hydrodynamic properties of the solutions and of the molecular mass distribution (MMD) of polyarylates based on 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes led to the discovery of the specific nature of the interaction with the solvent of the polyarylates containing 1,2- and 1,7-dicarbadodecaborane fragments in the chain.[43] Whilst the molecular masses of the polyarylates with the 1,7-diphenyldicarbadodecaborane fragments in the chain are similar, the latter have significantly higher specific viscosities than the analogous polymers with the 1,2-diphenyldicarbadodecaborane fragments regardless of the method of synthesis. This made it possible to postulate that the polyarylates based on 1,2-bis(4-carboxyphenyl)dicarbadodecaborane exists in solution as denser macromolecular coils than can be accounted for by both steric factors and by the greater influence of the dipole moment in the case of the polyarylates with the 1,2-dicarbadodecaborane groups.

The parameters K and a in the Mark–Houwink equation have been determined for the polyarylate obtained from 1,7-bis-(4-carboxyphenyl)dicarbadodecaborane and bis(4-hydroxyphenyl) ether.[43] In chloroform and tetrahydrofuran (THF), $K = 4.74 \times 10^{-4}$ and 2.7×10^{-4}, while $a = 0.71$ and 0.70 respectively. The polydispersity coefficient for the polymer under consideration, synthesised by acceptor-catalytic polyesterification, is 1.35, indicating its comparatively narrow MMD.[43]

The mechanisms of the relaxation processes in the polyarylates based on 1,2- and 1,7-bis(4-carboxyphenyl)dicarba-dodecaboranes have been investigated by dielectric proton magnetic resonance spectrometry and by the thermodepolarisation and radiothermoluminescence methods over a wide temperature range (from −196–300 °C).[44,45,50,58] This led to the establishment of the existence of two regions where the resonance line becomes narrower, one of which (the high-temperature region) is near the glass points of the polymers and is due to the segmental motion of the polymer chain, while the other (the low-temperature region −50 to 150 °C) is induced by the local mobility of the dicarbadodecaborane chain frag-ments. The temperature corresponding to the 'unfreezing' of the segmental mobility depends significantly on the chemical structure of the dihydric phenol and depends little on the structure of the diphenyldicarbadodecaborane fragments incorporated in the chain.

It has also been shown that the vibrations of the 1,2-dicarbadodecaborane nucleus are hindered compared with the 1,7-isomer both by the appreciable conjugation of the 1,2-dicarbadodecaborane fragment with the aromatic rings and due to steric effects. This is reflected in the relaxation processes in the dicarbadodecaborane-containing polyesters, the results of the study of which indicate an increase in the rigidity of the macrochain on passing from the 1,7- to the 1,2-dicarbadodecaborane-containing polymers.[44,58]

Colourless films, the strength parameters of which are listed in Table 2, are obtained from the 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaborane-based polyarylates by casting the latter from solution.

A series of studies have been carried out on the thermal properties of the 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaborane-based polyarylates in air and under an inert atmosphere — under both dynamic and isothermal conditions.[21,25,40–42,46–49,51,59] It was found that the initial polymer degradation temperature is 20–60 °C higher than for the usual polyarylates and, furthermore, the polyarylates have greater 'coke' residues (50%–90% relative to the initial mass on heating in air to 900 °C), whereas the usual polyarylates derived from terephthalic acid and 1,9-bis(4-hydroxyphenyl)fluorene are fully combusted at 650–700 °C. Table 2 shows that, after heating in air at 400 °C for 3 h, the mass of dicarbadodecaborane-containing polymers diminishes by 2%–15%, whereas the 1,9-bis-(4-hydroxyphenyl)fluorene polyterephthalate begins to decompose even before 400 °C and its degree of decomposition after 3 h is 35%. Analysis of the gaseous products of the degradation of the dicarbadodecaborane-containing polyarylates under consideration demonstrated the presence in them of a lower content of carbon oxides and an appreciable content of hydrogen.[21,25,48,49]

The survey of the data obtained established that the dicarbadodecaborane nuclei in the polymer chain have a stabilising effect on the thermal stability of the ester linkage, increasing thereby the thermal stability of the polymer. It has been suggested that this stabilising effect of 1,2-dicarbadodecaborane groups is associated with their conversion into dicarbaundecaborate groups.[48]

A comparative study of the thermal behaviour of the polyarylates obtained by the reaction of 9,9-bis(4-hydroxyphenyl)fluorene with 1,2-bis(4-carboxyphenyl)dicarbadodecaborane and terephthalic acid revealed an interesting feature:[47] in vacuo, gel formation in the 1,2-dicarbadodecaborane-containing polyarylates begins sooner than in polyfluoreneterephthalate [poly(9,9-fluorenylenediphenyl terephthalate)? (translator)] and reaches a maximum at 350 °C, whilst the gel content in the case of polyfluoreneterephthalate is only 2.7%. Under oxidation conditions, the dicarbadodecaborane-containing polyarylate is already fully cross-linked at 275 °C, whereas polyfluoreneterephthalate contains only 30% of the gel at 350 °C.

A study has been made of the structural-chemical transformations of 1,2- and 1,7-dicarbadodecaborane-containing polyarylates during isothermal heating in the temperature range 225–325 °C (at 25 °C intervals) in vacuo and in the presence of oxygen by means of IR spectroscopy and sol-gel analysis.[59] Analysis of the results led to the conclusion that, during vacuum heating and under oxidation conditions, the dicarbadodecaborane fragments participate in the cross-linking of the polymer chain of the dicarbadodecaborane-containing polyarylates, forming inorganic intermolecular B–O–B linkages. In terms of their ability to form three-dimensional structures, the 1,7-dicarbadodecaborane-containing polyarylates are superior to the 1,2-dicarbadodecaborane polymers.

The electrical conductivities of the solid pyrolysis products formed on heat treatment of the polyarylate obtained by the reaction of 1,7-bis(4-carboxyphenyl)dicarbadodecaborane and bis(4-hydroxyphenyl) ether for 1 h in vacuo (10^{-3} Torr) at 600, 900, and 1200 °C have been investigated by electronic spectroscopy.[60] The aromatic rings in the polymer chain of this polyarylate are separated (apart from the dicarbadodecaborane fragments) also by ester groups, which do not transmit π-conjugation along the chain, as a result of which the degree of conjugation of the initial system is low and the system does not exhibit semiconducting properties. The comparatively small changes in the electrical conductivities and activation energies for the specimens heated to 600 °C indicate a low degree of reorganisation of the internal structure of the polymer, leading to the formation of condensed polynuclear systems in the solid pyrolysis products. The electrical conductivity at 150 °C of the specimen heated to 900 °C increases by approximately

twelve orders of magnitude compared with the initial polymer and the electrical conduction process becomes nonactivated ($E \approx 2.89$ kJ mol^{-1}). In terms of the absolute value of the electrical conductivity, this pyrolysis product is at the boundary between semiconductors and metals. The observed change in electrical conductivity is due to the formation of highly conjugated polynuclear systems in the pyrolysis product.

The absolute values of the electrical conductivities of the specimens heated to 1200 °C increase slightly compared with the electrical conductivity of the specimen heated to 900 °C, but, after heating at 1200 °C, a negative temperature coefficient of the resistance, $\alpha = -0.12$ K^{-1} is observed, i.e. with increase in temperature the electrical conductivity of the specimens does not increase, as in typical semiconducting materials, but actually diminishes, which is characteristic of materials with the metallic type of conductivity. Consequently heat treatment of the specimens at 900–1200 °C is accompanied by a significant reorganisation of the internal structure. The thermal e.m.f.'s of the specimens obtained at 900 and 1200 °C are respectively 9.3 and 6.8 μVK^{-1} at 100 °C. The sign of the thermal e.m.f. shows that the principal electric current carriers are electrons. Thus the pyrolysis of the dicarbadodecaborane-containing polyarylate leads to the formation of an extended region of aromatic ring systems cross-linked in space by the residual dicarbadodecaborane fragments.

As noted above, 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane has been used to synthesise polyarylates with diphenyldicarbadodecaborane fragments in the chain.[21,54–56] 1,2-Bis(4-hydroxyphenyl)dicarbadodecaborane was subjected to acceptor-catalytic and high-temperature polycondensation with dicarboxylic acid chlorides (see Scheme 5). A number of characteristic features of these processes have been investigated in relation to the polycondensation of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane with isophthalic acid chloride: influence of the nature of the solvent, temperature, concentrations of initial substances, and the order in which they are introduced into the reaction sphere, on the reduced viscosities of the solutions of the polymers obtained and their structures.

It was found that, when the acceptor-catalytic polyesterification is carried out in acetone (heterogeneous conditions), changes in the process temperature, in the concentrations of the starting materials, and in the order in which they are introduced into the reaction zone did not lead to the formation of polymers with a high reduced viscosity of the solution. A positive result was not obtained either when the acceptor-catalytic polycondensation was carried out under homogeneous conditions (in dichloroethane, tetrahydrofuran, dioxane, and benzene) and also when the synthesis was performed by high-temperature polycondensation in Sovol and α-chloronaphthalene at 220 °C. In all cases, polymers with low reduced viscosities of the solutions (0.07–0.31 dl g^{-1} in tetrachloroethane) were obtained. The molecular mass of a polymer with a reduced viscosity of 0.07 dl g^{-1}, determined by the light scattering method in tetrahydrofuran, was 8600. The reason for the formation of polymers with low molecular masses is their limited solubility in the reaction medium due to the crystallisation of the polymers during their formation.[55]

The tendency of the 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane-based polyarylates to form highly ordered and sparingly soluble systems is manifested to an even greater extent in the polycondensation of 1,2-bis(4-hydroxyphenyl)-dicarbadodecaborane with terephthalic and biphenyl-4,4′-dicarboxylic acid chlorides. Such polyarylates, obtained by high-temperature polycondensation, have a highly ordered crystal structure according to X-ray diffraction data and do not dissolve in any of the solvents known for polyarylates even such as trifluoroacetic and sulfuric acids. Polymers with a lower degree of order are formed in the acceptor-catalytic polycondensation, but in this case too the terephthalic acid-based polyarylates are insoluble.[55]

Attempts have been made to obtain the above polyarylates by high-temperature polycondensation using finely dispersed magnesium as the catalyst and also by the rapid heating of the initial components in a high-boiling solvent to 250–340 °C with subsequent polycondensation at these temperatures for 1 h and rapid cooling of the initial solution to room temperature. In this case, the poly[1,2-bis(4-hydroxyphenyl)dicarbadodecaborane terephthalate] dissolved immediately after synthesis in a mixture of tetrachloroethane and phenol, but it soon precipitated and then no longer dissolved.[55]

On the other hand, under conditions where the polymers formed are amorphous and readily soluble, it is possible to attain high molecular masses. This occurs in the polycondensation of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane with the chlorides of oxybis(benzene-4-carboxylic)acid and bis(4-carboxyphenyl)-phthalide. In the former case, it was possible to obtain a polymer with a reduced viscosity in tetrachloroethane (TCE) of 0.92 dl g^{-1} (molecular mass 140 × 10^3), while in the latter the reduced viscosity was 0.62 dl g^{-1} (molecular mass 93 × 10^3). Both polymers are soluble in chloroform, tetrachloroethane, tetrahydrofuran, and benzene.

Since one of the ways of disturbing the order in the polymer is copolycondensation, a series of mixed polyarylates based on isophthalic (or terephthalic) acid, 1,2-bis(4-hydroxyphenyl)-dicarbadodecaborane, and phenolphthalein were obtained.[55] It was found that, for a relatively high content of phenolphthalein residues in such copolymers, the degree of order in the copolymer formed diminishes, which improves its solubility and the reduced viscosity is fairly high. For example, the copolymer obtained from 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane, phenolphthalein, and terephthalic acid chloride in molar proportions of 0.5 : 0.5 : 1 has a crystal structure with a relatively low degree of order, is soluble in chloroform, tetrachloroethane, and tetrahydrofuran, and its reduced viscosity in tetrachloroethane is 1.53–1.67 dl g^{-1}. With increase in the content of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane residues in the mixed polyarylates, the degree of order in the latter increases, while the reduced viscosity and the solubility diminish.

Mixed 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and chloro- or methylhydroquinone polyterephthalates have been synthesised recently by acceptor-catalytic polycondensation. The possibility of obtaining them from organoelement liquid-crystal polymers has been investigated.[41,52,53] The liquid-crystal properties of such dicarbadodecaborane-containing copolyarylates are indicated both by the composition of the copolymer and by its microstructure. For example, with increase in the molar proportion of the 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane residues in the copolyarylate derived from 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and chlorohydroquinone from 0.4 to 0.6, the temperature range corresponding to the existence of the mesophase expands from 245–400 °C to 230–400 °C. In all cases the 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane-based homo- and copolyarylates were obtained in high yields (85%–95%).

Table 3 presents data on certain properties of the 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane-based polyarylates. Comparison of the data in Tables 2 and 3 permits the conclusion that the softening temperatures of the polyarylates are hardly influenced by the presence between the 1,2-dicarbadodecaborane group with hydroxy- or carboxy-phenyl residues. Thus, whereas the softening temperature of the amorphous polyarylates derived from 1,2-(4-hydroxyphenyl)dicarbadodecaborane and oxybis(benzene-4-carboxylic) acid is 275–285 °C, that of the isomeric amorphous polyarylate derived from 1,2-bis(4-carboxyphenyl)dicarbadodecaborane and bis(4-hydroxyphenyl) ether is 280–290 °C. On the other hand, comparison of the melting points of the crystalline polyarylates derived from 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and terephthalic and isophthalic acids (~400 and 245 °C respectively) with those of the crystalline polyesters of 1,2-bis(4-hydroxymethyl)dicarbadodeca-

Table 3. Certain properties of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane polyarylates obtained by acceptor-catalytic (I) and high-temperature (II) polycondensation.

Acid chloride	Methods of synthesis	η_{red}/dl g^{-1} (TCE, 25 °C)	Structure[a]	Softening temperature[b]/°C	Temperature of onset of mass loss/°C		Coke residue at 900 °C (%)	
					in air[c]	in helium[d]	in air[c]	in helium[d]
Isophthalic	I	0.31	Crystalline, low	245				
	II	0.20	degree of order	240	350	360	70	90
Terephthalic	I	–	Crystalline, high	~400				
	II	–	degree of order	>400	380	380	82	88
Biphenyl-4,4'-dicarboxylic	I	0.20	Crystalline, moderate degree of order	~400				
	II	–	Crystalline, high degree of order	>400	370	370	85	85
Oxybis(benzene-4-carboxylic)	I	0.92	Amorphous	275				
	II	0.46	"	285	380	400	75	88
Of bis(4-carboxyphenyl)phthalide	I	0.62	"	330	400	410	77	85
	II	0.28	"	300				

[a] X-Ray diffraction data. [b] See footnote to Table 2. [c] See footnote to Table 2. [d] Heating rate 5 K min^{-1}.

borane and terephthalic and isophthalic acids[61] (221 and 88 °C respectively) clearly demonstrates that it is desirable to introduce the dicarbadodecaborane groups into the polymer chain in the form of diphenyldicarbadodecaborane fragments in order to create heat-resistant polymers.

As can be seen from Table 3, the 1,2-bis(4-hydroxyphenyl)-dicarbadodecaborane-based polyarylates are thermally stable and give rise to high amounts of coke residue on heating to 900 °C both under an inert atmosphere and in air.

A polyarylate with an increased content of diphenyldicarbadodecaborane fragments, the chain of which contains only 1,2-diphenyldicarbadodecaborane fragments together with the ester groups, has been synthesised by the high-temperature polycondensation of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane with the acid chloride of 1,2-bis(4-carboxyphenyl)dicarbadodecaborane in α-chloronaphthalene at 220 °C for 15–18 h (Scheme 6).[56] This polymer had the most crystalline structure (degree of crystallinity 55%) and was soluble only in tetrahydrofuran. The synthesis of polyarylates by acceptor-catalytic polycondensation in acetone or by high-temperature polycondensation in Sovol with rapid heating of the solution of the starting materials to 320 °C and the maintenance of the reaction mixture at this temperature for 1 h with subsequent rapid cooling to 0 °C gives rise to specimens with a lower degree of crystallinity. In the last case, the polymer is soluble not only in tetrahydrofuran but also in cyclohexanone. None of these polymers melt below 400 °C. Above this temperature, their thermal degradation begins.

However, it was observed that this dicarbadodecaborane-containing polyarylate can be converted into an amorphous form by reprecipitating the polymer from solution in tetrahydrofuran in cooled water or methanol. The specimens, converted into an amorphous form, dissolve in chloroform, tetrachloroethane, and even in benzene, softening at 260–290 °C. The amorphous specimen can be reconverted into a crystalline form by heating a 3% solution of the polymer in tetrachloroethane (from which the polymer begins to precipitate during the crystallisation process) or by slow (over a period of several days) evaporation of the polymer solution in chloroform. The specimens obtained in this way do not melt below 400 °C.

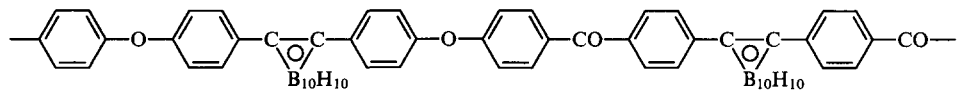
The degree of crystallinity of the polyarylates with 1,2-diphenyldicarbadodecaborane units can be altered also by heat treatment. Thus successive heating of the same specimen with a degree of crystallinity of 55% at 230, 290, and 330 °C in air for 30 min reduces the degree of crystallinity to 26%, 22%, and 16% respectively. On the other hand, when the specimen is heated at 450 °C, its degree of crystallinity falls to 5%–8%.

Thus, by manipulating the conditions in the synthesis or in the subsequent treatment of the polymer, it is possible to alter specifically the structure of this diphenyldicarbadodecaborane-containing polyarylate and hence its heat resistance.

The study of the characteristic features of the thermal and thermooxidative degradation of the polyarylates derived from 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and 1,2-bis(4-carboxyphenyl)dicarbadodecaborane[56,57] revealed a difference in the behaviour of the crystalline specimen and the specimen converted into an amorphous form on heating, which may be due to the difference between the molecular mobilities in the temperature range 280–380 °C.[57] It was established that the thermal stability of the amorphous polymer is higher. Thus the mass of a specimen of the latter does not change up to ~650 °C, whereas crystalline specimens exhibit a decrease in mass at 400 °C.[56]

The structural transformations of the polyarylate derived from 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and 1,2-bis-(4-carboxyphenyl)dicarbadodecaborane and, for comparison, the polyarylate obtained from 4,4'-dihydroxybiphenyl and 4,4'-dicarboxybiphenyl on heat treatment (for 1 h) in vacuo (10^{-3} Torr) in the temperature range 300–1200 °C have been investigated and the characteristic regions corresponding to the thermal transformations of the polymers have been determined.[62] The temperature range corresponding to the existence of the EPR absorption for the dicarbadodecaborane-containing polyarylate is much wider (400–1200 °C) than for the usual polyarylate (400–700 °C). The maximum concentration of paramagnetic centres is attained at 800 °C for the dicarbadodecaborane-containing polyarylate and at 600 °C for the usual polyarylate.

It was found that heating of the dicarbadodecaborane-containing polyarylate at 300 °C induces hardly any changes in the crystalline polymer specimen, while the amorphous specimen becomes crystalline under similar conditions. An increase in temperature to 400 °C leads to the complete disruption of the crystal structure of the polymer and to its conversion into an amorphous form. After heating to 500 °C, considerable chemical transformations take place and an appreciable amount of boric acid is formed. This may indicate the interaction of the dicarbadodecaborane groups and the products of their thermal transformations with the oxygen



1

bound chemically in the polymer and in its reaction products. At 600 °C, the polymer structure is fully disrupted and at 700 °C small amounts of graphite particles are formed. A further increase in temperature up to 1000 °C does not lead to significant changes in the structure of the specimen. The latter remains porous and the amount of graphite increases. According to the results of dynamic thermogravimetric analysis (DTGA) in helium at a heating rate of 5 K min^{-1}, specimens of the dicarbadodecaborane-containing polyarylate do not exhibit a region of vigorous decomposition up to 900 °C. The decrease in mass virtually ceases towards 750 °C and the rate of change of the mass in the temperature range 700–750 °C is only 0.01%–0.02% when the temperature is altered by 1 K.

Comparison of the results of X-ray diffraction and of the EPR spectra of the heat-treated polymers (the dicarbadodecaborane-containing and usual polymers) permits the conclusion that the principal difference between the polyheteroarylenedicarbadodecaboranes and their usual organic analogues is the displacement of the extensive decomposition processes and of the rearrangement of the initial structure to higher temperatures and also the specific interaction of the dicarbadodecaborane groups or the products of their thermal transformation with the chemically bound oxygen.[62]

2. Polyesterketones

Brief data have been published recently concerning simple aromatic polyesterketones in which the 1,2-, 1,7-, and 1,12-dicarbadodecaborane groups and phenylene units are joined via oxygen or CO groups (for example, as in a type **1** polymer).[63] These polymers are obtained by the interaction of diphenylenedicarbadodecaboranedicarboxylic acids having the corresponding structure and diphenoxyphenyl derivatives of the dicarbadodecaborane.

The polymers generally have an amorphous structure and a glass point of 180–220 °C and form films from solutions in methylene chloride and chloroform. According to DTGA data, the polymers begin to lose mass at 350–400 °C without fusion, the overall mass loss at 1000 °C amounting to about 10%–15%. This enabled the authors to postulate that the pyrolysis of such polymers under an inert atmosphere can lead to the formation of a ceramic boron carbide residue dispersed in the graphite matrix.

3. Polyamides

Polyamides with diphenylenedicarbadodecaborane fragments in the chain have been obtained by the reaction of the acid chlorides of 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes with aromatic diamines (Scheme 7) under the conditions of low-temperature polycondensation in solution or by polycondensation in an organic solvent–water–hydrogen chloride acceptor mixture.[21,64–67]

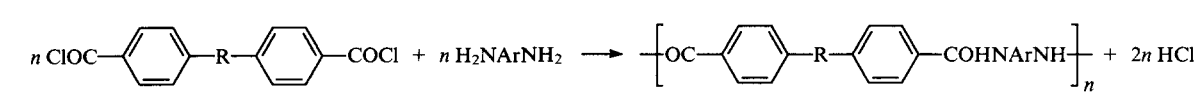
In order to discover the most favourable conditions of synthesis, certain features of the formation reactions of the polyamides (the nature of the solvent, reaction temperature, concentrations of the initial components, etc.) were investigated in relation to the polycondensation of the acid chloride of 1,2-bis(4-carboxyphenyl)dicarbadodecaborane with *m*-phenylenediamine and 1,2-bis(4-carboxyphenyl)dicarbadodecaborane with 9,9-bis(4-aminophenyl)fluorene. It was found that, in the case of the low-temperature synthesis of the polyamide, the polymers with the highest reduced viscosity are obtained when the process is carried out in dimethylacetamide at −30 °C (synthesis for 1 h at −30 °C and maintenance at room temperature for 1–2 h) at a concentration of the starting materials of 1.0 M.

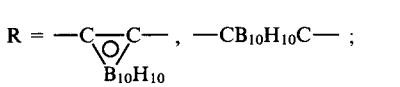
When the polycondensation was carried out in an organic solvent–water system, best results were obtained when tetrahydrofuran and a concentration of the starting material of 0.3 M were employed. In this case, $NaHCO_3$ was used as the hydrogen chloride acceptor. The process was carried out at room temperature for 20 min with vigorous stirring of the reaction mass. Both methods can be used successfully to obtain high-molecular-mass dicarbadodecaborane-containing polyamides.

As an example, Table 4 presents the intrinsic viscosities of 0.5% solutions of the polymers in *N*,*N*′-dimethylacetamide at 25 °C and their molecular masses determined by the light scattering method in *N*-methyl-2-pyrrolidinone.

Outwardly the aromatic polyamides derived from 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes are white fibrous or powdered substances. Many of them are soluble not only in amide solvents but also in tetrahydrofuran, cyclohexanone, a mixture of tetrachloroethane with phenol, and tricresol. The polyamide obtained from 1,4-phenylenediamine and 1,2-bis-(4-carboxyphenyl)dicarbadodecaborane is an exception. It does not dissolve in the solvents listed above and is insoluble even in sulfuric acid. The polyamides synthesised are also insoluble in tetrachloroethane.

Scheme 7





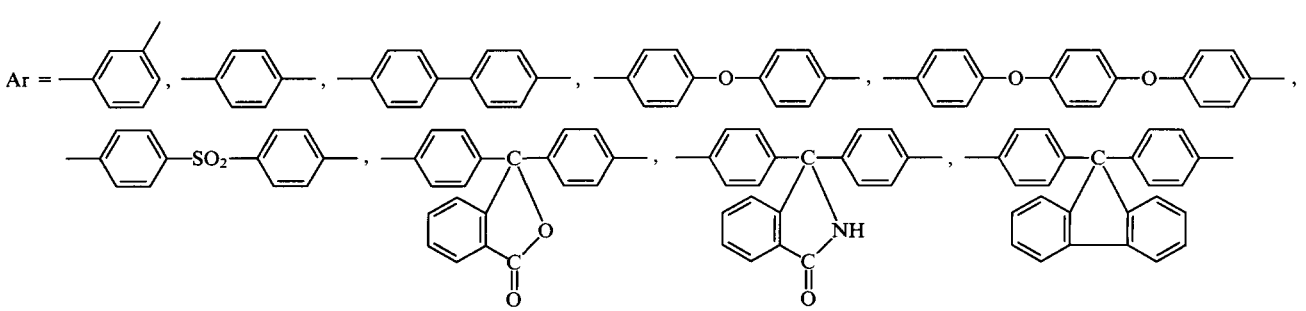


Table 4. The reduced viscosities and molecular masses of the polyamides obtained from various diamines and the acid chlorides of 1,2- (**A**) and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes (**B**) by low-temperature polycondensation in *N,N*-dimethylacetamide.

Initial components in the synthesis of polyarylates		η_{red}/dl g^{-1} (10^{-3} M_w)
diamine	acid chloride	
1,3-Phenylenediamine	**A**	0.74 (106)
	B	0.60
1,4-Phenylenediamine	**A**	Insoluble
	B	0.66
4,4′-Diaminobiphenyl	**A**	0.50
	B	1.05
Bis(4-aminophenyl) ether	**A**	0.91 (160)
	B	0.79
Bis(4-aminophenyl) ether of hydroquinone	**A**	0.81
	B	–
Bis(4-aminophenyl)sulfone	**A**	0.40 (19)
	B	0.40
9,9-Bis(4-aminophenyl)-fluorene	**A**	0.75 (70)
	B	1.50 (70)
Bis(4-aminophenyl)phthalide	**A**	0.75 (67)
	B	0.70
Bis(4-aminophenyl)phthalimide	**A**	0.50
	B	–

Strong films are formed from solutions of the diphenyldicarbadodecaborane-containing amides. For example, nonoriented films of the polyamides obtained by the reaction of 1,2-bis(4-carboxyphenyl)dicarbadodecaborane with anilinephthalein and the bis(4-aminophenyl) ether of hydroquinone have tensile strengths of 750 and 760 kgf cm^{-2} and relative elongations at breaks of 5% and 30% respectively. The tensile strength of the film obtained from the polyamide derived from 1,7-bis-(4-carboxyphenyl)dicarbadodecaborane and anilinefluorene is 940 kgf cm^{-2} with a relative elongation at break of 20%. At 300 °C, the film of this polymer retains a high strength (370 kgf cm^{-2}) and its relative elongation at this temperature is 111%.

The majority of the polyamides considered are amorphous. The polyamides obtained from anilinefluorene and both bis-(4-carboxyphenyl)dicarbadodecaborane isomers and also the polymer obtained by the reaction of benzidine and 1,7-bis-(4-carboxyphenyl)dicarbadodecaborane, which has a crystalline structure with a low degree of order, are exceptions.

Table 5 presents the thermal properties of aromatic polyamides based on 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes. Evidently high softening temperatures are characteristic of these polyamides. The polyamides derived from benzidine, 1,4-phenylenediamine, and diamines with cardo-groups have the highest softening temperatures (370–400 °C). Comparison of the results of a thermomechanical study of aromatic polyamides derived from 1,7-bis(4-carboxyphenyl)dicarbadodecaborane [64] and 1,7-dicarbadodecaboranedicarboxylic acid [69] permits the conclusion that the use of aromatic bifunctional derivatives of 1,7-dicarbadodecaborane leads to much more heat-resistant polyamides. For example, whereas the softening temperatures of the polyamides obtained by the reaction of 1,7-dicarbadodecaboranedicarboxylic acid with 1,4-phenylenediamine, benzidine, and bis(4-aminophenyl) ether are 210, 250, and 220 °C (in all cases with decomposition), the softening temperatures of the analogous polyamides based on 1,7-bis(4-carboxyphenyl)dicarbadodeca-borane are 380, 400, and 300 °C respectively.

The thermal and thermooxidative behaviour of dicarbadodecaborane-containing aromatic polyamides have been investigated in a number of studies. [64–66, 68, 70, 71]

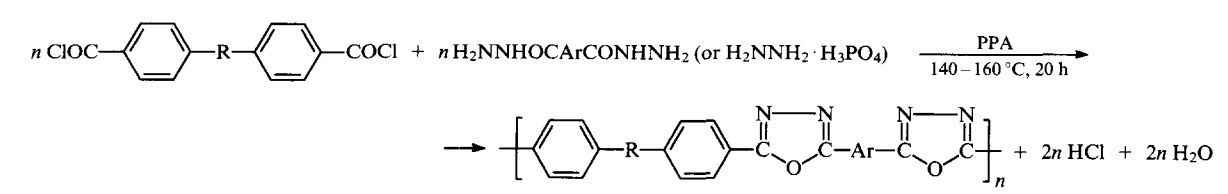
Table 5 (over) shows that the temperature of the onset of a change in mass is in the range 370–435 °C (in air) and 380–450 °C (in an inert medium) for diphenyldicarbadodecaborane-containing polyamides under the conditions of DTGA. [65] The overall rate of degradation of the dicarbadodecaborane-containing polyamides considered is appreciably lower than for the usual aromatic polyamides. On heating to 900 °C in air and especially under an inert atmosphere, the polyamides based on both isomers of bis(4-carboxyphenyl)dicarbadodecaborane give rise to a large amount of a coke residue (up to 30%–60% in air and up to 82%–96% in helium), whereas polyamides based on the reaction of terephthalic acid with cardo-diamines give rise to 13%–16% of coke residue (in air) and 48%–53% (in helium) (Table 5). [65] The nature of the thermal degradation of polyamides with 1,2- and 1,7-diphenyldicarbadodecaborane fragments is close to that of the degradation of polyamides based on 1,7-dicarbadodecaboranedicarboxylic acid, but the onset of vigorous decomposition is displaced towards higher temperatures. The amide groups in the dicarbadodecaborane-containing polyamides possess a greater hydrolytic stability compared with those in the usual polyamides. It is also noteworthy that the 1,2-dicarbadodecaborane groups stabilise the amide linkage in polyamides to a greater extent than the 1,7-dicarbadodecaborane groups. One of the reasons for the increase in the mass of the polyamidodicarbadodecaboranes when the latter are heated in air is believed to be the oxidation of the dicarbadodecaborane nucleus by atmospheric oxygen with formation of involatile oxygen-containing boron compounds. [68]

The electrophysical properties of polyamides based on 1,2- and 1,7-bis(4-hydroxyphenyl)dicarbadodecaboranes and anilinefluorene as well as their molecular mobility have been investigated. [72] It has been noted that the replacement of the 1,2-dicarbadodecaborane nucleus by the 1,7-dicarbadodecaborane nucleus is accompanied by a decrease in the rigidity of the macrochains.

4. Poly-1,3,4-oxadiazoles

For the synthesis of homogeneous and mixed poly-1,3,4-oxadiazoles with diphenyldicarbadodecaborane fragments in the chain, use has also been made of 1,2- and 1,7-bis-(4-carboxyphenyl)dicarbadodecaboranes. [73–75] The study of the characteristic features of this synthesis showed that, even after prolonged interaction of 1,2- and 1,7-bis(4-carboxyphenyl)-

Scheme 8



R = —C(O)—C— , —CB10H10C—
B10H10

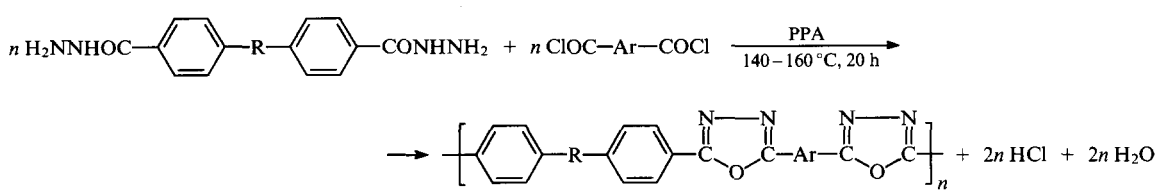
Table 5. Thermal properties of the polyamides obtained from the acid chlorides of 1,2- (**A**) and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes (**B**), terephthalic acid (**C**), and various diamines.

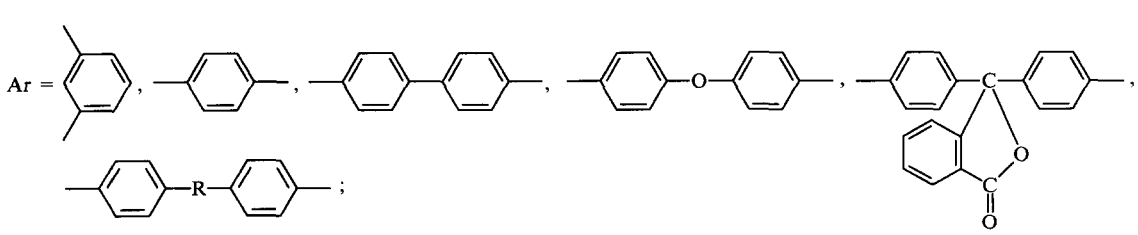
Initial components in the synthesis of polyarylates		Softening temperature[a]/°C	Temperature of onset of change in mass/°C		Maximum increase in mass of specimen in air (%)	Temperature of attainment of maximum increase in mass[b]/°C	Temperature range of intense decomposition in helium/°C	Coke residue at 900 °C (%)	
Diamine	Acid chloride		in helium	in air				in helium	in air
1,3-Phenylenediamine	**A**	310	420	410	14.9	520	470–580	96	67
	B	320	410	420	9.0	520	420–560	92	66
1,4-Phenylenediamine	**A**	360	420	410	7.9	490	435–550	94	47
	B	380	410	420	4.0	500	440–550	91	62
4,4′-Diaminobiphenyl	**A**	350	400	400	4.4	530	440–550	96	45
	B	400	410	420	4.0	500	470–560	89	52
Bis(4-aminophenyl) ether	**A**	325	410	410	12.7	460	420–560	92	49
	B	300	400	380	–	–	420–560	90	33
Bis(4-aminophenyl) ether of hydroquinone	**A**	280	–	–	–	–	–	–	–
Bis(4-aminophenyl)sulfone	**A**	305	380	410	9.0	490	400–570	87	45
	B	320	380	370	–	–	440–520	82	60
9,9′-Bis(4-aminophenyl)fluorene	**A**	370	415	420	2.2	–	440–540	87	30
	B	370	450	420	–	–	460–580	89	47
	C	–	410	390	–	–	450–620	53	13
Bis(4-aminophenyl)phthalide	**A**	380	400	400	–	–	450–580	87	36
	B	390	435	435	–	–	450–560	85	45
	C	–	360	380	–	–	440–600	48	16
Bis(4-aminophenyl)-phthalimide	**A**	385	–	–	–	–	–	–	–

[a] See footnote to Table 2. [b] The range between the two points of intersection of the tangents to the corresponding branches of the S-shaped thermogravimetric analysis curve was adopted as the temperature range.

dicarbadodecaboranes with hydrazine phosphate or dicarboxylic acid dihydrazides in polyphosphoric acid (PPA) at 180–200 °C, the corresponding poly-1,3,4-oxadiazoles are not formed. It was not possible to obtain the polymers also by the interaction of the dihydrazides of 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes with dicarboxylic acids. However, when one begins with the dichlorides of dicarboxylic acids, it is possible to synthesise homogeneous and mixed dicarbadodecaborane-containing poly-1,3,4-oxadiazoles with a fairly high molecular mass. In this case, the process proceeds in accordance with Scheme 8 or 9 and under comparable conditions leads to products differing appreciably in molecular mass and, in the case of 1,2-bis(4-carboxyphenyl)dicarbadodecaborane derivatives, in composition.

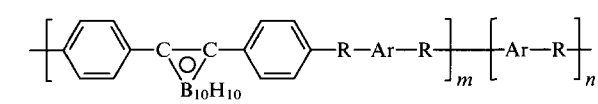
Scheme 9

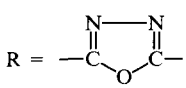




Thus the polymers obtained from the dihydrazides of the dicarbadodecaborane-containing dicarboxylic acids (Scheme 9) have lower reduced viscosities (0.10–0.70 dl g^{-1}) in a 3:1 (by weight) tetrachloroethane–phenol mixture than the products obtained in accordance with Scheme 8 (0.50–3.10 dl g^{-1}). The composition of the mixed poly-1,3,4-oxadiazoles based on 1,2-dicarbadodecaborane derivatives corresponds to the molar ratio of the starting materials only when one of them is the dihydrazide of 1,2-bis(4-carboxyphenyl)dicarbadodecaborane (Scheme 9). In the synthesis in accordance with Scheme 8, the corresponding polymers have a reduced content of the 1,2-bis-(4-carboxyphenyl)dicarbadodecaborane residues compared with the molar ratio of the starting materials. Presumably one of the causes of the formation of polymers with a lower molecular mass via Scheme 9 is the decrease in the reactivity of the NH_2 groups of the dihydrazides of the dicarbadodecaboranedicarboxylic acids caused by the presence in them of the dicarbadodecaborane nucleus and by its electron-accepting nature.

The high-temperature polycyclisation in polyphosphoric acid involves the homopolycondensation of the dicarboxylic acid dihydrazides with formation of poly-1,3,4-oxadiazoles. This process can take place simultaneously with the main one and can lead to the enrichment of the polymer in the aromatic dicarboxylic acid residues, incorporated in the polymer chain in the form of blocks of the corresponding homopoly-1,3,4-oxadiazoles.





The structure of the 1,7-bis(4-carboxyphenyl)dicarbadodecaborane derivatives, which are sterically more favourable, makes it possible to obtain from them mixed poly-1,3,4-oxadiazoles with a composition which is determined by the molar ratio of the starting materials (Scheme 8).[74]

The presence of dicarbadodecaborane groups, especially of the 1,2-dicarbadodecaborane group, in the polyoxadiazoles impart to the latter a high solubility in organic solvents. The softening temperatures of these polymers are in the range 260–350 °C depending on the chemical structure. The homopolyoxadiazoles based on the 1,2- and 1,7-bis(4-carboxyphenyl)-dicarbadodecaboranes and the mixed polyoxadiazole obtained from 1,7-bis(4-carboxyphenyl)dicarbadodecaborane and terephthalic acid have the highest softening temperatures (330–350 °C). Compared with the cardo-polyoxadiazoles based on bis(4-carboxyphenyl)phthalide (softening temperature 390 °C), the dicarbadodecaborane-containing homopolyoxadiazoles soften at a temperature lower by 40–50 °C, which is apparently associated with the fact that the 1,2- and 1,7-dicarbadodecaborane groups weaken the intermolecular interactions of the polymer chains to a greater extent than the phthalide groups.

Strong transparent films, which in a number of instances give rise to an appreciable elongation at break, were obtained from solutions of the polymers (for example, from solution in a tetrachloroethane–phenol mixture). For example, the tensile strength of the polyoxadiazole obtained from 1,7-bis-(4-carboxyphenyl)dicarbadodecaborane and isophthalic acid is 1140 kgf cm^{-2} and the relative elongation at break is ~200%.[74] The majority of the polymers obtained are amorphous or have an amorphous structure with signs of crystallinity. According to DTGA data, the mass of diphenyldicarbadodecaborane-containing polyoxadiazoles changes in air in the temperature range 380–440 °C. For the majority of the polyoxadiazoles with dicarbadodecaborane groups, an increase in mass is observed in air at a temperature of about 500 °C. On heating to 900 °C, the coke residue amounts to more than 90% in a number of instances [for example the coke residues produced by the polyoxadiazoles based on 1,2- and 1,7-bis(4-carboxyphenyl)dicarbadodecaboranes are 98% and 97% respectively].

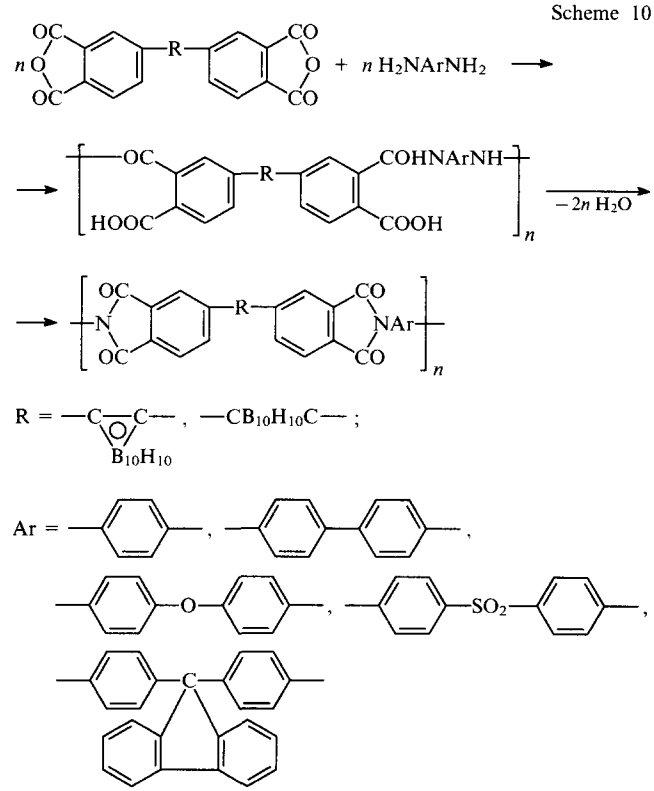
The study of the thermal degradation of polyoxadiazoles and the corresponding model systems led to the conclusion that at relatively low temperatures (300–400 °C) processes involving the hydrolytic decomposition of the oxadiazole ring becomes dominant whilst, with increase in temperature the role of the homolytic reactions is enhanced. The presence of 1,2- and 1,7-dicarbadodecaborane nuclei in the polyoxadiazoles hinders the occurrence of heterolytic decomposition reactions.[75]

5. Polyimides

The development of a method of synthesis of 1,2- and 1,7-bis(3,4-dicarboxyphenyl)dicarbadodecaboranes, presented in Scheme 3, led to the possibility of obtaining from these compounds and various aromatic diamines and of investigating polyimides with diphenyl-1,2- and diphenyl-1,7-dicarbadodecaborane fragments in the chain.[76–81]

Both two-stage and single-stage high-temperature polycondensations in solution have been used to synthesise dicarbadodecaborane-containing polyimides.[77] Scheme 10 presents the structures of the polyimides synthesised.

Scheme 10



In connection with the two-stage method of synthesis, a study was made of the influence on the formation of polyamidoacids in dimethylacetamide of various low-temperature polycondensation conditions: the concentrations of the reactants (0.3–0.7 M or 10 mass%–30 mass%), the basicity of the initial diamines, the reaction temperature (0–50 °C), and the reaction time (1.5–3.5 h).[77] Polyamidoacids with the maximum reduced viscosities (up to 1.84 dl g^{-1} in dimethylacetamide) were obtained in the case of the most basic diamine (benzidine); on passing from benzidine to bis(4-aminophenyl) ether and then to bis(4-aminophenyl) sulfone, the values of η_{red} diminish appreciably, which, incidentally, has been observed also for the usual polyamidoacids. In the experimental range, changes in reaction temperature and reaction time hardly affect the results of the synthesis. The

optimum conditions for the synthesis of 1,2- and 1,7-dicarbadodecaborane-containing polyamidoacids proved to be as follows: concentration 0.7 M for the 1,2-isomer and 0.3 M for the 1,7-isomer, temperature 20–25 °C, reaction time 1.5 h.

The single-stage polycyclisation method and the two-stage polycondensation method with thermal or chemical cyclisation in the second stage, known in connection with the preparation of the usual polyimides, have been used to synthesise polyimides with diphenyl-1,7-dicarbadodecaborane fragments in the chain. In the two-stage method of synthesis, higher-molecular-mass polyimides with diphenyl-1,7-dicarbadodecaborane fragments in the chain are obtained in the case of the chemical cyclisation. The reduced viscosities of the 0.5% solutions in dimethylacetamide are 1.24–1.70 dl g^{-1}; the molecular mass of the polyimide based on bis(4-aminophenyl) ether with η_{red}= 1.7 dl g^{-1}, determined by the light scattering method in dioxane, is 115 × 10^3.

It was observed that the 1,2-dicarbadodecaborane group in the dianhydride of 1,2-bis(3,4-dicarboxyphenyl)dicarbadodecaborane and in the macromolecules of the polyimides is unstable in relation to the action of aprotic dipolar solvents of the type of *N,N*-dimethylacetamide, *N,N*-dimethylformamide, and *N*-methylpyrrolidinone and also of the cyclising mixture in chemical cyclisation, being converted into derivatives of the dicarbaundecaborate anion. An increase in the pyridine content in the cyclising mixture shortens the cyclisation time, promoting simultaneously an increase in the yield of the dicarbaundecaborate derivative. In the case of the 1,2-bis(3,4-dicarboxyphenyl)-dicarbadodecaborane, the degradation of the dicarbadodecaborane nucleus was also observed in the single-stage method of synthesis, evidently under the influence of the initial diamine.[77] However, it was nevertheless found that polyimides with diphenyl-1,2-dicarbadodecaborane fragments can be synthesised successfully by single-stage polycondensation in a high-boiling solvent (nitrobenzene, *p*-chloronitrobenzene, *p*-nitrotoluene) at 170–190 °C in the presence of hydrogen chloride as the catalyst, provided that the basicity of the amino-group in the aromatic diamines is reduced by employing *N,N*-diacyl derivatives as the starting materials. Among the acyl derivatives of aromatic diamines with HCO, MeCO, PhCO, and CF_3CO groups, the first two are the most reactive.[78] This method makes it possible to avoid the degradation of the 1,2-dicarbadodecaborane nucleus during the synthesis and hence to achieve successfully the synthesis of polyimides with unaffected diphenyl-1,2-dicarbadodecaborane fragments in the chain. Polyimides with 1,2-dicarbadodecaborane groups can be synthesised also by the two-stage polycondensation with thermal cyclisation in the second stage.

Outwardly the dicarbadodecaborane-containing polyimides are powdered or fibrous yellow or greyish-white substances. According to X-ray diffraction data, these polymers are amorphous with the exception of polyimides based on bis(4-aminophenyl) sulfone, which show certain signs of crystallinity.

Polyimides with diphenyl-1,2- and diphenyl-1,7-dicarbadodecaborane fragments in the chain, which generally possess properties characteristic of aromatic polyimides (high heat resistance, satisfactory mechanical and electrical properties of films produced from them) are readily soluble in a wide range of solvents by virtue of the specific influence of the dicarbododecaborane groups. Among the dicarbadodecaborane-containing polyimides obtained, the highest solubility is shown by the polyimides based on bis(4-aminophenyl) ether and anilinefluorene, which are soluble even in dioxane and tetrahydrofuran. Strong films can be obtained by casting from a solution of these dicarbadodecaborane-containing polyimides. For example, the strength of the film obtained from the polyimide based on 1,7-bis-(3,4-dicarboxyphenyl)dodecaborane and bis(4-aminophenyl) ether by the two-stage method with chemical cyclisation of the polyamidoacid is 980 kgf cm^{-2} and their elongation at break is 88%.[77]

According to the results of thermomechanical tests, the dicarbadodecaborane-containing polyimides based on benzidine do not soften on heating. Among the remaining polyimides, polymers based on 1,7-bis(3,4-dicarboxyphenyl)dicarbadodecaborane with *p*-phenylenediamine and anilinefluorene exhibited the highest heat resistance, their softening temperatures being ~375 and ~380 °C respectively.

The characteristics of the molecular motion in dicarbadodecaborane-containing polyimides have been investigated by electron spectroscopic methods and it has been shown that the intramolecular relaxation process observed in the temperature range 160–180 °C is associated with the vibrations of the heterocyclic fragments adjoining the dicarbadodecaborane groups via the aromatic ring. It has been established that the rigidity of the chain increases on passing from 1,7- to 1,2-dicarbadodecaborane-containing polymers.[80]

The relative permitivities of 1,7- and 1,2-diphenyldicarbadodecaborane-containing polyimides are the same (3.8 at 23 °C and a frequency of 1 MHz) and hardly change in the temperature range from −170 to 270 °C. Numerically this value is close to the dielectric permitivity of polyimides not containing a dicarbadodecaborane fragment. The tangent of the dielectric loss angle at a frequency of 1 MHz is 1.4 × 10^{-3} at 23 °C for the 1,2-dicarbadodecaborane-containing polyimide based on bis-(4-aminophenyl) ether and 2.0 × 10^{-3} for the 1,7-dicarbododecaborane-containing polymer.[79]

According to DTGA data, dicarbadodecaborane-containing polyimides begin to undergo a change in mass in air and in an inert medium at higher temperatures than other polyheteroarylenes with diphenyldicarbadodecaborane fragments and their decomposition reaction is slower. In air, the mass of 1,2-dicarbadodecaborane-containing polyimides begin to change in the temperature range 430–450 °C and that of their analogues with 1,7-dicarbadodecaborane groups begins to change at 450–470 °C and the process takes place with some absorption of oxygen (~1%–9% relative to the initial mass). On heating under an inert atmosphere, the mass of dicarbadodecaborane-containing polyimides begins to change at 500–510 °C; it decreases by only 5%–7%, which is 8–10 times smaller than for the usual polyimides.[81] On heating to 900 °C, the coke residues from dicarbadodecaborane-containing polyimides are in most cases 92%–97% under an inert atmosphere.

On heating under isothermal conditions in air (4 h at 400 °C), the molecular mass of the polyimide based on 1,7-bis(3,4-dicarboxyphenyl)dicarbadodecaborane and *p*-phenylenediamine does not change. The polyimides containing dicarbaundecaborate anions in the chain begin to lose mass at low temperatures; the amounts of their coke residues at 900 °C are also fairly large (78%–95%).[77]

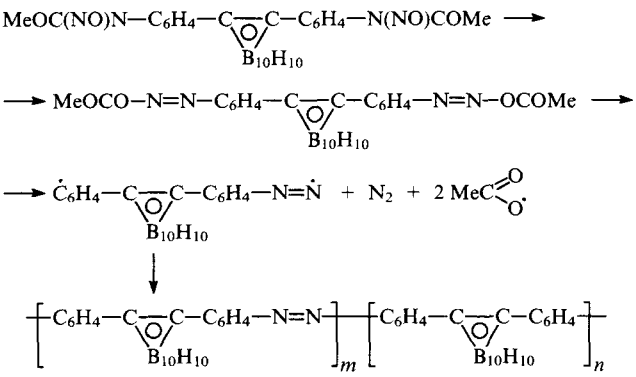
The pyrolysis at 1000 °C of the polyimides obtained from 1,2- and 1,7-bis(3,4-dicarboxyphenyl)dicarbadodecaboranes with bis-(4-aminophenyl) ether or anilinefluorene and, for comparison, also the polyimides based on the dianhydride of oxybis(benzenedicarboxylic)acid and bis(4-aminophenyl) ether under an argon atmosphere was investigated.[81] Analysis of the pyrolysis products demonstrated an appreciable difference between the dicarbadodecaborane-containing and the usual polyimides. This is manifested by an increased content of hydrogen, carbon monoxide, methane, and benzene in the pyrolysis products and by the absence of products such as aniline and benzonitrile characteristic of the pyrolysis of the usual polyimides. The formation of methane is a consequence of secondary reactions resulting from the increased content of hydrogen in the volatile pyrolysis products. It has been suggested that the absence of a very small amount of decomposition products containing nitrogen derived from the imide ring may be evidence for the binding of these products in the involatile residues, the yield of which is fairly high under the pyrolysis conditions. The products of the decomposition of the diphenyldicarbadodecaborane or diphenyl ether fragments apparently also remain in the carbonised matrix. These results suggested that the section of the polymer chain of the dicarbadodecaborane-containing polyimides most subject to homolytic decomposition is the diphenyldicarbadodecaborane

fragment with the adjacent imide ring, the primary products of the decomposition of which may in fact be hydrogen (from the dicarbadodecaborane nucleus), carbon monoxide, benzene, and also mono- and di-phenyldicarbadodecaboranes.[81]

6. Polyazophenylenedicarbadodecaborane

The synthesis and certain properties of polyazophenylene-1,2-dicarbadodecaborane have been described.[82,83] 1,2-Bis(*N*-nitrosoacetamidophenyl)-1,2-dicarbadodecaborane was used as the initial monomer. The recombination of the phenyl and azophenyl products of its decomposition actually leads to the formation of a dicarbadodecaborane-containing polyazophenylene (Scheme 11).

Scheme 11



The polyazophenylenedicarbadodecaborane was obtained in a suspension of cyclohexane in water in which the proportions of the two phases were 1:2. The monomer concentration was 7.5 g litre^{-1}, the temperature was 50 °C, and the reaction time was 4 h. The yield of the polymer was nearly quantitative. Outwardly, the polymer consisted of a pale-brown powder. It was readily soluble in chloroform, benzene, dimethylformamide, tetrahydrofuran, and, partially, in methanol and acetone. The molecular mass of its low-molecular-mass fraction (30%) was 820 and that of the higher-molecular-mass fraction (70%) was 1560. The presence of an EPR signal with an intensity of 3.3×10^{17} spins g^{-1} and the absorption in the long-wavelength part of the electronic spectrum indicated the presence of a conjugated bond system in this polymer.[82,83]

The polyazophenylenedicarbadodecaborane exhibits high thermal and thermooxidative stabilities. On isothermal heating in helium at 400 °C, a decrease in mass to 9% is observed initially, after which it hardly changes for 3 h. According to DTGA data (heating rate 4.5 K min^{-1}), the dicarbadodecaborane-containing polyazophenylene is stable up to 350 °C in air, after which an increase in the mass of the specimen is observed, amounting to approximately 30% at 600 °C. This apparently occurs owing to the addition of oxygen to the B–H bonds. The amount of the coke residue at 800 °C is ~90% of the initial mass.

It has been suggested that the ability of the dicarbododecaborane units of the polymer to combine with oxygen at high temperatures with formation of inactive products is of interest for the employment of such a polymer as a stabiliser[57] and for the inhibition of the thermooxidative degradation of thermally stable polymers.[82,83]

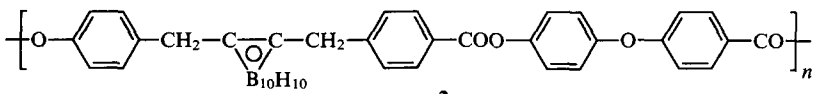
It has also been noted that 1,2-bis(*N*-nitrosoacetamidophenyl)-1,2-dicarbadodecaborane can be used for the synthesis of dicarbadodecaborane-containing copolymers by combining the processes involving the recombination of its decomposition products with those involving the radical polymerisation of various monomers.[82,83] For example, the copolymers of polyazo(hydroxyphenyl)dicarbadodecaborane with styrene, containing from 4 mass% to 38 mass% of polyazophenylenedicarbadodecaborane fragments, have been synthesised by emulsion copolymerisation. The introduction of polyazo(hydroxyphenyl)dicarbadodecaborane into polystyrene macromolecules significantly increases the thermal stability of the latter. Thus intense degradation of polystyrene begins at 300 °C, while that of the copolymer of styrene containing only 4% of polyazophenylenedicarbadodecaborane takes place at 350–360 °C.

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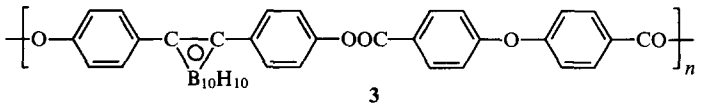
Summarising the foregoing, one should note that the development of new di- and tetra-functional aromatic derivatives of 1,2- and 1,7-dicarbadodecaboranes and the study of the characteristics of the formation of polymers from them have made it possible to obtain various new classes of linear heterochain polymers — polymers with diphenyldicarbadodecaborane fragments in the chain and a high molecular mass. These polymers possess a set of valuable properties and their thermal characteristics and in many cases also their solubilities are significantly superior to those of the usual organic analogues.[83] The introduction of dicarbadodecaborane groups into the polymer chain in the form of diphenyldicarbadodecaborane fragments increases significantly the heat resistance of such polymers compared with polymers based on bifunctional aliphatic derivatives of dicarbadodecaborane.

The study of the behaviour of linear polyheteroarylenedicarbadodecaboranes of the type of the polyarylates **2**–**5**, the polyamides **6** and **7**, and the polyimides **8** and **9** (see over) during the sorption process in the vapour of an effective solvent (THF) showed that structural changes take place in the amorphous polymers with formation of a thermodynamically improved structure.[85] It was found that the temperature for the onset of gel formation depends little on the isomerism of the dicarbadodecaborane nucleus and the framework surrounding it and depends more on the medium in which the heat treatment has been carried out. In air, the temperature for onset of gel formation is 15–20 °C lower than in vacuo. In the cardo-analogues (the polymers **10**–**12**), the gel fraction appears at temperatures higher by 50 °C. After the gel formation point (~280 °C) has been passed, the subsequent structure formation takes place much faster in the polymers with the 1,7-dicarbadodecaborane fragments in the chain, which may be due both to the greater segmental mobility of these polymers and to the smaller extent of the purely degradative reactions occurring simultaneously.

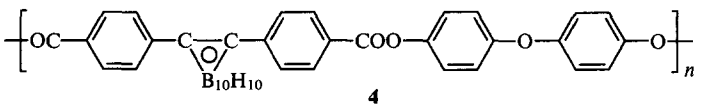
The significant difference between the behaviour of polyheteroarylenedicarbadodecaboranes and that of the usual organic analogues, both as regards the position of the initial gel formation point and the rate of accumulation of the gel fraction, suggested that intermolecular bonds are formed in the experimental temperature range (250–350 °C) mainly with participation of the dicarbadodecaborane groups. This is most characteristic of polymers with 1,7-dicarbadodecaborane fragments and has been confirmed by the fact that a nearly quantitative yield of the gel fraction is observed in these polymers at temperatures below that of the onset of gel formation in the polymers not containing dicarbadodecaborane groups.[85]



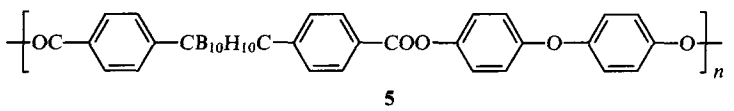
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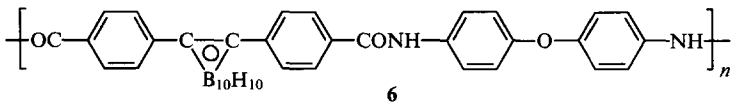
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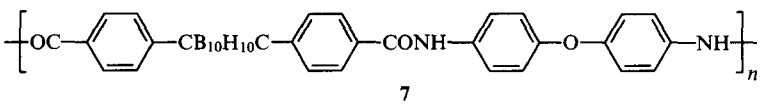
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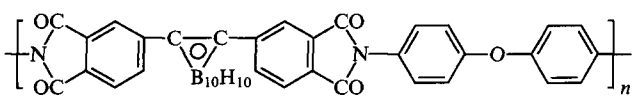
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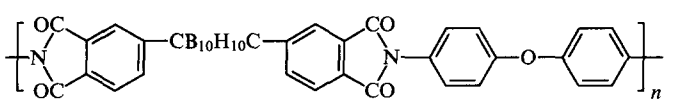
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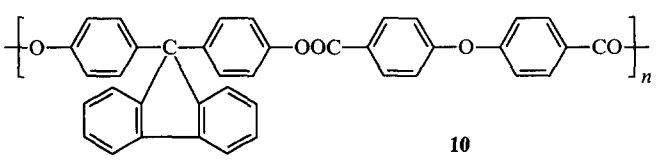
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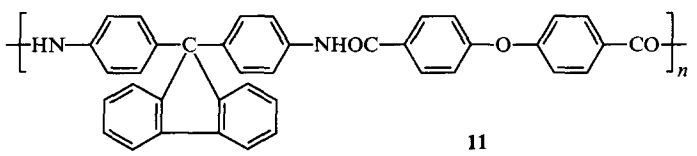
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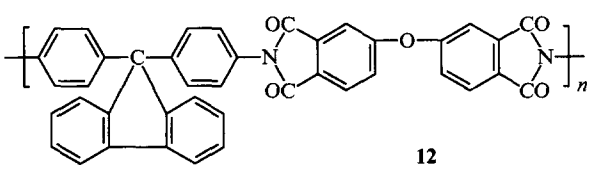
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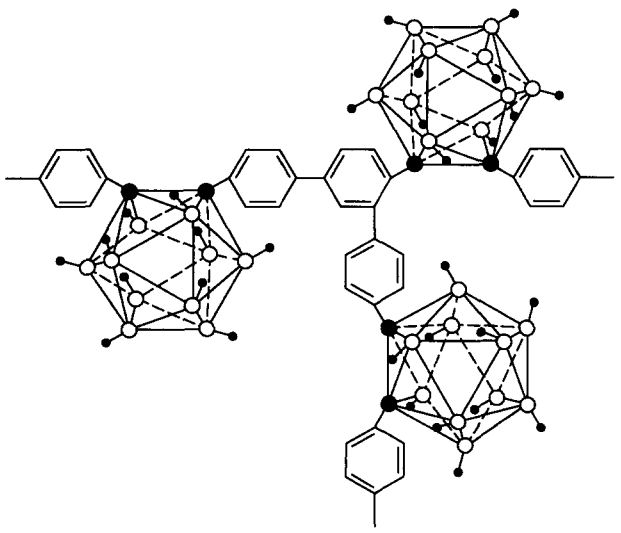
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IV. Phenylenedicarbadodecaborane-containing polymers of the thermoreactive type

The study of linear polyheteroarylenedicarbadodecaboranes of the type of polyarylates, polyamides, polyoxadiazoles, polyimides, etc. showed that the specific difference between these polymers and their usual organic analogues is their ability to form already in the temperature range 250–270 °C three-dimensional thermally stable polymers in which the inorganic networks are evidently combined with organic network molecules. It therefore appeared promising to employ this specific property of the aromatic derivatives of dicarbadodecaborane(12) in polymers of the thermoreactive type, containing reactive functional groups together with the dicarbadodecaborane groups. It might have been expected that, as a result of the introduction of dicarbadodecaborane groups into such systems, the properties of the thermoreactive and dicarbadodecaborane-containing polymers would be usefully mutually supplemented, in the first place in those applications, traditional for thermoreactive oligomers and polymers, where, together with the simplicity of processing, a high thermal stability and the formation of secondary coking products are required.

We shall now deal with phenylenedicarbadodecaborane-containing polymers of the polyphenylene, epoxide, phenolformaldehyde, and polycyanurate types.

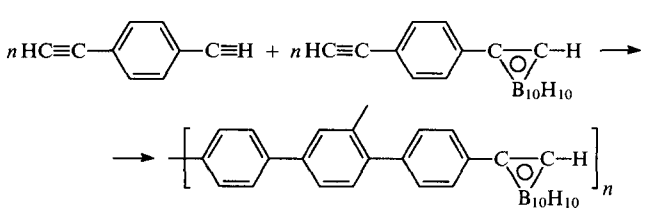
The 1,2-dicarbadodecaborane-containing oligophenylenes, obtained from diphenyl-1,2-dicarbadodecaborane, are presented below.



The polycondensation of diphenyl-1,2-dicarbadodecaborane was carried out in the presence of Lewis acids ($AlCl_3$, $MoCl_2$, etc.) and oxidising agents (MnO_2, $CuCl_2$, etc.) at 120–220 °C.[86,87] The oligomers have a molecular mass of 1300 and a softening temperature of about 300 °C. They do not melt up to 350 °C and are readily soluble in organic solvents (chloroform, benzene, acetone, etc.) According to DTGA data, the decrease in their mass in air is 1.6% at 600 °C and 11.6% at 900 °C.

The preparation of polydicarbadodecaboranephenylenes by the reaction of 1,7-$Cu_2C_2B_{10}H_{10}$ with *m*-$C_6H_4I_2$ in 1:1 molar proportions has been mentioned.[63] Together with the formation of a polymeric product, there is a possibility in this instance of the formation of macrocyclic systems in which the 1,7-dicarbadodecaborane fragments are linked to 1,3-disubstituted phenylene rings. When *m*-$C_6H_4I_2$ is replaced by 1,3- or 2,6-disubstituted pyridines, macrocyclic systems in which the 1,7-dicarbadodecaborane fragments are linked to pyridine rings are formed together with the polymeric product.

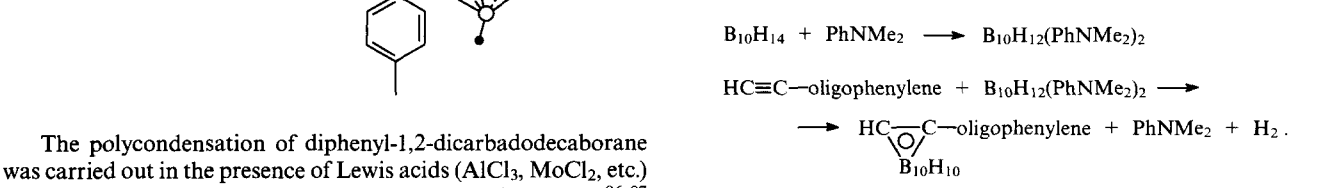
The synthesis of *p*-[1-(1,7-dicarbadodecaboranyl)]phenylethyne has been achieved by the reaction of diethynylbenzene with decaborane in the presence of dimethylaniline in toluene.[88] Dicarbadodecaborane-containing polyphenylenes were obtained by the joint polycyclotrimerisation of this dicarbadodecaborane-containing ethyne with diethynylbenzene (taken in equal proportions) in the presence of the $NiCl_2.2PPh_3.2NaBH_4$ system.



For an equimolecular ratio of the starting materials, fully soluble copolymers containing 18.7% of boron are formed in 75% yield. According to DTGA data, under a helium atmosphere their mass diminishes at 900 °C only to the extent of 6%, whereas the decrease in the mass of the homopolyphenylene obtained from diethynylbenzene is 15%. These boron-containing polyphenylenes are extremely heat-resistant: they undergo only slight deformations up to the temperatures of their thermal decomposition (above 600 °C).

In order to regulate the content of the dicarbadodecaborane groups in the copolymers, the joint polycyclotrimerisation of 1,2-dicarbadodecaboranylphenylethyne (CPE) with diethynylbenzene (DEB) and phenylethyne (PE) was also carried out. For the molar proportions of the starting materials CPE : DEB : PE = 0.5 : 1 : 1, copolymers containing 11% of boron were obtained in 73% yield. Up to 27% of an insoluble polymer was formed under these conditions as a result of partial structure formation. It was noted that the mixed dicarbadodecaborane-containing polyphenylenes exhibit an enhanced thermooxidative stability. Thus the mass of the triple copolymer initially increases somewhat (up to 4%) at 350 °C, after which it remains virtually unchanged for 5 h; the mass lost by the polymer after 5 h at 550 °C exceeds only slightly 40%.[88]

It has been shown that the oligophenylenedicarbadodecaboranes of the type considered could be used as the starting materials for the synthesis of π-arenetricarbonyl complexes of transition metals.[89] The introduction of 1,2-dicarbadodecaborane groups into an oligophenylene has also been achieved as a result of the chemical modification of the oligophenylene, containing triple bonds, by decaborane in accordance with the following scheme:[90]

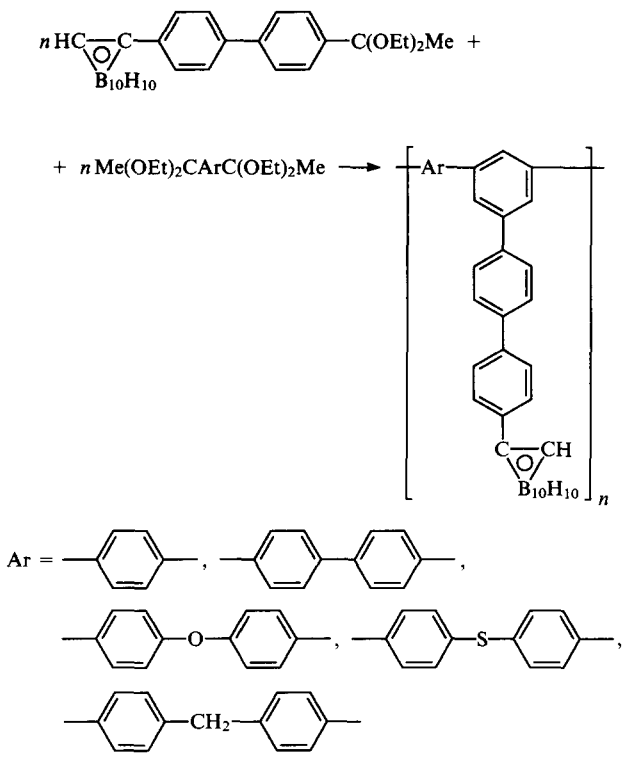


The oligophenylenedicarbadodecaborane is an amorphous pale-brown powder readily soluble in the usual organic solvents. Analysis of the polymer obtained permitted the conclusion that, under the selected chemical modification conditions, the replacement of the ethynyl groups of the oligophenylene by dicarbadodecaborane groups is almost quantitative. The absence from such an oligophenylenedicarbadodecaborane of residual ethynyl groups renders the latter (in contrast to oligophenylene) incapable of passing to an infusible and insoluble state during heating to 300 °C.

A higher thermal stability (both under an inert atmosphere and in air) is characteristic of the oligophenylenedicarbadodecaboranes than of the initial oligophenylene. According to DTGA data, the yield of the coke residue for the oligophenylenedicarbadodecaborane is 84.5% at 900 °C under a helium atmosphere, whereas for the usual oligophenylene it is 68%.

Polyphenylenes with phenyldicarbadodecaborane fragments in the chain can be obtained also by means of the trimerisation polycondensation of aromatic mono- and di-acetyl compounds in which one of the monomers is a dicarbadodecaborane-containing aromatic acetyl derivative.[91–97] In particular, when the 4′-(1,1-diethoxyethyl)biphenylyl-1,2-dicarbadodecaborane was used as the monomer, a prepolymer of the polyphenylene type was obtained.[91,92]

Different versions of the synthesis of the prepolymer were employed: at 0 and 20 °C in solution in benzene through which dry hydrogen chloride was passed; at −20 °C in solution in *o*-dichlorobenzene with dry HCl; at 100 and 150 °C in solution in *o*-dichlorobenzene or ditolylmethane in the presence of 10% toluene-*p*-sulfonic acid as the catalyst.[91,92] The final polymers were obtained by heat treatment at 450 °C.[92]



Dicarbadodecaborane-containing polyphenylenes have also been synthesised from bis(4-acetylbenzyl)- and 4-acetylbenzyldicarbadodecaboranes in which the phenylene group was separated from the dicarbadodecaborane nucleus by a methylene group.[94-96] It is noteworthy that the fraction of the enone side groups [...-R-CO-CH = C(Me)-R-...] and polyvinylene fragments in the oligomer increases (compared with their contents in the prepolymers without dicarbadodecaborane nuclei) in the polycondensation of acetyldicarbadodecaboranes or their ethyl ketals, i.e. heterounit polymers are formed in the polycyclocondensation process.[92,93]

Oligophenylenes containing diphenyl-1,2-dicarbadodecaborane groups were found to be less soluble than the prepolymers based on bis(acetylbenzyl)dicarbadodecaboranes: they dissolved fully only in the reaction solution, chloroform, and *o*-dichlorobenzene and did not dissolve in benzene, toluene and dioxane,[92] whereas the dicarbadodecaborane-containing oligophenylenes based on bis(acetylbenzyl)dicarbadodecaborane derivatives dissolve readily in toluene, cyclohexanone, dioxane, acetone, benzene, etc.[93]

The heat-treated dicarbadodecaborane-containing polyphenylene exhibits a high thermal stability. According to DTGA data, the mass of the polymers obtained from bis(acetylbenzyl)-dicarbadodecaboranes increases by 18% at 400 °C as a consequence of the oxidation of the dicarbadodecaborane groups at the B-H bonds; the decrease in mass at 800 °C in air is 17%. Under the conditions of isothermal heating at 700 °C for 7-8 h, the mass of the polymers hardly changes.[93]

It has been noted that[92] the thermal stability of the polymers based on the ethyl ketal of acetylbiphenylyl-1,2-dicarbadodecaborane is higher than that of the analogous polymers based on the ethyl ketal of acetylbenzyl-1,2-dicarbadodecaborane with the same or higher boron content in the latter and for approximately the same intrinsic viscosities of the initial prepolymers. Thermomechanical tests on polymers with biphenylyl-1,2-dicarbadodecaborane groups in the macromolecules on a plastometer showed that they are not deformed up to 280 °C and for loads up to 200 kgf cm^{-2}.[92]

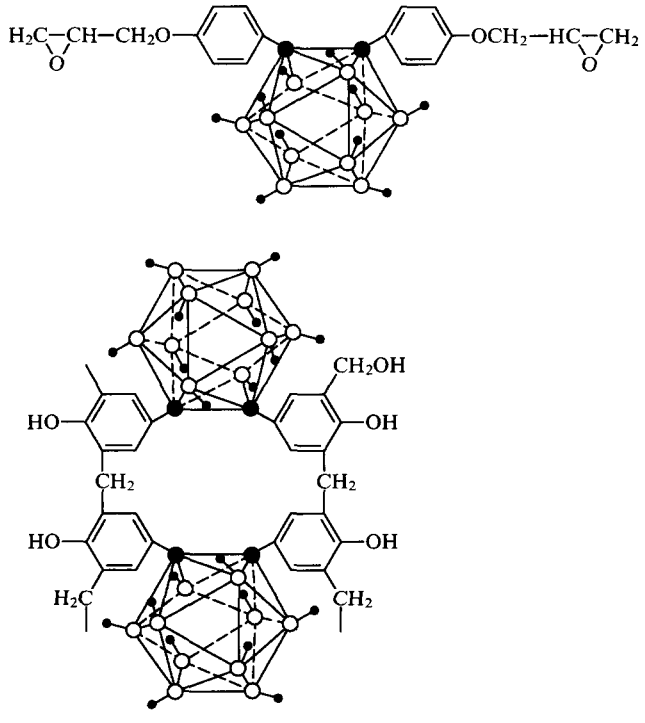
Epoxides and phenolformaldehyde oligomers based on 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane have been developed.

Not only the individual 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane but also mixtures of boroxyphenylenedicarbadodecaboranes [usually mono-, di-, and trisubstituted 1,2-bis-(4-hydroxyphenyl)dicarbadodecaboranes without their separation into the individual substances], obtained by the hydrolysis of (*B*-1,7-dicarbadodecaboranyl)phenyl borates and (*B*-1,7-dicarbadodecaboranyl)phenyl silicates, synthesised by the high-temperature condensation of 1,2-dicarbadodecaborane with the phenylesters of orthosilicic and orthoboric acids, may be used successfully for the synthesis of epoxide and phenol-formaldehyde phenylenedicarbadodecaborane-containing oligomers and polymer systems based on them.[98-100]

The synthesis and properties of the thermoreactive epoxyphenylenedicarbadodecaborane and 1,2-bis(4-hydroxyphenyl)-dicarbadodecaborane formaldehyde oligomers have been examined.[19,21,98-111]

Epoxide oligomers based on 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane have been synthesised by a two-stage method.[101] The reaction of the 1,2-bis(4-hydroxyphenyl)-dicarbadodecaborane with epichlorohydrin was initially carried out in the presence of catalytic amounts of a tertiary amine at 50-90 °C for 6-12 h. The dichlorohydrin formed was isolated and treated in a dry inert solvent (chlorinated hydrocarbons, etc.) with solid alkali in stoichiometric proportions at a temperature not exceeding 40-50 °C. Depending on the selected 1,2-bis-(4-hydroxyphenyl)dicarbadodecaborane : epichlorohydrin molar ratio selected, oligomeric products with different molecular masses or the diglycidyl ether of 1,2-bis(4-hydroxyphenyl)-dicarbadodecaborane (see compound **13**) were obtained. For a 1 : 5 component ratio, a compound with the composition closest to that of the diglycidyl ether is formed; its melting point is 130-135 °C. The 1,2-dicarbadodecaborane-containing epoxide oligomers are readily soluble in ethanol, acetone, chloroform, tetrahydrofuran, benzene, etc.

An epoxyphenyldicarbadodecaborane oligomer with a molecular mass of 400 and a softening temperature of 30 °C was synthesised in one stage from a mixture of mono-, di-, and trihydroxyphenylenedicarbadodecaboranes[98,99] in epichlorohydrin in the presence of a 40% aqueous solution of sodium hydroxide [with boroxyphenylenedicarbadodecaboranes : epichlorohydrin : alkali molar ratios of 1 : 10 : (2-4)] at 60 °C for 2-3 h.



13

The epoxyphenylenedicarbadodecaborane oligomers obtained are hardened with the aid of familiar hardening agents (acid anhydrides, amines).[99,101] The study of the hardening of oligoepoxyphenylenedicarbadodecaborane in the presence of 30 mass% of an anilinoformaldehyde oligomer (specimen 1) or 15 mass% of a polyethyleneamine (specimen 2) showed that the oligopeptide is structured most vigorously in the latter case.[97] Heating of a composition comprising the oligoepoxide and the polyethyleneamine for 1 h at 100 and 125 °C leads to ~97% hardening. The structure formation process takes place more slowly for the composition comprising the oligoepoxide and the anilinoformaldehyde oligomer. The degree of hardening of this composition in the temperature range 100–200 °C increases continously, attaining approximately 91% after heating for 8 h. According to DTGA data, in air (at a heating rate of 5 K min^{-1}) both oligoepoxide specimens, hardened at 200 °C, begin to lose mass in the temperature range 250–300 °C, the rate of degradation of specimen 1 being somewhat higher than that of specimen 2: at 350 and 600 °C, the mass of specimen 1 diminishes by 24% and 37%, while that of specimen 2 diminishes by 8% and 21% respectively. However, the overall decrease in the mass of both specimens is the same at 900 °C and amounts to 35%. On the other hand, the usual (not containing dicarbadodecaborane groups) epoxyoligomer, hardened by the anilinoformaldehyde oligomer, is fully combusted at 600 °C.[97]

Homogeneous and mixed phenolformaldehyde polymers with diphenylenedicarbadodecaborane fragments in the chain have been synthesised by the reaction of formaldehyde with 1,2-bis-(4-hydroxyphenyl)dicarbadodecaborane or with a mixture of the latter and phenol using different ratios of the starting materials.[21,100,101,104,109] The study of the polycondensation of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane with formaldehyde (the reaction was carried out in isopropyl alcohol at 93–94 °C in the presence of NaOH using an aqueous formaldehyde solution) and of the structure of the product showed that, according to IR spectroscopic data, dicarbaundecaborate derivatives are not formed in this process.[103] It has been noted that, depending on the nature of the catalyst, the process conditions, and the ratio of the initial components, oligomers of both the resol and novolac type may be obtained.[111] Oligomers of the resol type are formed in the presence of basic catalysts [for example, NaOH, NH_4OH, and $Ba(OH)_2$] whereas oligomers of the novolac type are formed in the presence of acid catalysts (for example, hydrochloric acid and toluene-*p*-sulfonic acid) for 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane : formaldehyde at molar ratios ranging from 1 : 0.8 to 1 : 4.

The synthesis of mixed resols based on 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and phenols taken in proportions ranging from 1 : 3 to 1 : 21 for a 1.5 : 1 molar ratio if the formaldehyde and phenolic components has been described.[107] The polycondensation was carried out without a solvent in the presence of a 25% aqueous solution of ammonia (0.3 mol per mole of phenols) at 90 °C for 3 h. With decrease in the content of the dicarbadodecaborane-containing groups in the oligomer, the softening temperature of the latter fell from 110 to 60 °C, while its molecular mass increased from 650 to 890. In contrast to the resol obtained solely from the 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane, the mixed dicarbadodecaborane-containing resols exhibit an increased fluidity. These oligomers are hardened under the conditions usual for phenolformaldehyde resols, forming resites containing only 2%–4% of the acetone-soluble fraction.

The study of the chemical transformations on heating dicarbadodecaborane-containing resols and the corresponding resites showed that, in the temperature range from 50 to 200 °C, structure formation in the dicarbadodecaborane-containing oligomer takes place via the mechanism usual for resols. At temperatures of 200–300 °C and above, the dicarbadodecaborane groups of the resites undergo appreciable chemical transformations, the extent of which depends significantly on the heating conditions (air, vacuum).[104] It has been suggested that the chemical transformations involving the dicarbadodecaborane groups of the resites are in fact responsible for their enhanced thermal stability and the high yields of the coke residue compared with the known polymers.

The greatest differences between the stabilities of the usual phenolformaldehyde and dicarbadodecaborane-containing resites are observed in thermooxidative degradation. According to DTGA data, in air the mass of the dicarbadodecaborane-containing resite begins to increase at 350 °C and above (at 900 °C the increase is 4%), whereas the usual hardened resol decomposes fully under these conditions.[104]

The mixed dicarbadodecaborane-containing resites based on 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and phenol also exhibit an increased thermal stability, the decrease in their mass on heating in air depending in a definite manner on the content of the dicarbadodecaborane groups. However, the introduction of even small amounts of dicarbadodecaborane groups into the copolymer decreases significantly the mass loss. Thus the decrease in the mass of the hardened cooligomer obtained for the 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane : phenol = 1 : 21 molar ratio is 45% at 900 °C.[106]

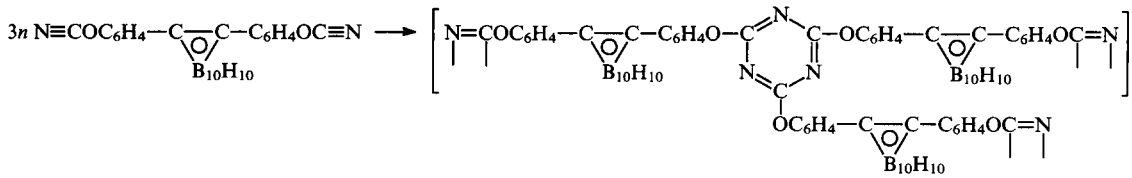
A number of studies have been devoted to the elucidation of the nature of the high thermal stability of the dicarbadodecaborane-containing resites.[105,107–110] Analysis of the structural transformations in the dicarbadodecaborane-containing resites over a wide temperature range (200–2500 °C), resorting to X-ray diffraction and various spectroscopic research methods, suggested that the oxidation of the B–H groups of the dicarbadodecaborane fragments and other processes involving their consumption, which is accompanied by the evolution of an appreciable amount of hydrogen, is most characteristic of the 1,2-bis(4-hydroxyphenyl)dicarbadodecaboraneformaldehyde resites in the temperature range 300–450 °C. This leads to an increase in the density of the network in the resites as a result of the formation of the energetically strong B–B, B–O–B, and B–C bonds.

By virtue of the presence of such a thermally stable macronetwork system, the radical species produced (large molecular formations or low-molecular-mass degradation products) are unable to emerge from the 'cage' and undergo secondary recombination processes. Nor can one rule out the possibility that the hydrogen split off from the B–H groups may interact with the radical species, inhibiting further polymer decomposition processes.[108]

The high thermal stability of the 1,2-bis(4-hydroxyphenyl)-dicarbadodecaboraneformaldehyde and epoxyphenylenedicarbadodecaborane polymers has also been used to enhance the thermal characteristics of the hardened polymer compositions based on the usual polymers of this type.[98,112] Thus the hardened compositions comprising phenolphthaleinformaldehyde and 1,2-bis(4-hydroxyphenyl)dicarbadodecaboraneformaldehyde (based on boroxyphenylene-1,7-dicarbadodecaboranes) resols are destructured to a lesser extent than the phenolphthaleinformaldehyde resite. According to DTGA data, the decrease in the mass of a hardened specimen (obtained for a 1 : 1 mass ratio of the resols) in air at 900 °C is 40%, whereas the phenolphthaleinformaldehyde resite decomposes almost completely at the same temperature. In the presence of 50 mass% of the epoxyphenylenedicarbadodecaborane oligomer, the yield of the coke residue is 60% greater than in the case of the unmodified phenolphthaleinformaldehyde resite.[98]

Modification of an epoxide oligomer [based on 1,1,3-tris-(hydroxyphenyl)propane and epichlorohydrin] by a dicarbadodecaborane-containing phenolformaldehyde oligomer [based on 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane and formaldehyde] makes it possible to increase the thermal stability and the coke number of the hardened epoxyphenolformaldehyde polymer.[112] Thus, whereas for the hardened polymer obtained for the epoxide : dicarbadodecaborane-containing resol = 3.3 : 1 mass

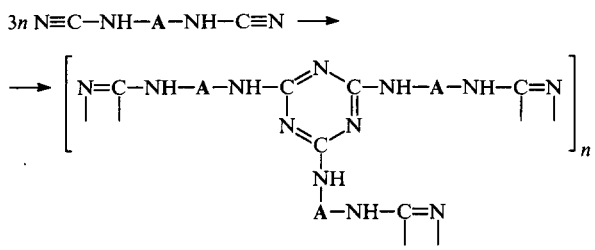
Scheme 12



ratio, the temperature of the onset of decomposition in air is about 260 °C, the yield of the coke residue on heating to 600 °C is 60%, and the decrease in mass on heating in vacuo at 350 °C for 3 h is 15%, for the corresponding hardened epoxyphenolformaldehyde polymer based on the same oligoepoxide and an anilinephenolformaldehyde oligomer the temperature of the onset of decomposition in air is about 200 °C, the yield of the coke residue on heating to 600 °C is 20%, and the decrease in mass on heating in vacuo at 350 °C for 3 h is 45%.

We shall consider yet another type of polymer with diphenyldicarbadodecaborane fragments in the chain. The diphenyldicarbadodecaborane fragments were introduced into the macromolecules by means of the thermal polycyclotrimerisation of the dicyano-esters of 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane (Scheme 12).[113] Such dicarbadodecaborane-containing polymers with *s*-triazine rings in the macromolecule are obtained with a high degree of conversion (98%) of the functional groups, i.e. in the final stage of the process these polymers are regularly cross-linked dense-network systems. The temperature of the onset of the deformation of such a polymer is 375 °C when a load of 0.8 kgf cm^{-2} is applied to the specimen; according to DTGA data, the temperature of the onset of decomposition in air is 385 °C; the polymer has an amorphous structure.

Dicarbadodecaborane-containing cross-linked thermally stable and heat-resistant polymers containing melamine structures in the main chain have been synthesised by the polycyclotrimerisation of diphenyl-1,7-dicarbadodecaborane-containing biscyanamides or their mixtures with aromatic mono- and bis-cyanamides.[113,114]



A = C_6H_4—$CB_{10}H_{10}C$—C_6H_4

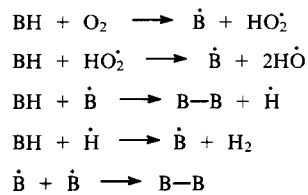
The temperature of the deformation of the polymelamine based on 4,4′-bis(4-cyanamidophenyl)dicarbadodecaborane is 490 °C; the temperature of the onset of the decrease in mass in air is 370 °C. According to X-ray diffraction data, the polymer has an amorphous structure with signs of crystallinity.

V. The mechanism of the thermal transformations of polyarylenedicarbadodecaboranes and the radical arylation of dicarbadodecaborane(12)

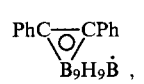
The study of the linear polyheteroarylenedicarbadodecaboranes showed (see Section III) that the formation under comparatively mild conditions (250–300 °C) of three-dimensional networks as a result of reactions involving the dicarbadodecaborane groups is most characteristic of these polymers. In the presence of oxygen, the formation of new bonds in the dicarbadodecaborane-containing polymers occurs more vigorously under these conditions compared with an inert medium or a vacuum. There is no doubt that the elucidation of the nature and mechanism of the formation of new thermally stable bonds with participation of the dicarbadodecaborane groups is of fundamental importance for the explanation of the behaviour of polyarylenedicarbadodecaboranes at elevated temperatures and of the formation of thermostable secondary products. Taking this into account, a study of the thermal transformations of 1,2-diphenyl-1,2-dicarbadodecaborane was undertaken.[115]

It was established that, when diphenyl-1,2-dicarbadodecaborane is heated in air in the temperature range 260–300 °C, the product of the reaction occurring with evolution of hydrogen contains, together with the initial compound, a substance which is a diphenyl-1,2-dicarbadodecaborane dimer according to gel-permeation chromatographic, ebullioscopic and mass-spectrometric data. Detailed analysis of this compound by various spectroscopic methods suggested that under these conditions the diphenyldicarbadodecaborane fragments in the dimer are linked by a single B–B bond, the formation of which most probably involves the boron atoms in the 9- or 12-position which are most remote from the carbon atoms in the dicarba-*closo*-dodecaborane(12) icosahedron.

The study of the conditions under which this reaction is carried out showed that, in the presence of phenols (familiar inhibitors of free-radical reactions), the yield of the dimer falls sharply, whereas heating of 1,2-diphenyl-1,2-dicarbadodecaborane in the presence of *tert*-butyl peroxide—a source of free radicals—is accompanied by the formation of the dimer under much milder conditions. The results suggested that the reaction constituting the basis of the dimerisation of 1,2-diphenyl-1,2-dicarbadodecaborane is of a radical type and, when the dicarbadodecaborane is heated in air, the reaction is initiated by oxygen.



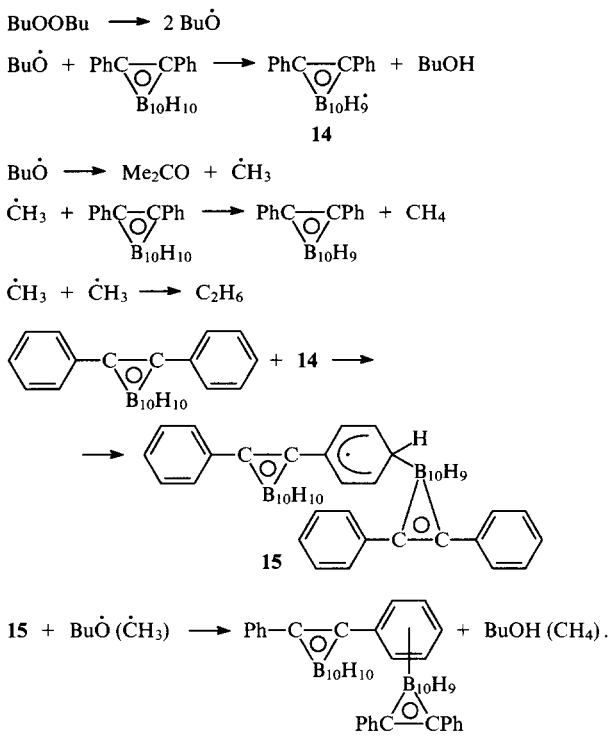
It is noteworthy that the dimer is also formed on heating in vacuo, but this requires much more severe conditions (500 °C and above). Evidently during the high-temperature heat treatment, homolytic dissociation of the B–H bond of the dicarbadodecaborane nucleus takes place with formation of the radicals



the recombination of which leads to the dimer. Such severe conditions, necessary for the formation of the dimer in vacuo, indicate that oxygen is an initiator of both the formation of the diphenyl-1,2-dicarbadodecaborane dimer and evidently of the structure formation in the dicarbadodecaborane-containing polymers.

The study of the thermal decomposition of *tert*-butyl peroxide in 1,2-diphenyl-1,2-dicarbadodecaborane at 150 °C for 5 h showed that it results in the formation of *tert*-butyl alcohol, acetone, methane, ethane, and small amounts of hydrogen together with polymeric dicarbadodecaborane-containing products with the maximum degree of polarisation (n = 10)

determined from gel-permeation chromatographic data.[116] The yield of the polymeric products is directly proportional to the amount of decomposed peroxide and amounts to 58%–70% of theoretical. The calculated yield of the products of the polymerisation of 1,2-diphenyl-1,2-dicarbadodecaborane and the total amount of the butyl alcohol and methane obtained are similar. The study of the structure of the dicarbadodecaborane-containing products by ^{13}C and ^{11}B NMR spectroscopy permitted the conclusion that dimers and oligomers (via a boron–carbon bond) are formed under these conditions. They are mixtures of isomers in terms of the boron atoms of 1,2-diphenyl-1,2-dicarbadodecaborane and the position in the aromatic ring. The reactions occurring in the thermolysis of *tert*-butyl peroxide can be represented schematically as follows:

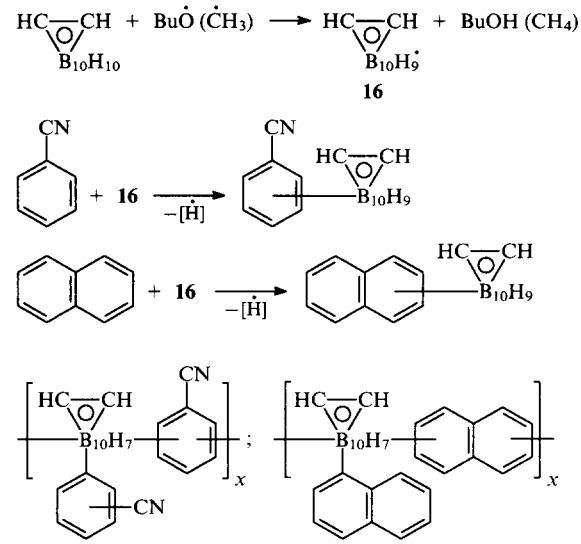


The virtually total absence of molecular hydrogen from the reaction products, the agreement between the total molar amounts of methane and butyl alcohol and the total number of B–C bonds in the products of the oligomerisation of 1,2-diphenyl-1,2-dicarbadodecaborane, and the formation of a B–C bond suggested that the mechanism of the radical reaction of 1,2-diphenyl-1,2-dicarbadodecaborane involves bimolecular aromatic homolytic substitution via the formation of an intermediate radical σ-complex between the 1,2-dicarbadodecaboranyl radical and the aromatic compound.

The boron-centred dicarbadodecaboranyl radicals were obtained as a result of the abstraction of the hydrogen atom from the B–H groups in 1,2-, 1,7-, and 1,12-dicarbadodecaboranes by the *tert*-butoxyl radicals. They were detected by the EPR method in the form of spin-adducts with 2,4,6-tri-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one.[117]

In order to confirm this mechanism of the dimerisation and oligomerisation of 1,2-diphenyl-1,2-dicarbadodecaborane in the presence of a free radical source, a study was made of the interaction of 1,2- and 1,7-dicarbadodecaboranes with aromatic compounds such as benzonitrile and naphthalene in the presence of *tert*-butyl peroxide at 200 °C.[118] It was established that the reactions occur in this case in accordance with the following scheme:





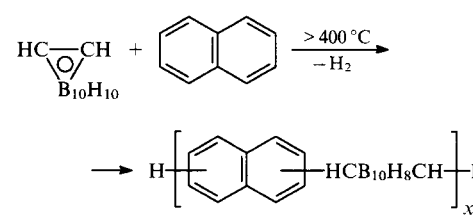
x = 5–10

Under conditions where the intermediates are not removed, only oligomeric products with x = 5–10 are formed. The products of the recombination of the dicarbadodecaboranyl radicals and the aromatic compounds were not detected.

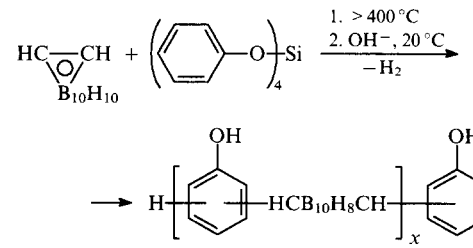
Since the products of the homolysis of the bonds at elevated temperatures can also serve as sources of free radicals, the dicarbadodecaboranes(12) were heated at 350–490 °C in the presence of aromatic compounds (naphthalene)[119] and also in the gas phase at 630–750 °C.[120] It was indeed established that under these conditions the dicarbadodecaboranes(12) undergo thermal radical condensation with the aromatic compounds in both condensed and gas phases with evolution of hydrogen.

In the condensed phase for degrees of conversion of 85%–95% [with respect to the dicarbadodecaborane(12)], oligomers soluble in aromatic hydrocarbons, ketones, and other solvents are formed (Scheme 13).

Scheme 13



x = 8–10



x = 2–3

The thermal condensation in the gas phase (at 630–750 °C) was investigated in relation to the interaction of 1,7-dicarbadodecaborane with benzene.[120] It was found that the products of this condensation for low degrees of conversion of 1,7-dicarbadodecaborane (up to 33%) are isomeric boron-substituted phenyl-1,7-dicarbadodecaboranes, namely 2-, 4-, 5-, and 9-phenyl-1,7-dicarbadodecaboranes, 2-phenyl-1,12-dicarbadodecaborane, and biphenyl. For high degrees of conversion, attained by

reintroducing the reaction solution into the reactor, the appearance of unidentified products with a higher molecular mass, tentatively disubstituted 1,7-dicarbadodecaboranes, was observed. An increase in the reaction temperature led to an increase in the yield of biphenyl, which is apparently due to the higher activation energy for this side reaction compared with the activation energy for the thermal condensation of 1,7-dicarbadodecaborane and benzene. The latter evidently proceeds, as in the condensed phase, via a stage involving the formation of an intermediate boron-centred radical. The products of the thermal condensation in the gas phase are similar to those of the condensation in the condensed phase and constitute a mixture of all possible isomers of 1,7-dicarbadodecaborane, their content in the mixture corresponding to the number of equivalent boron atoms in the 1,7-dicarbadodecaborane molecule and being almost independent of the temperature in the experimental temperature range. The carbon atoms of 1,7-dicarbadodecaborane do not participate in this reaction.[120]

The study of the kinetics of this process was undertaken in relation to the interaction of 1,7-dicarbadodecaborane with naphthalene at 350–490 °C.[119] The reaction was carried out in glass bulbs in the gas phase. The concentrations of the initial reactants were measured with the aid of gas–liquid chromatography.

The partial reaction orders with respect to each component were calculated from the equation

$$\ln W_0 = \ln k + n \ln[HCB_{10}H_{10}CH]_0 + m \ln[C_{10}H_8]_0 \ ,$$

where W_0 is the initial rate of consumption of 1,7-dicarbadodecaborane (mol litre^{-1} s^{-1}), k the reaction rate constant, n the reaction order with respect to 1,7-dicarbadodecaborane, m the reaction order with respect to naphthalene, $[HCB_{10}H_{10}CH]_0$ the initial molar concentration of 1,7-dicarbadodecaborane, and $[C_{10}H_8]_0$ the initial molar concentration of naphthalene. It was found that the reaction orders with respect to 1,7-dicarbadodecaborane and naphthalene are close to unity. The effective activation energy for the reaction in the temperature range 440–490 °C is 221 ± 6 kJ mol^{-1}, which is significantly less than the C–H bond stength in naphthalene, the latter amounting to ~419 kJ mol^{-1}.[119]

It was established that the rate of the reaction between 1,7-dicarbadodecaborane and naphthalene is described by the following equation for degrees of conversion between 0% and 30% and at temperatures in the range 440–490 °C:

$$-\frac{d[C_{10}H_8]}{d\tau} = \frac{d[HCB_{10}H_{10}CH]}{d\tau} = k[HCB_{10}H_{10}CH]_0^{0.95\pm0.04}[C_{10}H_8]_0^{1.01\pm0.03} \ ,$$

where

$$k = 6.3 \times 10^{11.0\pm1.0} \exp\left(-\frac{221 \pm 6}{RT}\right) \Big/ \text{litre mol}^{-1}\ \text{s}^{-1}.$$

Hence it was concluded that the interaction of the dicarbadodecaborane(12) with aromatic compounds at high temperatures is described by the following scheme:

$$ArH \xrightarrow{k_0} Ar^{\cdot}$$

$$Ar^{\cdot} + BH \xrightarrow{k_1} ArH + \dot{B}$$

$$\dot{B} + ArH \underset{k_3}{\overset{k_2}{\rightleftharpoons}} ArH\dot{B}$$

$$ArH\dot{B} + BH \xrightarrow{k_4} ArH_2B + \dot{B}$$

$$ArH_2B \xrightarrow{k_5} ArB + H_2$$

$$ArH\dot{B} + \dot{B} \xrightarrow{k_6} ArB + BH$$

where ArH is the aromatic compound and BH is the dicarbadodecaborane(12).

In principle, this scheme is analogous to the mechanism of the reaction involving chain radical addition to alkenes known as the Kharasch reaction.[119] In conformity with this scheme, the rate of reaction of the dicarbadodecaborane(12) is then equal to the rate of reaction of the aromatic compound:

$$-\frac{d[BH]}{d\tau} = -\frac{d[ArH]}{d\tau} = k_4[ArHB^{\cdot}][BH] \ ,$$

and subject to the conditions $k_3 \gg k_4[BH]$, we obtain

$$-\frac{d[BH]}{d\tau} = -\frac{d[ArH]}{d\tau} = k_4\left(\frac{k_2}{k_3}\right)^{1/2}\left(\frac{k_0}{k_6}\right)^{1/2}[ArH][BH] \ .$$

Since the reactants in this reaction are polyfunctional, it is possible to employ the initial concentrations instead of the current concentrations for low degrees of conversion. In this scheme, the bimolecular abstraction reaction is an aromatic homolytic substitution reaction.[119]

The proposed reaction scheme and the experimental data yield an overall reaction order of 2, which is due to the appreciable acceleration of the reaction under the influence of the radical fragments formed. It is to be expected that the factor determining the rate of the molecular chain propagation in the reaction investigated is the stability (thermodynamic stability) of the σ-radical complex at high temperatures.

This is confirmed by the data obtained in the condensation of monosubstituted benzene derivatives, which leads, as can be seen from Table 6, to the formation of two isomers (*ortho*- and *para*-) in terms of the position of the dicarbadodecaboranyl group in the aromatic ring, each of which consists of four isomers in terms of the position in which the aryl group is substituted in the 1,7-dicarbadodecaborane nucleus.

Table 6 shows that the nature of the substituent influences the ratio of the isomers involving the 2- and 9-positions in the 1,7-dicarbadodecaborane. Since the 1,7-dicarbadodecaboranyl group exhibits different inductive effects in the 2- and 9-positions[122] (positive in the 9-positive and negative in the 2-position), it is to be expected that the presence of an electron-donating substituent in the benzene ring increases the stability of the radical complex with the 1,7-dicarbadodecaboranyl radical involving the 2-position, whilst the presence of an electron-accepting substituent increases the stability of the complex involving the 9-position, increasing thereby the rate of formation, i.e. the content, of a particular isomer in the reaction products.

Table 6. The compositions of the *B*-aryl-1,7-dicarbadodecaboranes obtained from PhX and 1,7-dicarbadodecaborane by thermal condensation at 440 °C and for the molar ratio arene:1,7-dicarbadodecaborane = 1:15.

Substituent X	Content of *para*-isomers (%)			Content of *ortho*-isomers (%)			*para*:*ortho*
	2-	4-, 5-	9-	2-	4-, 5-	9-	
H	21.5	6.5	15.0	–	–	–	–
Me	20.1	62.8	17.1	24.9	59.0	16.1	1.62
Ph	19.6	62.4	18.0	20.7	60.3	19.0	1.73
$(Me)_3Si$	20.1	62.5	17.4	22.0	63.0	15.0	2.02
MeO	22.3	61.9	15.8	24.4	63.5	12.1	1.41
PhO	16.9	67.6	15.5	19.2	65.2	15.6	1.65
Cl	17.8	62.0	20.2	24.6	47.2	28.2	2.34
CF_3	15.3	61.4	23.3	20.2	58.0	21.8	1.46

Note. The totals for isomers of the *B*-aryl-1,7-dicarbadodecaborane with the aryl group in the 4- and 5-positions in the dicarbadodecaborane nucleus are given.

Oligophenylene-, oligonaphthalene-, and oligoanthracenedicarbadodecaboranes, obtained by the high-temperature polycondensation of 1,2-dicarbadodecaborane with the corresponding aromatic compound under pressure at 400–460 °C, are coloured powders, the colours of which range from pale-yellow (benzene) to dark-brown (anthracene). For a degree of reaction of 95%, the oligomers are readily soluble in acetone, benzene, and chloroform. It was found that the Mark–Kuhn–Houwink equation for oligophenylenedicarbadodecaborane is

$$[\eta] = 4.622 \times 10^{-4} M^{0.59\pm0.09}.$$

(The reduced viscosity was determined in toluene). The average length of the Kuhn segment for this oligomer, which is 12.0 Å, makes it possible to assign the structure to the flexible-chain type.[123]

Thermal condensation of dicarbadodecaborane(12) with ferrocene is also possible. In order to investigate the mechanism of this reaction, a study was made of the process kinetics at 440 °C. It was found from the dependences of the initial rates of consumption of ferrocene on the initial concentration in the absence of dicarbadodecaboranes(12) that the rate of consumption of ferrocene under these conditions is described by the relation

$$-\frac{d[(C_5H_5)_2Fe]}{d\tau} = k[(C_5H_5)_2Fe]^{2.48\pm0.17},$$

where $k = (1.2 \pm 0.5) \times 10^3\ s^{-1}$.

The study of the dependence of the initial rates of consumption of ferrocene and the dicarbadodecaborane(12) on the initial concentration of the dicarbadodecaboranes(12) showed that variation of the concentration of the latter hardly affects the rate of consumption of ferrocene. Thus the rate of consumption of ferrocene in the course of the reaction with dicarbadodecaboranes(12) is also described by the relation presented above.

The rate of consumption of dicarbadodecarboranes(12) is proportional to their concentration in accordance with the relation

$$\frac{d[C_2B_{10}H_{12}]}{d\tau} \sim [C_2B_{10}H_{12}]^{1.76\pm0.12}.$$

The data obtained permitted the conclusion that the condensation of ferrocene with dicarbadodecaborane(12) differs fundamentally from the reaction of dicarbadodecaborane(12) with aromatic compounds[119] apparently mainly as a consequence of the high rate of the thermal degradation of ferrocene.

One can assume with a high degree of justification that the condensation of ferrocene with dicarbadodecaboranes(12) is achieved exclusively as a result of the presence of the radical products of the degradation of ferrocene, which is in its turn a heterogeneous autocatalytic process. The rate of the radical degradation of the radical products is then higher than the rate of their diffusion into the bulk of the gas phase, which is the reason for the strong dependence of the rate of consumption of dicarbadodecaboranes(12) on their concentration.

The presence of cyclopentadiene and its dimer among the products of the degradation of ferrocene in the presence of dicarbadodecaborane(12) at temperatures in excess of 350 °C shows that the primary products are cyclopentadienyl radicals.

$$(C_5H_5)_2Fe \xrightarrow{>350\ ^\circ C} 2\,C_5H_5^{\bullet} + Fe$$

$$C_5H_5^{\bullet} + 1,2\text{-},1,7\text{-}C_2B_{10}H_{12} \longrightarrow C_5H_6 + 1,2\text{-},1,7\text{-}C_2B_{10}H_{11}$$

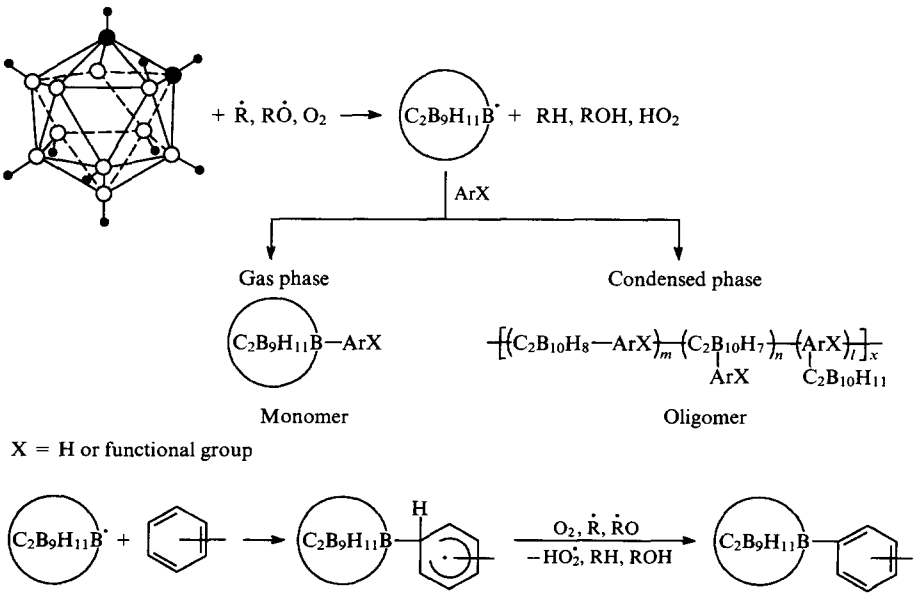
$$2\,C_5H_6 \longrightarrow \text{cyclopentadiene dimer.}$$

The formation of the unstable and reactive 1,2- and 1,7-dicarbadodecaboranyl radicals apparently constitutes a sufficient condition for the formation of the products of the condensation of *B*-ferrocenyl-1,2- and *B*-ferrocenyl-1,7-dicarbadodecaboranes in the course of their further transformations as a result of reactions analogous to homolytic aromatic substitution reactions.

The reaction involving the direct thermal arylation of dicarbadodecaboranes(12) differs from the arylation reaction examined at the beginning as regards the mechanism of the homolytic radical aromatic substitution in the presence of a free-radical source evidently only in the mechanism of the formation of the boron-centred radicals. In a general form, the radical arylation of dicarbadodecaboranes(12) may be represented by Scheme 14.

The results of the investigation presented above are important for the understanding and practical solution of the problem of the preparation of polymers based on dicarbadodecaboranes(12) and having a high thermal stability. Firstly, the transformations in such polymers at elevated temperatures, leading to the formation of dense network three-dimensional systems and giving rise to materials with a long useful life, become comprehensible. Secondly, dicarbadodecaboranes(12) can be and should be regarded as inhibitors of the thermal and thermooxidative degradation, since the radical products of the degradation of the organic fragments of the polymers interact with the

Scheme 14



dicarbadodecaborane groups and are converted into an inactive form. The dicarbadodecaborane groups are capable of forming new stable bonds of the B–C type with the boron-centred radicals (Scheme 14); nor can one rule out the formation of B–B bonds by a recombination reaction. Thus one can represent the dicarbadodecaborane-containing polymer matrix at elevated temperatures as a system involving a definite dynamic equilibrium in which the thermal destruction of the chemical bonds is compensated by the formation of new ones. A necessary consequence of these results is also that the dicarbadodecaborane groups must be introduced into polymer systems in combination with aromatic compounds in order to ensure the conditions for the transformations examined above. Thirdly, an important factor is undoubtedly the fact that the observed direct arylation of dicarbadodecaboranes(12) permits a new and much simpler solution of the problem of the synthesis of dicarbadodecaborane-containing monomers and reactive oligomers. For this purpose, it is essential to introduce the corresponding aromatic compounds into the thermal condensation reaction.

The example involving tetraphenoxysilane, presented in Scheme 13, the product of the interaction of which with 1,2-dicarbadodecaborane affords a reactive monomer with the more stable 1,7-dicarbadodecaborane groups, capable of being employed as such, constitutes an adequate illustration of the process in the condensed phase. On the other hand, the products of its hydrolysis are dicarbadodecaborane-containing phenols, which serve as starting materials for the synthesis of polymers of practical importance, in particular those of the phenolformaldehyde and epoxide types.[98] For the gas-phase arylation of dicarbadodecaboranes(12) in a flow system, it is sufficient to employ the corresponding benzene derivatives.

VI. Conclusion

Since the end of the 1960s, an extensive series of studies have been carried out on the development of new polymers with arylenedicarbadodecaborane fragments in the chain. Novel methods have been developed for the synthesis of various bifunctional dicarbadodecaborane-containing aromatic monomers and processes involving the formation from the latter of new high-molecular-mass dicarbadodecaborane-containing polymers have been investigated. A detailed study has been made of the mechanisms of the chemical reactions of polyarylenedicarbadodecaboranes, which makes it possible to understand the causes of their unusual thermal behaviour and to find new promising methods of synthesis of dicarbadodecaborane-containing monomers and polymers.

Naturally, dicarbadodecaborane-containing polymers are not produced on a large scale and in the foreseeable future will not be produced on such a scale, which, incidentally, applies also to many other interesting polyheteroarylenes with specific properties. Dicarbadodecaborane-containing polymers are special-purpose polymers used primarily in those fields where improved thermal characteristics are required for the polymeric materials.[17,19–25,124–133]

Thus the employment of dicarbadodecaborane-containing phenolformaldehyde polymers as a base for adhesive compositions proved to be promising[125,132] because hardened dicarbadodecaborane-containing resols are distinguished by a high thermal stability. Dicarbadodecaborane-containing resites hardly undergo any change in mass during ageing for 1000 h at 350 °C, whereas the usual phenolformaldehyde polymers are fully destructured under these conditions.

The combination of effective thermal properties of the dicarbadodecaborane-containing resites with the improved adhesion characteristics which are in general specific to phenolformaldehyde polymers made it possible to obtain adhesive compositions with a long useful life at 350–500 °C. The strength characteristics of certain adhesives hardly change after prolonged ageing at 500 °C. Thus when steel components are glued together by means of the adhesive based on the dicarbadodecaborane-containing phenolformaldehyde polymer, the breaking stress is 120 kgf cm^{-2} when the glued junction is subjected to shear before ageing at 20 °C and 500 °C, while after ageing for 500 h at 20 and 500 °C the breaking stresses are 116 and 118 kgf cm^{-2} respectively.

The use of the dicarbadodecaborane-containing epoxide polymers in thermostable adhesive compositions also proved successful.[19,22,23,25,125,130,132] The employment of epoxydicarbadodecaborane oligomers in compositions with furan polymers, as activators of the graphitisation process, in the technology for the preparation of carbon materials has also had a positive effect.[131]

The application of dicarbadodecaborane-containing polyphenylenes, synthesised by the polycyclocondensation of dicarbadodecaborane-containing aromatic acetyl compounds and their ketals, as thermostable binders for glass plastics with a working temperature of 400 °C and in the manufacture of thermostable constructional materials has been described.[97,126–128]

It has been suggested that dicarbadodecaborane-containing polymers of various classes be used to obtain thermostable antifriction self-lubricating coking plastics ensuring the operation of dry friction units at extreme temperatures of 350–500 °C and above: polyamides, polyarylates, polyimides, and polyoxadiazoles, capable of being converted during the preparation of the material into a high-strength coke which consists of a three-dimensionally structured polymer system, without change in the initial mass and shape of the article.[124,129,133] For example, heat-treated materials derived from dicarbadodecaborane-containing polyarylates [obtained from the acid chloride of 1,2-bis(4-carboxyphenyl)dicarbadodecaborane and 1,9-bis(4-hydroxyphenyl)fluorene or 1,2-bis(4-hydroxyphenyl)dicarbadodecaborane] and graphite has the following physicomechanical characteristics: hardness of 18–20 kgf mm^{-2}, coefficient of friction 0.05–0.09, intensity of linear wear $(2.5–5) \times 10^{-9}$, and limiting working temperature 500 °C. The use of the polyoxadiazole based on 1,2-bis(4-carboxyphenyl)dicarbadodecaborane or the polyimide based on 1,7-bis(3,4-dicarboxyphenyl)dicarba-dodecaborane and bis(4-aminophenyl) ether as dicarbadodecaborane-containing polymers in compositions makes it possible to obtain materials with a limiting working temperature of 600 °C whilst retaining effective physicomechanical characteristics.

By virtue of their specific behaviour at elevated temperatures, dicarbadodecaborane-containing polymers can also be used as stabilisers in the thermal and thermooxidative degradation of other polymers,[11,21,25,82,83,134,135] in the preparation of thermostable thermoprotective materials, and for other purposes.

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