HIGHLY BRANCHED POLYCARBOSILANES AS PRECURSORS FOR SiC CERAMICS

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Abstract

The Grignard reaction of (chloroalkyl)chlorosilanes affords a series of highly branched polycarbosilanes featuring two types of terminal groups. The thermophysical properties of the resulting compounds are studied. The effect of the structure of the highly branched polymer and the nature of its terminal groups on the formation of a carbon residue (pyrolysate) is evaluated. The potential of application of poly(chloromethyl)-trichlorosilane with terminal SiH groups as a precursor for SiC ceramics is demonstrated.

Key words: highly branched polycarbosilanes, Grignard reaction, (chloroalkyl)chlorosilanes, terminal groups, precursors of SiC ceramics.
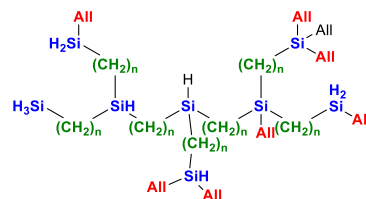
Introduction

Nowadays, some of the most promising constructional materials are silicon carbide (SiC) and ceramic composite materials on its base. Silicon carbide exhibits unique properties: thermal conductivity of 180–200 W/(m·K) (as aluminum), operating temperatures above 1350 °C (as heat-resistant steel), melting/decomposition point of 2830 °C, and stability in the oxidizing and reducing media higher than titanium. By the chemical inertness, SiC approaches gold and platinum, while by the resistance to abrasive wear, it is comparable to diamond. The materials based on silicon carbide that display the mentioned properties find application, first of all, in the extremal fields such as space and aircraft industries [1–3]. Owing to the high chemical stability, fire and wear resistance, silicon carbide is used as a fire-proof material in metallurgy, machinery for coating heat-treating furnaces, and chemical apparatus engineering. The materials based on SiC are utilized in the production of corrosion and erosion-resistant inserts for nozzles, caps and diffusers, components of heat-exchange equipment and pumps for the transfer of acidic solutions and other corrosion-active liquids, in the manufacture of heaters of high-temperature resistance furnaces (globars), lightning arresters for current-flow lines, and electroinsulating devices [1]. Over recent years, many reports have been devoted to the production of different details from SiC ceramics by means of 3D printing [4, 5].

The main methods for producing silicon carbide ceramics are the carbothermal reduction of silicon dioxide, chemical gas-phase deposition of silicon carbide particles, and the preparation from polymer precursors.

The production of silicon carbide from polymer precursors has a range of advantages over other methods. First of all, the structure of the initial polymer determines the structure and properties of the resulting ceramics. Second, ceramic items of various shapes can be obtained: starting from fibers and film coatings to 3D figures. Finally, the application of polymer precursors for the production of SiC ceramics bearing other elements (O, B, N, Ti, Al, Fe, *etc.*) does not require the development of special methods for introducing these elements into ceramics since they are already included in the composition of the initial polymer [6–11]. The drawbacks of the production of ceramics from polymer precursors are large changes in the volume and the release of large amounts of gaseous products during the pyrolysis at the formation of amorphous ceramics.

The polymer precursors for SiC ceramics are polycarbosilanes (PCSs) which main chains consist of silicon and carbon atoms.

There are several main methods for the synthesis of polycarbosilanes (PCSs). The most popular method is the synthesis of PCSs from cyclic and linear polysilanes by the Kumada rearrangement which can be carried out at both elevated and ambient pressure [12–15]. Other methods include the ring-opening polymerization (ROP) of the derivatives of 1,3-disilacyclobutane [16, 17], hydrosilylation of vinylhydridosilanes [18, 19], and the Grignard reaction of (chloroalkyl)chloro- or alkoxysilanes with alkenylmagnesium halides [20–22]. Fuchise *et al.* [23] obtained polycarbosilanes by the polycondensation of di-, trichlorosilanes with dichloromethane or chloroform in the presence of magnesium and titanium tetrachloride (catalyst) at room temperature in THF followed by the reduction of the remaining chlorosilyl groups with $NaAlH_2(2\text{-MeO(CH)}_2O)_2$. Yet another method for producing polycarbosilanes from chlorosilanes and chloroalkylchlorosilanes is the Wurtz reaction. The process occurs either upon refluxing in a solvent (toluene) or a metallic sodium melt (110–120 °C) [24]. If the process does not involve

chloroalkylchlorosilanes, then polysilane is subjected to the Kumada rearrangement in order to obtain polycarbosilane [25–27].

The drawbacks of the production of ceramics from polycarbosilane precursors are significant changes in the volume and the release of large amounts of gaseous products during the pyrolysis at the formation of amorphous ceramics. The presence of alkene, alkyne, and hydride groups in the PCS structure, which are able to form a network during the pyrolysis, essentially increases the yield of a carbon residue (20–30 wt %) [28]. The amount of the carbon residue can be increased by ~30% also by the introduction of a structuring agent (divinylbenzene or diallylbisphenol A) into PCS [29, 30].

Hyperbranched polycarbosilanes (HPCSs) offer certain advantages as preceramic polymers. The application of HPCSs results in the direct formation of a branched SiC structure, which does not require a separate step such as the Kumada rearrangement. The bulk structure of the polymer with the functional groups uniformly distributed over the macromolecule volume, which are able to form intra- and intermolecular network structures, leads to a reduction in the gas release during the pyrolysis and, as a consequence, the high (almost stoichiometric) yields of a ceramic phase.

The diversity and inconsistency of the literature data on the synthesis of HBPCs by the Grignard reaction published over the last 30 years do not allow one to choose an optimal method for obtaining hyperbranched polycarbosilanes by this approach. The main problem in the synthesis of hyperbranched poly(chloromethyl)trichlorosilanes blocked with the allyl groups is the involvement of a solvent during the alkylation of chlorosilanes (opening of a tetrahydrofuran (THF) ring and cleavage of an ether bond in diethyl ether). However, even these facts are not supported by all the publications, not to mention the contradictory details [31, 32]. Due to the side processes and relatively low average molecular masses, the polycarbosilanes synthesized by the Grignard reaction can hardly be called hyperbranched, although they were synthesized based on (chloroalkyl)chlorosilanes—the AB$_3$-type monomers. Therefore, many researchers [31, 33] as well as we call them highly branched polycarbosilanes (HBPCSs).

This work is devoted to the synthesis and properties of highly branched poly(chloroalkylchlorosilanes) blocked with allyl or hydride groups that are able to form a three-dimensional structure. The monomers in use were chloromethyl-, chloroethyl- and chloropropyltrichloro- and methyldichlorosilanes. The applications of the chloroalkyl groups of variable lengths and different amounts of the chlorosilyl groups in the monomer allowed us to evaluate the effect of the monomer structure on their activity in the Grignard reaction. The investigation of the properties of the HBPCSs based on the mentioned monomers with different terminal groups allowed for outlining the main relationships between the structure of HBPCS and the pyrolysate yield that serves as a precursor for SiC ceramics.

Results and discussion

Peculiarities of the synthesis of HBPCSs

The synthesis of HBPCS from (chloroalkyl)trichlorosilanes by the Grignard reaction affords a polymer with a high content of chlorosilyl groups (Scheme 1) which are readily hydrolyzed to silanol groups in the air. The latter can undergo condensation resulting in the release of water and the formation of siloxane bonds. In order to avoid this, the target polymer is isolated only after the blocking of the chlorosilyl groups with the less reactive groups that can form a network structure upon heating. Usually, these groups are allyl, vinyl, ethynyl, and hydride functionalities. Traditionally, the alkylation with unsaturated groups is carried out simultaneously with the formation of a hyperbranched polymer: a mixture of (chloromethyl)trichlorosilane and allyl chloride is added to magnesium in a polar solvent (THF, diethyl ether). To synthesize HBPCSs, we decided to separate these two processes in order to obtain a polymer with a higher molecular mass and to gain insight into the roles of the reagents in the cleavage of the solvent molecules. In a single-step synthesis of HBPCSs, allyl chloride can act not only as an alkylating agent for chlorosilyl groups but also as a chain-terminating agent due to the possible alkylation of chloromethyl groups of the initial monomer. It is impossible to believe that the COC bonds of the solvents are cleaved by the chlorosilyl groups under reaction conditions (in the case of diethyl ether, at 34 °C) [31, 32]. Some researchers use this to explain the appearance of alkyl and alkoxy groups in the polymer that do not refer to the initial monomer and alkylating agent. The ether bonds are likely to be cleaved by the organomagnesium compounds that are formed during the synthesis of HBPCSs, -SiCH$_2$MgCl and AllMgCl. The separate synthesis will allow for evaluating the effect of each reagent on the solvent.

The following (chloroalkyl)trichlorosilanes featuring different lengths of the alkyl substituents were chosen as the monomers: (chloromethyl)trichlorosilane, (2-chloroethyl)trichlorosilane, (3-chloropropyl)trichlorosilane,
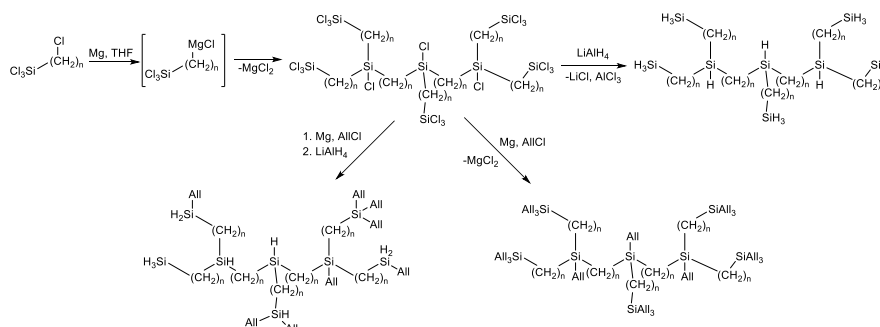
Scheme 1. Synthesis of HBPCSs with different terminal groups.

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which refer to the AB$_3$-type monomers, and (chloromethyl)methyldichlorosilane, which represents an AB$_2$ monomer. This choice of the monomers can allow for evaluating the effect of the monomer structure on the synthesis of HBPCSs and the properties of the resulting HPCSs: molecular mass, polydispersity, density, yield of a carbon residue, *etc*. The AB$_2$-type monomer was implied to be used as a comonomer in the synthesis of poly(chloromethyl)trichlorosilane for thinning the HBPCS dendrite structure, which has a short methylene linker between the silicon atoms, and thereby to improve its properties.

The one-step synthesis of HBPCSs from (chloroalkyl)trichlorosilanes includes two steps: the synthesis of HBPCS by the Grignard reaction and blocking of the chlorosilyl groups by the Grignard reaction or reduction of the chlorosilyl groups with lithium aluminum hydride (LAH) (Scheme 1). The full consumption of the chloromethyl groups at the first step of the production of poly(chloroalkyl)trichlorosilanes was controlled using IR spectroscopy by the disappearance of absorption bands of the Si–CH$_2$ group vibrations at 1192 cm^{-1} and ClCH$_2$ group vibrations at 700–750 cm^{-1}. An aliquot for the IR spectroscopic analysis was preliminarily washed with water till the neutral pH. The completion of the second step, namely, the alkylation of the chlorosilyl groups with allyl chloride was controlled by measuring the pH value of the reaction mixture.

The reduction of the chlorosilyl groups at the second step of the synthesis of HBPCS with terminal SiH groups was carried out by the addition of the required amount of LAH in the form of a THF suspension to the reaction mixture with poly(chloroalkyl)trichlorosilane. The completion of the process was controlled by measuring the reaction mixture pH.

Table 1 presents the synthesis conditions and yields of the blocked highly branched polycarbosilanes.

The resulting HBPCSs with the allyl terminal groups represent colorless, flowing, viscous oils, while the polycarbosilanes with the hydride terminal groups are colorless, almost not flowing, highly viscous oils. Such an aggregate state of the polycarbosilanes with the hydride terminal groups can be explained by the formation of a physical network.

Effect of the length of the alkyl spacer in the monomer on the activity of (chloroalkyl)trichlorosilanes in the Grignard reaction

The investigations on the structures of the resulting HBPCSs by NMR and IR spectroscopy confirmed the presence of tetrahydrofuran moieties. The signals in the range of 3.0–4.0 ppm in the ^{1}H NMR spectra (Figs. 1–3) and the absorption bands at 1070–1100 cm^{-1} in the IR spectra evidence the presence of CH$_2$O and SiO groups in the structures of the HBPCSs. Comparing the NMR spectra of HBPCSs **I**, **III**, and **V** with the allyl terminal groups based on (chloromethyl)trichlorosilane, (2-chloroethyl)trichlorosilane, and (3-chloropropyl)trichlorosilane, one should note that the amount of the THF moieties included in the polymer structure reduces in the mentioned series of the chlorosilanes. Taking into account that the alkylation of the chlorosilyl groups with allyl chloride was carried out at the second step for all the HBPCSs under similar conditions, it can be concluded that a THF ring opens under the action of the Grignard reagent based on the

Table 1. Conditions for the synthesis of HBPCSs

HBPCS	Initial monomer	Blocking agent	Solvent	Time, h	Yield, %
I	ClCH$_2$SiCl$_3$	AllCl	THF	30	91
II	ClCH$_2$SiCl$_3$	LiAlH$_4$	THF	40	62
III	Cl(CH$_2$)$_2$SiCl$_3$	AllCl	THF	35	83
IV	Cl(CH$_2$)$_2$SiCl$_3$	LiAlH$_4$	THF	40	60
V	Cl(CH$_2$)$_3$SiCl$_3$	AllCl	THF	35	81
VI	Cl(CH$_2$)$_3$SiCl$_3$	LiAlH$_4$	THF	40	67
VII	ClCH$_2$SiCl$_3$	AllCl + LiAlH$_4$	THF	80	69
VIII	ClCH$_2$SiCl$_3$	AllCl	Et$_2$O	100	55
IX	ClCH$_2$SiCl$_3$	AllCl	MTBE	100	–
X	ClCH$_2$SiCl$_3$ + Cl(CH$_2$)$_3$SiCl$_3$	AllCl	THF	30	82
XI	ClCH$_2$SiCl$_3$ + ClCH$_2$(CH$_3$)SiCl$_2$	AllCl	THF	40	89
XII	Mixture of polymers **1** and **2**				

chloroalkyl groups (SiAlkMgCl), most probably, belonging to the monomers, during the synthesis of highly branched poly(chloroalkyl)trichlorosilanes (Scheme 2).

A reduction in the content of the CH$_2$O groups in the HBPCSs (Figs. 1a, 2a, and 3a) correlates with the elongation of the alkyl substituent at the silicon atom. The removal of the ClCH$_2$ groups, which take part in the formation of organomagnesium intermediates, from the chlorosilyl groups in the monomer reduces the polarity of the Cl–C bonds owing to a reduction in the inductive effect of the chlorosilyl groups (Scheme 3). The high polarity of the chloromethyl group explains its active participation in the form of the Grignard reagent in the cleavage of THF molecules and significant content of the oxygen-containing structural units in the HBPCSs derived from (chloromethyl)trichlorosilane. The elongation of the alkyl substituent reduces the activity of the chloroalkyl groups and decreases the content of admixture moieties in the structures of the HPCSs based on (2-chloroethyl)- and (3-chloropropyl)trichlorosilanes.
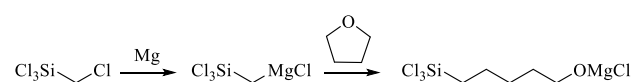
Scheme 2. Opening of a THF ring under the action of the Grignard reagent during the synthesis of highly branched poly(chloromethyl)trichlorosilane.
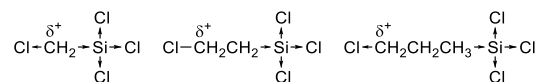
Scheme 3. Reduction in the activity of the chloroalkyl groups in a series of the (chloroalkyl)trichlorosilanes with an increase in the length of the alkyl substituent at the silicon atom.

The analysis of the ^{1}H and ^{29}Si NMR spectra suggests the presence of different oxygen-containing structures in the HBPCSs due to the opening of a THF ring. The presence of only a broad multiplet at about 0 ppm (Fig. 1b) along with the presence of the peaks in the range of 3–4 ppm (Fig. 1a) in the ^{1}H NMR spectrum of the HBPCS based on (chloromethyl)trichlorosilane with the terminal allyl groups indicates that the structure of the resulting highly branched poly(chloromethyl)trichlorosilane contains the oxygen-contain-
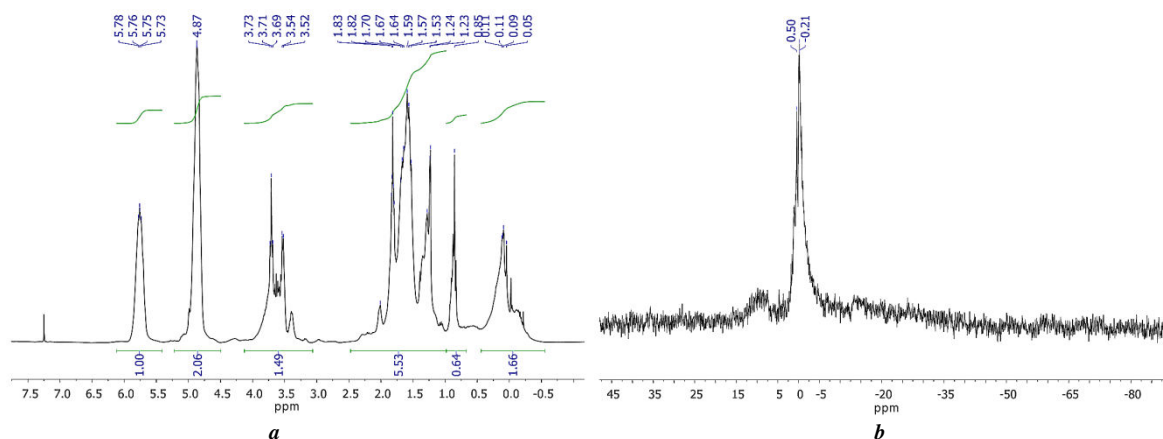
Figure 1. ^{1}H NMR (*a*) and ^{29}Si (*b*) NMR spectra of poly(chloromethyl)trichlorosilane blocked with allyl chloride (**I**).
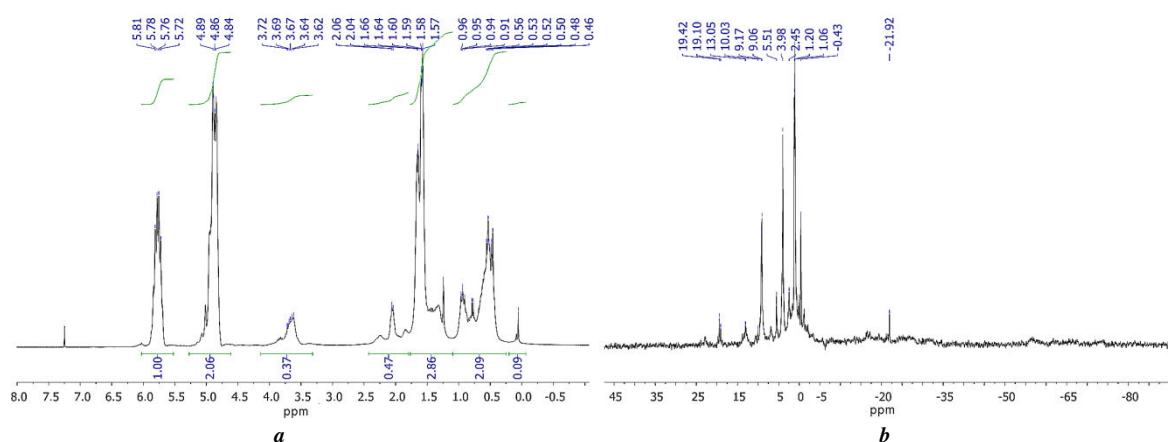

Figure 2. ^{1}H NMR (*a*) and ^{29}Si (*b*) NMR spectra of poly(2-chloroethyl)trichlorosilane blocked with allyl chloride (**III**).
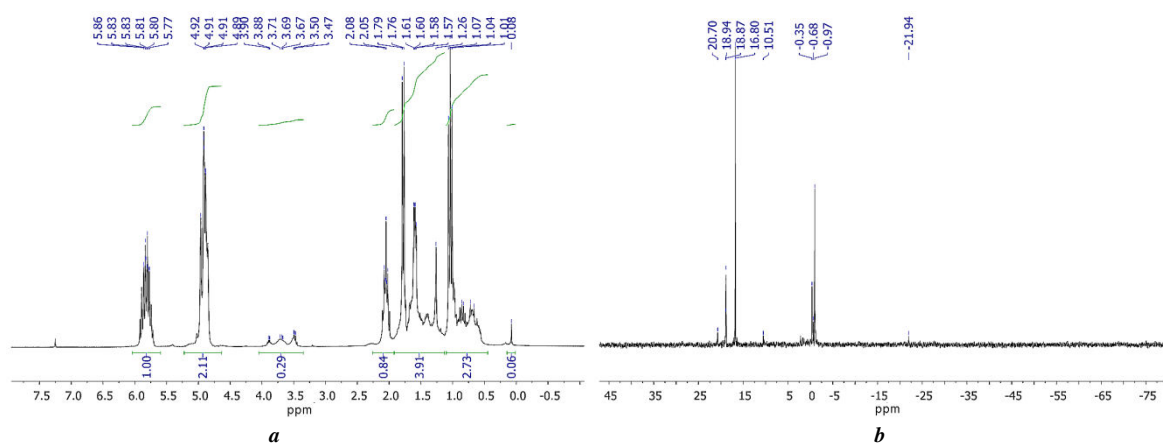

Figure 3. ^{1}H (*a*) and ^{29}Si (*b*) NMR spectra of poly(3-chloropropyl)trichlorosilane blocked with allyl chloride (**V**).

ing moieties of only CH_2OCH_2 type. The organomagnesium intermediate based on the chloromethyl group, opening a THF ring and thus affording the new Grignard reagent, alkylates both the chlorosilyl and chloroalkyl groups (Scheme 4). Then, the resulting alkoxysilyl groups are likely to be alkylated with $ClMgCH_2SiCl_3$, leading to an organomagnesium intermediate analogous to that which was obtained as a result of the opening of a THF molecule. The less reactive CH_2OCH_2 are prone to this type of cleavage in a lesser extent; therefore, they are accumulated in the HBPCS structure during the polymerization course. The reactivities of $ClMgCH_2CH_2SiCl_3$ and

$ClMgCH_2CH_2CH_2SiCl_3$ are lower; their ability to alkylate the alkoxy groups reduces. Therefore, the structure of the HBPCS based on trichlorosilanes with chloroethyl and chloropropyl substituents according to the NMR spectroscopic data contain the alkoxy groups of $SiOCH_2$ type (peaks in the range from –20 to –25 ppm in the ^{29}Si NMR spectra, Figs. 2b and 3b).

The synthesis of hyperbranched polycarbosilanes is a complex process. The structures of the resulting HBPCSs contain the units that are formed as a result of a whole series of side reactions. The main side reaction, after the cleavage of the solvent molecules, is hydrolysis.
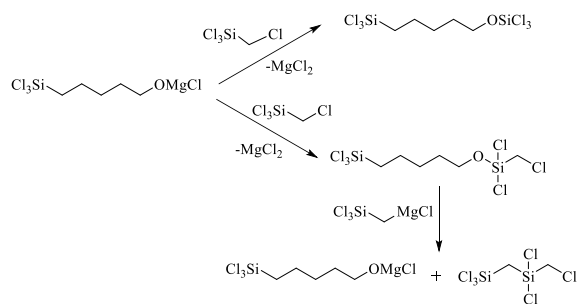
Scheme 4. Formation of the ether and alkoxy bonds during the synthesis of the highly branched poly(chloromethyl)trichlorosilane in THF.

Structural features of the HBPCSs containing the allyl terminal groups

During the synthesis of the HBPCS with the terminal allyl groups, the isolation of the target product requires rinsing with water to remove the magnesium salts. Since the Grignard reaction at the second step proceeds almost completely, the probability of the hydrolysis of the resulting chlorosilyl groups under the action of water with the formation of silanol groups and siloxane bonds is very low. However, the reaction mixture contains the alkoxy groups that result from the cleavage of THF (Scheme 4) and the residual organomagnesium compounds which hydrolysis leads to the formation of alkyl and hydroxyalkyl substituents at the silicon atom (Schemes 4 and 5). This explains the appearance of a weak absorption band of OH stretches at 3500–3350 cm^{-1} in the IR spectra of the HBPCSs (Fig. 4a).
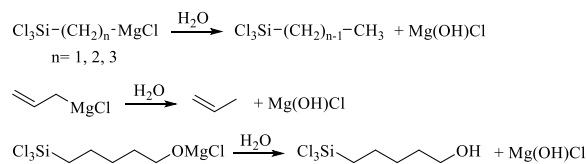

**Scheme 5.** Hydrolysis of the organomagnesium intermediates during the synthesis of HBPCSs.

Structural features of the HBPCSs containing the hydride terminal groups

The reduction of the chlorosilyl groups is complicated by the high hydrolytic instability of LAH. Upon storage, the surface of LAH powder is hydrolyzed to LiOH and Al(OH)$_3$ and adsorbs water. This process is almost impossible to estimate quantitatively; therefore, the addition of LAH to the reaction mixture introduces also a certain amount of water and lithium hydroxide. The appearance of water and alkali in the reaction mixture during the reduction of poly(chloroalkyl)trichlorosilane with LAH leads to the hydrolysis of the chlorosilyl and hydride groups (in the alkali presence), which results in the formation of silanol groups and siloxane bonds (Scheme 6). Therefore, the IR spectra of the HBPCSs with the terminal hydride groups also demonstrate the absorption bands of OH stretches (Fig. 4b).

Of particular interest is the synthesis of HBPCS which structure would contain both the allyl and hydride groups (Scheme 1). It was found that there is a strict order in the blocking of the chlorosilyl groups: their partial reduction must be performed prior to the alkylation of the resulting chlorosilyl
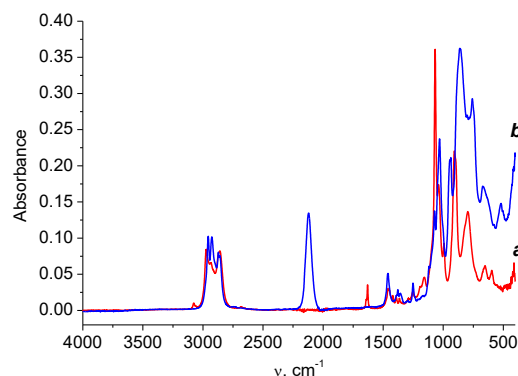
Figure 4. ATR IR spectra of the highly branched poly(chloromethyl)trichlorosilanes with the terminal alkyl (*a*) or hydride (*b*) groups.
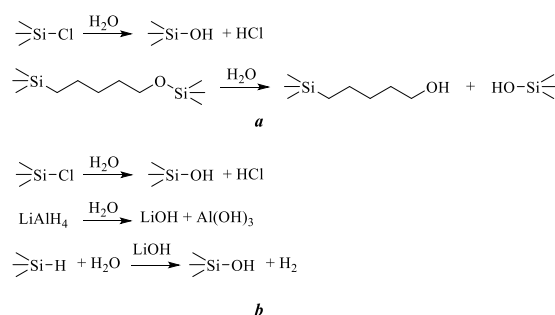

Scheme 6. Hydrolysis of the chlorosilyl and alkoxy bonds during the synthesis of the HBPCSs with the allyl (*a*) and hydride (*b*) groups.

groups with allyl chloride (Fig. 5). The reverse synthetic approach, *i.e.*, the alkylation followed by the reduction, leads, according to the NMR and IR spectroscopic data, to the complete reduction of the allyl groups to the propyl ones. It should be noted, however, that some researchers stated the formation of the HBPCSs with the allyl and hydride terminal groups even at this order of reactions [32].

Grignard reaction in diethyl and methyl *tert*-butyl ethers

Due to a side process of the solvent cleavage during the synthesis of HBPCSs in tetrahydrofuran, we tried to replace this solvent for diethyl and methyl *tert*-butyl ether. The Grignard reaction in methyl *tert*-butyl ether does not proceed. After 100 h of refluxing the reaction mixture (at the solvent boiling point of 56 °C), there were no signs of the precipitation of magnesium chloride, which is indicative of the reaction. The solution after magnesium deposition appeared to be transparent. The reaction was not initiated even by heating magnesium in iodine vapor or the addition of iodine crystals to the reaction mixture. The probable reason is the lower (compared to tetrahydrofuran) polarity of methyl *tert*-butyl ether. The dipole moments (μ_0) of THF, diethyl ether, and methyl *tert*-butyl ether compose 1.65, 1.15, and 0.55 D, respectively. In diethyl ether, the Grignard reaction does proceed but much slower due to the lower boiling point. In 100 h of the Grignard reaction (alkylation with allyl chloride proceeds only in 14 h), the yield of target hyperbranched poly(chloromethyl)trichlorosilane was 56% of the theoretical value (**VIII**, Table 1). The analogous HBPCS

a

b
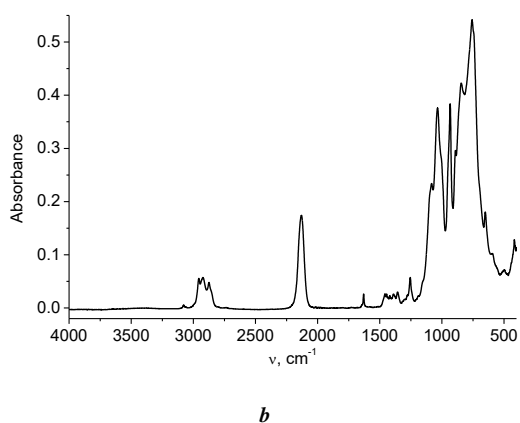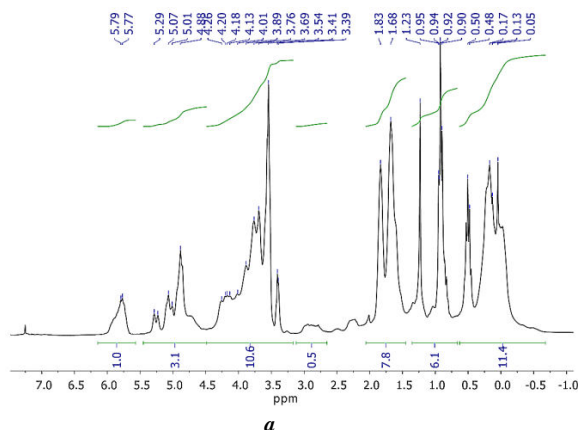
Figure 5. ^{1}H (*a*) and IR (*b*) spectra of the highly branched poly(chloromethyl)trichlorosilane with the terminal allyl and hydride groups (**VII**).

was obtained in THF three times faster with a significantly higher yield (**I**, Table 1). However, diethyl ether almost does not undergo cleavage. The peaks at 3.5–4.0 ppm that correspond to the ether protons are almost absent (Fig. 6).

Investigation of the resulting HBPCSs by GPC

Table 2 summarizes the results of the gel permeation chromatography (GPC) studies of the resulting highly branched polycarbosilanes.

The analysis of the molecular mass characteristics of the resulting HBPCSs allows for concluding that the average molecular mass of poly(chloroalkyl)trichlorosilanes depends on the activity of the chloroalkyl substituent in the monomer during the Grignard reaction: M_w and M_n reduce in the following mono-

Table 2. Molecular mass characteristics of the HBPCSs obtained from the GPC analysis

HBPCS	M (elem. unit)	M_w	M_n	D
I	124.259	8969	1904	4.71
II	44.129	1736	877	1.98
III	138.286	4043	1135	3.56
IV	58.156	1267	815	1.55
V	152.313	1321	760	1.74
VI	72.183	428	225	1.90
VIII	124.259	1669	1078	1.55
X	138.286	1739	985	1.76
XI	222.48	5722	1413	4.05
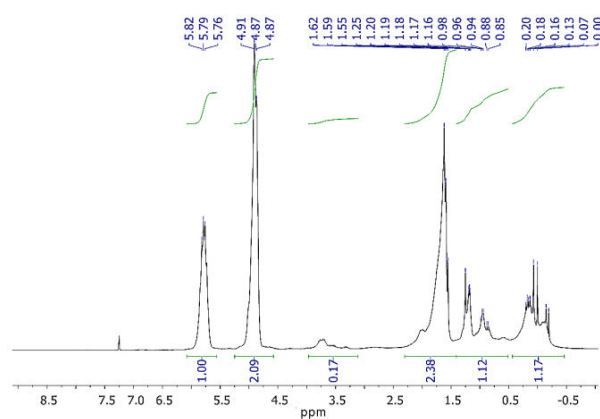
Figure 6. ^{1}H NMR spectrum of the highly branched poly(chloromethyl)trichlorosilane with the terminal allyl groups (**VIII**) obtained in diethyl ether.

mer series $ClCH_2SiCl_3 > ClCH_2CH_2SiCl_3 > ClCH_2CH_2CH_2SiCl_3$ (Table 2, Scheme 3). A change in the polydispersity of the polymers in the mentioned series is also explained by the activity of the chloroalkyl groups in the initial monomer. The lower molecular masses of the HBPCSs bearing the terminal hydride groups (**II**, **IV**, and **VI**) compared to those of the polymers with the terminal allyl groups (**I**, **III**, and **V**) are caused by the lower masses of polymer units (Table 2). The sample of the HBPCS with the allyl groups (**VIII**) obtained in diethyl ether features a significantly lower molecular mass (in 5 times) than polymer **I** obtained in THF. Presumably, the Grignard reaction at the first step did not come to completion even in ~90 h. The highly branched polycarbosilane with the allyl terminal groups obtained by the statistical copolymerization of $ClCH_2SiCl_3$ and $ClCH_2CH_2CH_2SiCl_3$ in a 1:1 molar ratio (**X**) has the lower molecular mass than the homopolymers (**I** and **VI**), while the copolymer based on $ClCH_2SiCl_3$ and $ClCH_2Si(CH_3)Cl_2$ (**XI**) features the molecular mass being average between those of the homopolymer based on (chloromethyl)trichlorosilane and the copolymer based on $ClCH_2SiCl_3$ and $ClCH_2CH_2CH_2SiCl_3$ (**X**) (Table 1). This can evidence that the monomer activity in the Grignard reaction reduces more markedly with an increase in the length of the alkyl substituent than upon substitution of one chlorine atom in the chlorosilyl group for the methyl one.

Thermogravimetric investigation of the HBPCSs

Prior to the thermogravimetric investigations, the resulting HBPCSs were subjected to preliminary thermal cross-linking. The polymer samples were heated in an argon atmosphere at 170 °C for 7 h. These conditions of the preliminary thermal processing of the polycarbosilanes are the most popular ones. The thermogravimetric analysis was carried out in an argon atmosphere at a heating rate of 10 °C/min. The polycarbosilanes, which initially represented liquids, slowly converted (without a significant weight loss, Fig. 7) into white to yellow solids during the preliminary cross-linking. A change in the aggregate state of the HBPCSs after the preliminary thermal processing is explained by the formation of a network in the polymer owing to the terminal groups. This assumption is confirmed by the IR spectroscopic data: the intensities of the absorption bands of the

allyl (1629 cm^{-1}) and hydride (2130 cm^{-1}) groups in the thermally processed samples reduce.

Table 3 lists the results of the thermogravimetric analysis by the carbon residues for the resulting highly branched polycarbosilanes.
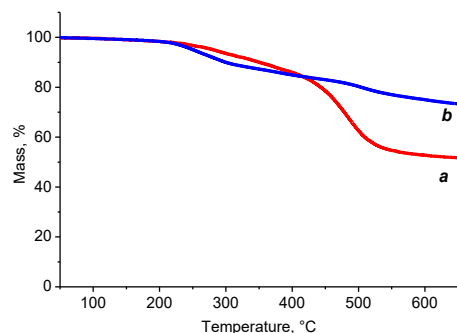
Figure 7. Thermograms of HBPCSs **I** (*a*) and **II** (*b*) with the maximal carbon residues.

Table 3. Formation of a carbon residue in the HBPCSs

HBPCS	Carbon residue, % (TGA)	HBPCS	Carbon residue, % (TGA)
I	51	**VII**	63
II	72	**VIII**	61
III	46	**X**	47
IV	55	**XI**	50
V	39	**XII**	56
VI	49		

During the analysis of the TGA data, particular attention should be drawn first of all to the high efficiency of the hydride groups in the formation of a carbon residue during the thermal decomposition of the resulting polycarbosilanes. Despite the lower molecular masses, the polycarbosilanes with the hydride terminal groups (**II**, **IV**, and **VI**) afford the greater carbon residue for all the monomers. The values of a carbon residue are in good agreement with the activity of the monomers in the Grignard reaction and reduce in the following monomer series: $ClCH_2SiCl_3 > ClCH_2CH_2SiCl_3 > ClCH_2CH_2CH_2SiCl_3$ from 51% to 39% for the polymers with the allyl terminal groups (**I, III,** and **V**) and from 72% to 49% for the polymers with the hydride terminal groups (**II, IV,** and **VI**). The resulting dependence of the formation of a carbon residue in the mentioned series can be explained by a reduction in the molecular mass and density of the polycarbosilane with the elongation of the alkyl spacer in the initial monomer, which leads to an increase in the yield of volatile products and reduction in the degree of network formation.

The presence of the admixture THF moieties in the HBPCS structures reduces the value of a carbon residue from 61% for polymer **VIII** obtained in diethyl ether to 51% for polymer **I** synthesized in THF, although the molecular mass of polycarbosilane **VIII** is five times lower.

The samples of the HBPCSs which structures include simultaneously the allyl and hydride groups (**VII**, **XII**) afford the intermediate amounts of a carbon residue relative to the polymers bearing only allyl (**I**) or hydride (**II**) groups. It should be noted that the more uniform distribution of the reactive groups over the HBPCS volume for polymer **VII**, in which the

hydride and allyl groups were obtained from poly(chloromethyl)trichlorosilane by the partial hydrogenation with LAH followed by the alkylation with allyl chloride, leads to the formation of a greater amount of a carbon residue compared to polycarbosilane **XII**, which represents a mixture of the poly(chloromethyl)trichlorosilane with the allyl groups (**I**) and the poly(chloromethyl)trichlorosilane with the hydride groups (**II**). The hydrogenation and alkylation reactions during the synthesis of HBPCS **VII** were carried out to obtain 50% of the SiH groups and 50% of the SiAll groups; sample **XII** represents a mixture of polycarbosilanes **I** and **II** in a 1:1 molar ratio. The values of carbon residue for samples **VII** and **XII** evidence the low probability of the formation of additional bonds during the thermal destruction owing to the hydrosilylation reaction.

The investigation of the thermal decomposition of copolymers **X** and **XI** showed that they feature the values of a carbon residue equal to 47% and 50%, respectively. The average values of a carbon residue for these samples are explained by the effect of divergent factors. For sample **X**, the carbon residue increases owing to a reduction in the admixture solvent moieties in the HBPCS structure (displacement of $ClCH_2SiCl_3$ moiety capable of breaking tetrahydrofuran for $ClCH_2CH_2CH_2SiCl_3$ that is not able to do this) and a reduction in the carbon residue owing to the application of $ClCH_2CH_2CH_2SiCl_3$, which reduces the molecular mass and density of the HBPCS due to the lower activity in the Grignard reaction and the longer alkyl spacer. The value of a carbon residue in sample **XI** can be explained analogously.

The use of the AB$_2$-type monomer along with the AB$_3$ monomer during the synthesis of a highly branched polycarbosilane also leads to a reduction in the polymer density and, as a consequence, to a reduction in the network formation degree and amount of a carbon residue. However, the use of the AB$_2$ monomer that does not decompose tetrahydrofuran and, thus, reduces the content of admixture structural units, which destruction leads to an increase in the amount of volatile products, increases the carbon residue value.

It should also be noted that the conditions for the preliminary thermal processing of polycarbosilanes strongly affect the amount of a carbon residue. According to the results of the TGA investigations (Fig. 7), the HBPCS samples do not lose mass until 220–250 °C. An increase in the temperature of the preliminary thermal processing from 170 to 250 °C enhanced the content of a gel fraction in the polycarbosilanes from 17% to 85% [33]. The optimization of the conditions for the preliminary thermal processing of the highly branched polycarbosilanes allows for improving the yield of a carbon residue by ~10%.

Experimental

General remarks

The ^1H, ^{13}C, and ^{29}Si NMR spectra were measured on an AM-300 Bruker spectrometer. The IR spectra were registered on a Nicolet iS50 FTIR spectrometer with an ATR device (diamond prism, resolution 4 cm^{-1}, scan number 32). The thermogravimetric analysis was performed on a Shimadzu DTG-60 H derivatograph in an argon atmosphere at the heating rate of 10 °C/min (the masses of the samples were about 10 mg). The

GPC analysis was carried out on a Khromatek Analitik 5000 unit (Russia) using a column with the sizes of 2 m × 3 mm (immobile phase SE-30 (5%) applied to Chromaton-H-AW), evaporator temperature 350 °C, katharometer temperature 310 °C, and helium supply rate 30 L/min. To measure the chromatograms, the controlled heating of the column in the temperature range from 50 to 300 °C with the rate of 20 °C/min was used. The GPC analysis of the polycarbosilanes was carried out on a chromatographic system that consisted of a Staier series II high-pressure pump (Akvilon, Russia), a Smartline RI 2300 refractometer detector (Knauer, Germany), and a Jetstream 2 Plus column thermostat (Knauer, Germany). The thermostating temperature was 40 °C. The eluent was THF, the flow rate was 1.0 mL/min. The columns with a length of 300 mm and a diameter of 7.8 mm (300 × 7.8 mm) were filled with Phenogel 75 kDa sorbent (Phenomenex, USA), the particle size was 5 μm, and the pore size varied from 500 to 5000 Å. The results of the analysis were processed with the MultiKhrom 1.6 GPC software (Ampersend, Russia). The molecular masses of the resulting polymers were evaluated relative to the polystyrene standards.

(Chloromethyl)trichlosilane (97%), (chloromethyl)methyl-dichlorosilane (97%), (2-chloroethyl)trichlorosilane (97%), and (3-chloropropyl)trichlorosilane (97%) were purchased from Alfa Aesar and ABCR.

All the organic solvents were dried over CaH$_2$ and distilled prior to the syntheses.

Syntheses

General procedure for the synthesis of the highly branched poly(chloroalkyl)chlorosilanes by the Grignard reaction. A solution of (chloroalkyl)trichlorosilane (0.05 mol) in absolute THF (15 mL) was added dropwise to a stirred suspension of magnesium powder (0.10 mol) in absolute THF (15 mL), heated in an inert gas flow and activated with iodine. The addition rate was controlled by the condensation rate. Then, the reaction mixture was stirred at the condensation temperature until the disappearance of the signals of the chloroalkyl groups in the IR spectrum (~20 h).

The following blocking of the chlorosilyl groups was carried out using the reaction mixture obtained, without isolating the resulting highly branched poly(chloroalkyl)chlorosilane due to the high concentration of the active chlorosilyl groups.

The reactions in diethyl and methyl *tert*-butyl ether were carried out analogously.

General procedure for the synthesis of the HBPCSs with the terminal allyl groups. Magnesium powder (0.15 mol) and allyl chloride (0.12 mol) were added sequentially to the mixture obtained after the synthesis of the highly branched polychloroalkylcarbosilane (0.05 mol), controlling the rate of the addition of allyl chloride by the condensation rate (~1 drop/s). Then, the stirred mixture was heated at the condensation temperature for 8–10 h. After the addition of hexane (50–60 mL), the resulting precipitate was carefully quenched with slightly acidic water. The organic layer was separated, rinsed with distilled water until neutral reaction, dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated. The yields of the polymers ranged within 70–90%.

The reactions in diethyl and methyl *tert*-butyl ether were carried out analogously.

General procedure for the synthesis of HBPCSs with the terminal hydride groups. A suspension of LiAlH$_4$ (0.60 mol) in absolute THF (30 mL) was added in small portions to the mixture obtained after the synthesis of the highly branched polychloroalkylcarbosilane (0.05 mol). Then, the resulting mixture was stirred upon heating to the condensation temperature for 20–25 h. The solvent was maximally removed under vacuum. The resulting mixture was diluted with hexane (50 mL). The decanted solution was evaporated to give the target polyhydridocarbosilanes in 50–70% yield.

Synthesis of HBPCS VII containing the terminal hydride and allyl groups. A suspension of LiAlH$_4$ (0.25 mol) in absolute THF (20 mL) was added in small portions to the mixture obtained after the synthesis of the highly branched polychloroalkylcarbosilane (0.05 mol). Then, the resulting mixture was stirred upon heating to the condensation temperature for 20–25 h. The solvent was maximally removed under vacuum. The resulting mixture was diluted with hexane (50 mL). After retention, the liquid phase was decanted from the resulting precipitate. Then, magnesium powder (0.60 mol) and allyl chloride (0.70 mol) were added sequentially. The stirring was continued upon heating at the condensation rate for 24–30 h. THF was removed under vacuum, and the resulting mixture was diluted with hexane (50 mL). The solution was decanted from the resulting precipitate. The solvents and the excess of allyl chloride were removed on a rotary evaporator.

Synthesis of the statistical copolymer of (chloromethyl)trichlorosilane and (3-chloropropyl)trichlorosilane blocked with allyl chloride (X). This highly branched polycarbosilane was synthesized according to the general procedure for the synthesis of the poly(chloromethyl)trichlorosilanes blocked with allyl chloride from (chloromethyl)methyltrichlorosilane (3.96 g, 21.50 mmol) and (3-chloropropyl)trichlorosilane (4.56 g, 21.50 mmol).

Synthesis of the statistical copolymer of (chloromethyl)trichlorosilane and (chloromethyl)methyldichlorosilane blocked with allyl chloride (XI). This highly branched polycarbosilane was synthesized according to the general procedure for the synthesis of the poly(chloromethyl)trichlorosilanes blocked with allyl chloride from (chloromethyl)methyltrichlorosilane (4.43 g, 24.00 mmol) and (chloromethyl)methyldichlorosilane (3.92 g, 24.00 mmol).

General procedure for the preliminary thermal cross-linking of the HBPCSs. Before the thermogravimetric analysis, the resulting highly branched polycarbosilanes were thermally cross-linked without the use of any cross-linking agent. The polymer sample (0.50 g) was placed in a flask and heated in an argon flow over an oil bath at 170 °C for 7 h.

Highly branched poly(chloromethyl)trichlorosilane with the terminal allyl groups (THF) (I). Yield: 92%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ –0.5–0.5 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.7–1.5 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.5–2.0 (m, C$\underline{H}_2$CH$_2$O, CH$_2$=CHC$\underline{H}_2$), 3.2–4.0 (m, C$\underline{H}_2$O), 4.7–5.2 (m, C$\underline{H}_2$=CHCH$_2$), 5.5–6.0 (m, CH$_2$=C$\underline{H}$CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ –6.02, –2.99, –2.61, 1.05, 14.01, 21.65, 21.80, 22.53, 23.57, 23.97, 25.48, 25.59, 29.07, 29.45, 29.56, 29.77, 31.46, 44.74, 61.68, 62.47, 62.63, 67.79, 69.76, 70.46, 113.38, 113.76, 114.17, 134.19, 134.41 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –2.50–2.50 (br. m, CH$_3$$\underline{Si}$, CH$_2$$\underline{Si}$) ppm. IR (ATR),

cm^{-1}: 3390, 3075, 2970, 2931, 2871, 2853, 1629, 1459, 1418, 1390, 1347, 1254, 1192, 1154, 1086, 1066, 1029, 991, 930, 891, 785, 649, 592, 483, 413. Elementary unit C$_7$H$_{12}$Si, unit mass 124.26. Anal. Calcd: C, 67.66; H, 9.73; Si, 22.60. Found: C, 54.42; H, 8.15; Si, 18.59%.

Highly branched poly(chloromethyl)trichlorosilane with the terminal hydride groups (II). Yield: 62%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ –0.5–0.5 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.7–1.5 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.5–2.0 (m, C$\underline{H}_2$CH$_2$O), 3.2–4.2 (m, C$\underline{H}_2$O, Si$\underline{H}$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ –10.83, –6.33, –2.99, –4.07, 7.00, 13.96, 19.56, 22.53, 24.29, 29.21, 29.53, 29.86, 31.42, 31.76, 35.86, 36.91, 37.21, 63.05, 70.43 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –13.65 (s, H$\underline{Si}$CH$_2$), –35.13 (s, H$\underline{Si}$O) ppm. IR (ATR) cm^{-1}: 2956, 2926, 2872, 2851, 2121, 1460, 1378, 1251, 1109, 1072, 1031, 936, 862, 757, 672, 510, 403. Elementary unit C$_1$H$_4$Si, unit mass 44.13. Anal. Calcd.: C, 27.22; H, 9.14; Si, 63.64. Found: C, 34.13; H, 9.72; Si, 60.01%.

Highly branched poly(2-chloroethyl)trichlorosilane with the terminal allyl groups (III). Yield: 80%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.06–0.7 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.7–1.2 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.2–2.5 (m, C$\underline{H}_2$CH$_2$O, CH$_2$=CHC$\underline{H}_2$), 3.5–4.0 (m, C$\underline{H}_2$O), 4.7–5.2 (m, C$\underline{H}_2$=CHCH$_2$), 5.5–6.0 (m, CH$_2$=C$\underline{H}$CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 0.50, 2.29, 2.96, 5.82, 10.87, 13.67, 13.81, 18.93, 18.99, 19.37, 19.44, 21.80, 22.39, 29.59, 37.20, 37.28, 37.50, 67.60, 81.58, 113.12, 113.45, 114.08, 114.31, 114.42, 114.61, 133.04, 133.41, 134.25, 134.58, 138.42 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –21.94, –1.21, –0.43, –0.05, 1.06, 1.20, 2.45, 3.98, 5.51, 6.89, 9.06, 9.17, 13.05, 19.10, 19.42, 22.90 ppm. IR (ATR) cm^{-1}: 3371, 3076, 3059, 2995, 2971, 2913, 2879, 2799, 1796, 1629, 1456, 1418, 1391, 1340, 1300, 1255, 1192, 1155, 1134, 1053, 1032, 990, 929, 891, 776, 669, 620, 595, 418. Elementary unit C$_8$H$_{14}$Si, unit mass 138.29. Anal. Calcd: C, 69.49; H, 10.20; Si, 20.31. Found: C, 61.37; H, 9.45; Si, 17.66%.

Highly branched poly(2-chloroethyl)trichlorosilane with the terminal hydride groups (IV). Yield: 60%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.04–0.7 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.7–1.4 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.4–2.2 (m, C$\underline{H}_2$CH$_2$O), 3.2–4.5 (m, C$\underline{H}_2$O, Si$\underline{H}$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ –0.20, 0.76, 0.91, 2.43, 3.48, 4.88, 6.38, 13.84, 13.99, 18.59, 22.58, 29.63, 31.52, 34.46, 63.72, 67.66 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –65.54, –55.25, –54.64, –22.49, –21.93, –21.36, 0.50, 0.87 ppm. IR (ATR) cm^{-1}: 3360, 2957, 2926, 2872, 2852, 2141, 1462, 1378, 1152, 1119, 1055, 923, 824, 607, 408. Elementary unit C$_2$H$_6$Si, unit mass 58.16. Anal. Calcd: C, 41.31; H, 10.40; Si, 48.29. Found: C, 38.22; H, 8.01; Si, 44.99%.

Highly branched poly(3-chloropropyl)trichlorosilane with the terminal allyl groups (V). Yield: 81%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.08–0.7 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.7–1.6 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.6–2.2 (m, C$\underline{H}_2$CH$_2$O, CH$_2$=CHC$\underline{H}_2$), 3.3–4.0 (m, C$\underline{H}_2$O), 4.7–5.2 (m, C$\underline{H}_2$=CHCH$_2$), 5.6–6.0 (m, CH$_2$=C$\underline{H}$CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 0.71, 8.90, 11.10, 11.79, 11.96, 12.02, 14.04, 15.74, 17.80, 17.88, 18.22, 19.32, 19.47, 19.54, 22.33, 22.80, 29.63, 32.66, 33.26, 47.60, 65.59, 113.19, 113.35, 113.40, 113.45, 113.60, 113.84, 114.19, 133.52, 133.90, 134.25, 134.33, 138.75 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –0.97, –0.68, –0.35, 2.18, 10.51, 16.80, 18.87, 18.94, 20.70 ppm. IR (ATR), cm^{-1}:

3078, 3070, 2992, 2967, 2919, 2874, 2851, 1797, 1629, 1463, 1418, 1392, 1253, 1189, 1150, 1119, 1030, 989, 927, 893, 860, 782, 716, 664, 598, 453, 408. Elementary unit C$_9$H$_{16}$Si, unit mass 152.31. Anal. Calcd: C, 70.97; H, 10.59; Si, 18.44. Found: C, 62.75; H, 9.53; Si, 13.88%.

Highly branched poly(3-chloropropyl)trichlorosilane with the terminal hydride groups (VI). Yield: 68%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ –0.09–1.0 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 1.0–1.20 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.25–2.0 (m, C$\underline{H}_2$CH$_2$O), 3.2–4.0 (m, C$\underline{H}_2$O, Si$\underline{H}$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 1.82, 12.68, 13.98, 18.97, 21.57, 22.56, 23.03, 29.60, 31.50, 36.20, 62.77, 64.91, 66.53 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –61.27, –59.94, –58.35, –30.54, –29.26, –22.07, –14.72 ppm. IR (ATR), cm^{-1}: 3360, 2956, 2918, 2862, 2141, 1457, 1404, 1189, 1075, 1029, 919, 893, 823, 757, 606, 522, 403. Elementary unit C$_3$H$_8$Si, unit mass 72.18. Anal. Calcd: C, 49.92; H, 11.17; Si, 38.91. Found: C, 40.32; H, 8.07; Si, 33.16%.

Highly branched poly(chloromethyl)trichlorosilane with the terminal hydride and allyl groups (VII). Yield: 70%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ –0.20–0.50 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.50–1.50 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.50–2.20 (m, C$\underline{H}_2$CH$_2$O, C$\underline{H}_2$CH=CH$_2$), 3.30–4.40 (m, C$\underline{H}_2$O, Si$\underline{H}$), 4.50–6.00 (m, CH$_2$CH=C$\underline{H}_2$, CH$_2$C$\underline{H}$=CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ –10.57, –5.95, 0.91, 6.15, 6.53, 6.67, 7.36, 10.25, 13.79, 14.06, 22.61, 26.04, 27.00, 29.05, 29.60, 31.83, 61.58, 62.06, 63.31, 64.07, 69.75, 70.49, 113.90, 114.44, 117.06, 118.48, 128.68, 130.76, 134.14, 136.49 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –64.61, –34.47, –21.90, 2.89 ppm. IR (ATR), cm^{-1}: ~3400, 3078, 2962, 2922, 2874, 2129, 1630, 1467–1405, 1257, 1255, 1052, 1035, 933, 849, 757, 657, 595, 417. Elementary unit C$_4$H$_8$Si, unit mass 84.19. Anal. Calcd: C, 57.06; H, 9.58; Si, 33.36. Found: C, 49.12; H, 9.01; Si, 27.86%.

Highly branched poly(chloromethyl)trichlorosilane with the terminal allyl groups (diethyl ether) (VIII). Yield: 56%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ –0.3–0.5 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.5–1.0 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.1–2.0 (m, C$\underline{H}_2$CH$_2$O, CH$_2$=CHC$\underline{H}_2$), 3.5–4.0 (m, C$\underline{H}_2$O), 4.6–5.3 (m, C$\underline{H}_2$=CHCH$_2$), 5.5–6.0 (m, CH$_2$=C$\underline{H}$CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ –6.27, –5.97, –2.91, –2.48, 1.10, 18.33, 20.22, 20.75, 21.72, 21.79, 21.87, 22.77, 22.96, 23.64, 29.28, 29.65, 45.25, 58.75, 63.26, 72.66, 113.44, 113.53, 113.86, 116.07, 134.29, 134.52, 134.91, 137.33 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –2.50–2.50, 9.16. IR (ATR), cm^{-1}: 3075, 2968, 2931, 2871, 2853, 1629, 1459, 1418, 1404, 1390, 1347, 1254, 1192, 1154, 1066, 1029, 991, 930, 891, 785, 649, 592, 483, 413. Elementary unit C$_7$H$_{12}$Si, unit mass 124.26. Anal. Calcd: C, 67.66; H, 9.73; Si, 22.60. Found: C, 66.91; H, 9.95; Si, 21.90%.

Statistical copolymer of (chloromethyl)trichlorosilane and (3-chloropropyl)trichlorosilane blocked with allyl chloride (X). Yield: 82%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ –0.25–0.5 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.5–1.2 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.5–2.5 (m, C$\underline{H}_2$CH$_2$O, CH$_2$=CHC$\underline{H}_2$), 3.3–4.5 (m, C$\underline{H}_2$O), 4.7–5.4 (m, C$\underline{H}_2$=CHCH$_2$), 5.6–6.2 (m, CH$_2$=C$\underline{H}$CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ –8.38, –4.14, –2.70, 6.80, 19.09, 19.60, 19.86, 21.83, 22.38, 28.35, 29.38, 32.32, 33.44, 36.17, 61.49, 64.54, 68.35, 70.27, 71.64, 113.12, 113.31, 113.55, 133.81, 134.13, 138.18 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –22.03, –2.50–2.50, 4.35, 7.22–10.20, 16.98, 18.95, 19.56, 21.43, 22.05 ppm. IR (ATR), cm^{-1}: 3354, 3076, 3071, 2956, 2917, 2872, 1629, 1468, 1422, 1391, 1253, 1192, 1154,

1071, 1032, 990, 929, 891, 856, 784, 669, 594, 417. Elementary unit $C_{16}H_{28}Si_2$, unit mass 276.57. Anal. Calcd: C, 69.49; H, 10.20; Si, 20.31. Found: C, 60.12; H, 8.85; Si, 16.07%.

Statistical copolymer of (chloromethyl)trichlorosilane and (chloromethyl)methyldichlorosilane blocked with allyl chloride (XI). Yield: 89%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ –0.5–0.5 (m, C$\underline{H}_3$Si, C$\underline{H}_2$Si), 0.5–1.5 (m, CH$_2$C$\underline{H}_2$CH$_2$), 1.5–2.0 (m, C$\underline{H}_2$CH$_2$O, CH$_2$=CHC$\underline{H}_2$), 3.1–3.9 (m, C$\underline{H}_2$O), 4.7–5.2 (m, C$\underline{H}_2$=CHCH$_2$), 5.4–6.0 (m, CH$_2$=C$\underline{H}$CH$_2$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ –6.02, –2.93, –2.60, 1.05, 14.031, 21.61, 21.83, 22.50, 23.57, 23.96, 25.48, 25.55, 29.07, 29.43, 29.55, 29.71, 31.45, 44.74, 61.68, 62.44, 62.63, 67.80, 69.76, 70.45, 113.35, 113.77, 114.10, 134.19, 134.42 ppm. ^{29}Si{^{1}H} NMR (59.60 MHz, CDCl$_3$): δ –2.50–2.50 (br. m, CH$_3\underline{Si}$, CH$_2\underline{Si}$) ppm. IR (ATR), cm^{-1}: 3390, 3075, 2965, 2931, 2870, 2853, 1629, 1459, 1424, 1390, 1347, 1333, 1261, 1253, 1192, 1154, 1081, 1057, 1029, 991, 932, 894, 788, 651, 591, 483, 413. Elementary unit $C_{12}H_{22}Si_2$, unit mass 222.48. Anal. Calcd.: C, 64.78; H, 9.97; Si, 25.25. Found: C, 58.96; H, 8.85; Si, 21.54%.

Mixture of poly(chloromethyl)trichlorosilane blocked with allyl chloride and poly(chloromethyl)trichlorosilane reduced with lithium aluminum hydride (XII). This sample represents a mixture of poly(chloromethyl)trichlorosilane with the allyl terminal groups (**I**) and poly(chloromethyl)trichlorosilane with the hydride terminal groups (**II**) obtained according to the corresponding procedures. A mixture of sample **I** (0.41 g, 3.30 mmol) and sample **II** (0.14 g, 3.20 mmol) was homogenized in absolute THF (5 mL). Then, the solvent was removed under vacuum.

Conclusions

The investigation of the structures of the highly branched poly(chloroalkyl)trichlorosilanes with the terminal hydride and allyl groups showed that the properties of the HBPCSs are affected by the activity of the chloroalkyl substituent at the silicon atom in the Grignard reaction, which reduces in the following monomer series: ClCH$_2$SiCl$_3$ > ClCH$_2$CH$_2$SiCl$_3$ > ClCH$_2$CH$_2$CH$_2$SiCl$_3$. The division of a single-step synthesis of the HBPCSs into two stages allowed for establishing that the cleavage of ether molecules at the first step occurs under the action of the Grignard reagent, ClMg(CH$_2$)$_n$SiCl$_3$, obtained from the initial (chloroalkyl)trichlorosilane and magnesium. The elongation of the alkyl substituent in the initial monomer and reduction in the polarity of a solvent used in the Grignard reaction decreases the content of solvent structural units in the resulting hyperbranched polymers. The terminal hydride groups afford higher efficiency in the processes of network formation during the thermal decomposition of the HBPCSs than the terminal allyl groups. The simultaneous presence of the allyl and hydride groups in the highly branched polycarbosilanes gives rise to additional bonds for the network formation during the thermal destruction owing to the hydrosilylation reaction.

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