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Synthesis of s- and p-Element Organosiloxanes by Mechanochemical Activation

Vitaliy Viktorovich Libanov, Alevtina Anatol'evna Kapustina and Nikolay Pavlovich Shapkin

Abstract

The interaction of some organosilicon compounds with oxides, hydroxides, and organic derivatives of s- (beryllium, magnesium, calcium) and p-elements (boron, aluminum, gallium, and tin) under conditions of mechanochemical activation was studied. Based on polyphenylsilsesquioxane and boric acid, the conditions for the synthesis of polyelementorganosiloxanes were selected, which included the activation time, carrier rotation speed, and the ratio of the nozzle mass to the payload mass. The influence of the nature of the heteroatom and the organic substituent of the heteroatom on the process has been studied. The effect of organic substituents at the silicon atom and the functionality of the organosilicon derivative on the mechanochemical interaction with acetylacetonates of boron difluoride and tin dichloride were also studied. The mechanisms of solid-phase reactions are proposed.

Keywords: mechanochemical activation, mechanisms of solid-phase reactions, organosilicon compounds, acetylacetonates of s- and p-elements

1. Introduction

Currently, the urgent task of chemistry is the search for new environmentally friendly methods for the synthesis of chemical compounds and materials based on them. One of these methods is mechanochemical, which excludes the use of solvents not only at the synthesis stage but in some cases when isolating the target product. In addition to the fact that mechanochemical activation excludes the use of solvents at the synthesis stage, the generated mechanical energy leads to the breaking of bonds and the creation of various radicals that cannot be formed in solution. Therefore, as a result of mechanochemical reactions, new compounds are formed that cannot be synthesized under the conditions of the use of solvents. This is due to the fact that most solvents interfere with the reagents or irreversibly bind to the product, changing their structure and reactivity.

In addition to the environmental component, this method has a number of economic advantages due to the short reaction time (in the case of using planetary activators, 3 minutes) and energy costs. Mechanochemical synthesis and mechanochemical activation are now widely used in various industries, for example, the production of catalysts [1], processing of materials, pharmaceuticals, utilization of carcinogenic organic derivatives, pyrite concentrates, etc. Mechanochemical

activation can be used to decompose polyamides [2], to synthesize nanotubes [3], and to destroy toxic chlorine compounds, for example, DDT ([2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane]) [4].

Recently, mechanochemical activation is often used in medicine and pharmacology, since the use of this method leads to an increase in the solubility of drugs and, as a consequence, to an increase in bioavailability.

It is promising to use the method of mechanochemical activation for the synthesis of organoelement, in particular organosilicon compounds.

Organosilicon compounds have a number of practically important properties, such as heat resistance, adhesion to metals, good electrical insulation characteristics, mechanical strength, and resistance to cold and water. Thus, organosilicon compounds containing indium ions have high catalytic activity [5] and containing magnesium atoms in their structure can be used to modify the surface of layered silicate to obtain an antifriction coating [6, 7]; siloxanes that simultaneously contain magnesium and titanium atoms in their structure are used as catalysts [8]. Siloxanes containing calcium ions in their structure are widely introduced into medicine [9, 10], while siloxane esters containing lithium salts are used in lithium-ion batteries [11].

Organosilicon polymers are used in electronics and semiconductor instrumentation [12]. Siloxanes modified with boron and aluminum compounds increase the fire resistance and mechanical properties of materials [13], improve the hydrophobic qualities of materials [14, 15], and are used as heat-conducting composites [16]. Thymine-modified siloxanes can be widely used in optoelectronics and impart biological properties of materials [17]. The introduction of borsiloxanes into rubbers greatly increases their elasticity [18], and the high corrosion resistance of materials is acquired when tin atoms are introduced into siloxanes [19].

Possible applications of polymetallorganosiloxanes are also described in review [20].

2. The choice of synthesis conditions based on polyphenylsilsesquioxane and boric acid

The conditions for the synthesis of polyelementorganosiloxanes containing s- and p-atoms were selected on the basis of the reaction of polyphenylsilsesquioxane (PPSSO) and boric acid. This choice is due to two important points. First, due to the presence of hydroxyl groups and coordination of water in the initial organosilicon compound, a heterofunctional condensation reaction can occur, and secondly, boric acid itself can split the siloxane chain.

To select the conditions of mechanochemical synthesis, the following activation parameters were varied: synthesis time, number of mill turns (rotation speed), and ratio of nozzle mass to payload mass.

Mechanochemical activation was carried out in the planetary monomill "Pulverisette 6." A stainless steel beaker and grinding balls made of the same material were used as a reactor. The activation time ranged from 30 seconds to 7 minutes, the rotational speed of the mill drove from 100 to 600 rpm.

The estimated reaction scheme for the interaction of PPSSO and boric acid is as follows:



where the original $x = 1, 2$ or 3 .

After milling, reaction mixture was extracted with toluene. As a result of the syntheses, two fractions were isolated. The toluene-insoluble fractions were

gray-white powdery substances, which, according to elemental and X-ray phase analysis and IR spectroscopy, were unreacted boric acid. Soluble fractions of all syntheses according to gel permeation chromatography were high molecular weight compounds (≥ 5000).

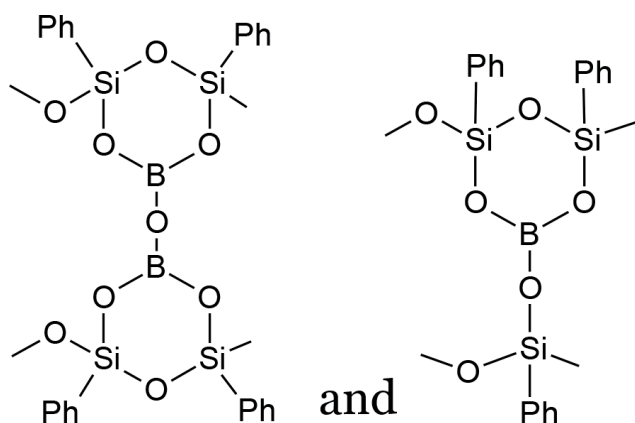
Mass fractions of soluble fractions in polymers slightly increased with an increase in activation time. At the same time, a slight increase in the content of boron in the polymer chain occurred. The Si/B ratio in the soluble fractions differed from the predetermined one and was approaching (or equal to) to 2:1. By fractional precipitation from solutions of polymers, only one fraction was isolated, which indicates the homogeneity of the obtained compounds.

Since the obtained Si/B ratios were approximately equal to 2, a number of syntheses were carried out in which PPSSO and boric acid were introduced under similar conditions in the initial ratios of 2:1.

The Si/B ratios obtained in this case are close to the given value. This fact makes it possible to assume that the ratios obtained under mechanochemical activation conditions are determined by the nature of the heteroatom introduced into the siloxane chain to a greater extent than the initial Si/B ratio. The ratio Si/B = 2:1 may indicate the formation of a cyclolinear structure with stable six-membered boronsiloxane fragments.

An increase in the initial Si/B ratio to 3:1 led to the formation of soluble fractions with a larger mass fraction, which is associated with an increase in the length of the siloxane fragment in the polymer chain.

Based on the data of elemental analysis, gel permeation chromatography, and IR spectroscopy, we can conclude that polymers consist of two types of structural units:



Since the optimal ratio for polyboronphenylsiloxanes obtained by mechanochemical activation was 2:1, to study the influence of activation parameters for all subsequent syntheses, the initial Si/B ratios were taken to be 2:1.

To study the effect of activation time on the entry of boron into the polymer chain, we carried out syntheses in which the activation time was 30 seconds and 2, 4, 6, and 7 minutes.

As a parameter showing the entry of boron into the polymer chain, we used the concept of “degree of conversion,” which was calculated by the formula:

$$\alpha = \frac{n_1}{n_2},$$

where n_1 is the amount of boron included in the polymer chain and n_0 is the initial amount of boron.

For greater clarity, the dependence of the degree of conversion on the activation time [$\alpha = f(t)$] is given in **Figure 1**.

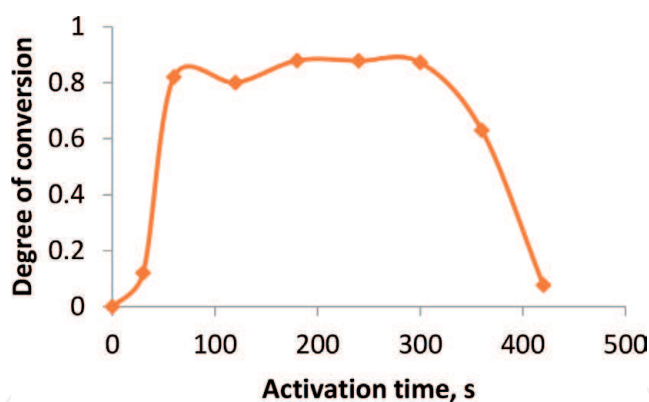


Figure 1.
The dependence of the degree of conversion on activation time.

Analyzing the obtained dependence, it can be seen that the degree of boron conversion remains practically unchanged in the time interval from 3 to 5 minutes. Therefore, in order to save energy, it is advisable to carry out syntheses precisely at 3 minutes of activation. After 5 minutes of activation, both the degree of conversion and the boron content in the polymer chain decrease, since an increase in the activation time leads to a break in the -O-B- bond in the Si-O-B fragment and the boron is removed from the polymer chain.

The entry of boron into the siloxane chain is also affected by such an important parameter as the rotational speed of the mill. With an increase in the rotation frequency, the mass fraction of the soluble fraction increases, and the degree of entry of boron into the polymer chain increases. Due to the fact that the mill mode at a frequency of 100–300 revolutions per minute is abrasive, under the influence of grinding media, the friction force between the balls and the reaction mixture increases, and, as a result, the local temperature increases. This can also explain the fact that, as a result of activation, the insoluble fraction is a mixture of metaboric acid, unreacted PPSSO, and silicon oxide formed as a result of the separation of the phenyl radical. The data obtained do not contradict to the previously described in the literature [21, 22]. **Figure 2** shows the dependence of the percentage of boron and the degree of conversion on the rotational speed of the mill.

With an increase in the ratio of the mass of the nozzle to the mass of the payload, an increase in the impact force from the grinding bodies occurs.

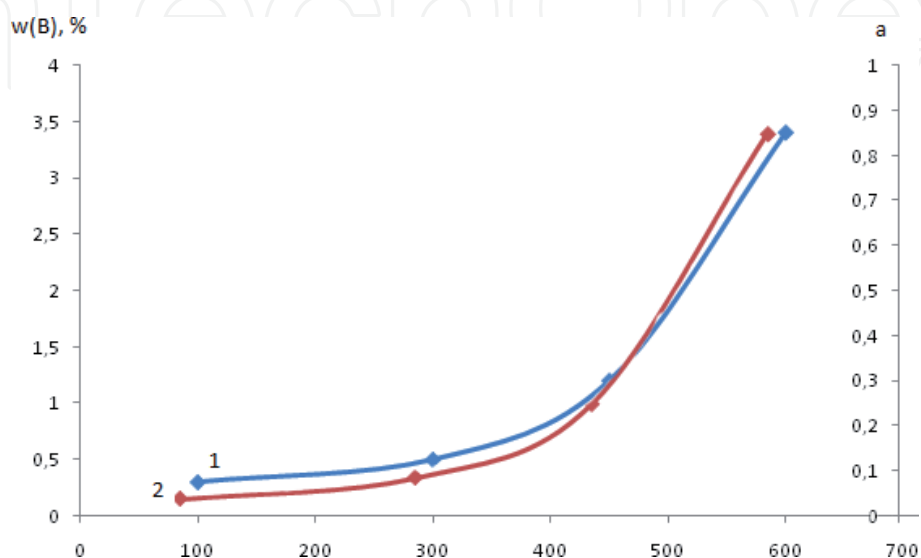


Figure 2.
Dependence of boron content $w(B)$ (1) and degree of conversion a (2) on carrier speed.

An increase in the ratio of the mass of the nozzle to the mass of the payload to 3.04 leads to a decrease in the entry of boron into the polymer chain and to a decrease in the mass fractions of soluble fractions with an increase in the activation time. Apparently, an increase in impact force does not favor the entry of boron into the polymer chain.

Thus, the decisive factors on which the degree of conversion and the percentage of boron included in the polymer chain depend on are the rotational speed of the mill, the activation time, and the ratio of the nozzle mass to the payload mass. Moreover, the optimal conditions for the selected model reaction are conditions under which the synthesis time is 3 minutes, the ratio of the mass of the nozzle to the mass of the payload is 1.8, and the frequency is 10 Hz (600 revolutions per minute), providing shock operation.

3. Syntheses based on PPSSO and oxides of *s*- and *p*-elements

The synthesis of polyelementophenylsiloxanes based on PPSSO and oxides of *s*- and *p*-elements was carried out under the optimized conditions defined in Section 2 of this work. Beryllium, magnesium, and calcium oxides were used as starting compounds containing an *s*-element heteroatom.

The proposed reaction scheme for the interaction of PPSSO and alkaline earth metal oxides is as follows:



where the original $x = 1$ or 2 .

The beryllium atom did not enter the polymer chain at all, which can be explained by the extremely high energy of the crystal lattice and Gibbs energy. Beryllium oxide has a very high thermal conductivity, which at 100°C is 209.3 W/(mK). This can also explain the fact that the resulting high local temperature at the impact boundary of grinding media does not go to the excitation of radical ions but to the heating of the crystal.

The low percentage of magnesium entering the polymer chain can be explained from the standpoint described by Butyagin [23]. A magnesium oxide crystal consists of chemically inert Mg^{2+} and O^{2-} ions with electron shells like noble gases. The energy of electrostatic interaction for small doubly charged ions is quite high, so the crystal of magnesium oxide is sufficiently strong and inert. The crystal lattice energy of this oxide is 3810 kJ/mol. In calcium oxide, this energy is not much less (3520 kJ/mol), which also explains its inertness in the reactions initiated by mechanical activation.

Thus, the synthesis of polymetallophenylsiloxanes based on PPSSO and oxides of beryllium, magnesium, and calcium by this method under the selected conditions is not possible.

The opposite picture is observed for oxides of *p*-elements.

The proposed reaction scheme for the interaction of PPSSO with oxides of elements of group XIII is as follows:



The relative mass fraction of soluble fractions with increasing time is first increased and then slightly decreased. The ratio of $n \text{ Si/B}$ in soluble fractions differed from the predetermined one and approached 2:1 values, which confirms our earlier assumption that stable six-membered rings are formed.

A comparison of the results obtained during the mechanochemical activation of PPSSO with boron oxide and similar syntheses into which boric acid was introduced showed that using boric acid, products of a composition closer to the specified one are obtained. Apparently, the passage of the process was facilitated by the presence of protons in the system. This assumption is consistent with the conclusions of the authors of the work, which showed that “acidic” protons in mechanochemical reactions diffuse, as the most mobile, to the surface oxygen atoms (Lewis main centers). The consequence of this is the formation of water molecules and new metal-oxygen-metal bonds.

The interaction of PPSSO with alumina under conditions of mechanochemical activation in a vibrating ball mill was first described by us [24].

In the planetary ball mill, three syntheses based on PPSSO and alumina were performed, which differ in the initial ratios Si/Al = 1:1, 2:1, and 3:1.

It was found that regardless of the initial ratio, soluble polyaluminophenylsiloxanes with a Si/Al ratio of approximately 4 are obtained, which corresponds to the optimal coordination number of the aluminum atom.

A comparison of the results obtained in the planetary-type activator with the results in a vibration mill shows that the use of a more energy-intensive activator, such as the planetary monomill, leads to an increase in the mass fraction of the soluble fraction and to obtain a higher ratio of silicon to aluminum in the obtained soluble products with the same initial ratio of reagents.

The introduction of a more basic gallium oxide into the reaction led to the formation of products with trace amounts of metal, which indicates the effect of the nature of the introduced oxide on the ability to cleave the siloxane bond. Thus, the cleavage of the siloxane bond under the action of an oxide under the conditions of mechanochemical activation occurs easier, with a higher acidity of the corresponding oxide.

Based on the synthesized PPSSO with oxides of alkaline earth metals, boron, aluminum, and gallium, we can conclude that the heteroatom incorporation into the siloxane chain decreases with an increase in the basic properties of the oxide and an increase in the ionicity and strength of the crystal lattice:



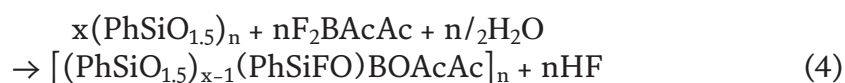
This conclusion is consistent with our conclusion [25], on the interaction of PPSSO with tin and germanium oxides under conditions of mechanochemical activation.

4. Study of the interaction of organosilicon compounds with different functionalities and boron difluoride acetylacetonate

In order to study the effect of the nature of the initial derivatives of the heteroatom on the process, boron difluoride acetylacetonate was used as the starting material. The initial Si/B ratios were 1:1, 2:1, and 3:1.

The choice of boron difluoride acetylacetonate is due to the great reactivity of this compound: in addition to reactive fluorine atoms, the interaction can be carried out at the hydrogen atom located in the gamma position of the acetylacetonate ring [26–28].

The proposed reaction scheme for the interaction of PPSSO and boron difluoride acetylacetonate is as follows:

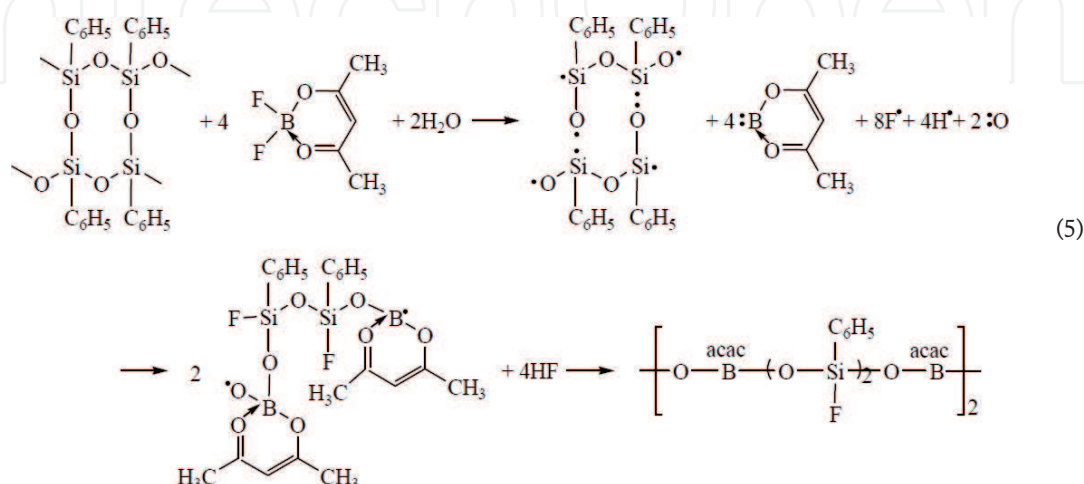


where the original $x = 1, 2$ or 3 .

Linear polyboronphenylsiloxanes containing fluorine atom at silicon and acetylacetonate group at boron have been synthesized by mechanochemical activation. Mechanochemical activation of polyphenylsilsesquioxane and boron difluoride acetylacetonate taken into molar ratio of 1:1 was shown to lead to the formation of polyboronphenylsiloxane with the given Si/B ratio.

The increase of the starting ratio Si/B enhances side processes and formation of polydisperse products with the Si/B ratio different from the desired one.

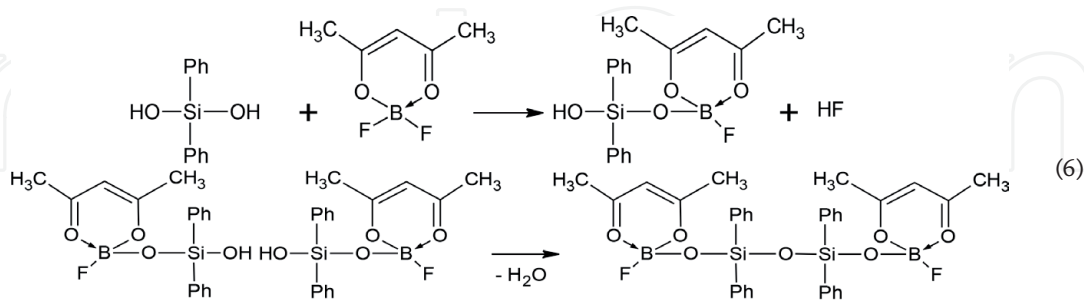
For the initial ratio Si/B = 1:1 by various physicochemical methods of analysis, including MALDI TOF, it was found that the synthesis is carried out according to the following scheme:



This synthesis was described in detail in previous work [29].

To study the effect of the functionality of the organosilicon derivative, diphenylsilanediol, triphenylsilanol, and octa(phenylsilsesquioxane) (Ph8T8 cubane) were used.

According to gel permeation chromatography, the soluble fraction of synthesis based on diphenylsilanediol is a low molecular weight substance with a relative molecular weight of 660. It was found that at the first stage of the synthesis, the starting materials condensed with the release of hydrogen fluoride, and then the reaction was carried out by hydroxide groups:



With a decrease in the functionality of the organosilicon derivative to unity (the use of triphenylsilanol), the formation of various degradation products of the starting compounds was observed. Only 1,3-difluoro-1,1,3,3-tetraphenyldisiloxane was isolated from a mixture of the resulting substances in an individual form, and the remaining substances were determined by chromat-mass-spectrometric analysis. Thus, tetraphenylsilane, triphenylfluorosilane, triphenylformylsilane, triphenylsilyl formic acid ester, and other products were discovered.

This synthesis was described in detail in previous work [30].

In continuation of the study of the influence of the functionality of the organosilicon compound on the course of mechanochemical activation, the

Ph8T8 cubane was introduced into the synthesis (it does not have functional reaction groups).

The interaction of the cubane with boron difluoride acetylacetonate did not occur due to the absence of water or hydroxyl groups, which were present in PPSSO, diphenylsilanediol, and triphenylsilanol and, according to the previously proposed scheme, taking part in the synthesis process.

The addition of the calculated amount of water to the “cubane-boron difluoride acetylacetonate” system resulted in the formation of a polymer product, the same as described for synthesis with PPSSO.

5. Interaction of PPSSO and acetylacetonates of alkaline earth metal and some p-elements

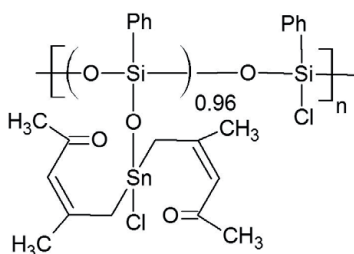
During the mechanochemical activation of PPSSO and beryllium, magnesium, and calcium oxides, the atoms of these elements did not enter the siloxane chain, which was associated with a high degree of ionicity of the corresponding oxides and, as a consequence, the high strength of the crystal lattice. Therefore, milder compounds, organic salts, and 2,4-pentanedionates were used.

In the case of the use of beryllium and magnesium acetylacetonates, the occurrence of a heteroatom did not occur. Apparently, during the activation process, these acetylacetonates were destroyed with the formation of stable oxides. However, when using a calcium salt, the heteroatom enters the siloxane chain (low metal percentage still remains). Thus, as in the interaction of PPSSO with alkaline earth metal oxides, an increase in the atom size facilitated the process of heterolytic polycondensation under these conditions, increasing the polarization of the compound and breaking of the bond in it.

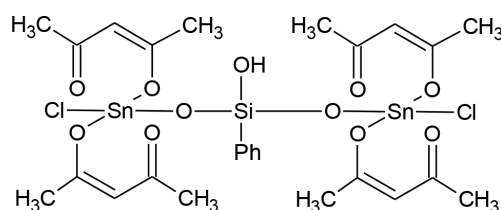
When aluminum tris-acetylacetonate is introduced into the reaction, products with a Si/Al ratio of 3:1 are formed (compared with the synthesis based on aluminum oxide). In the case of using gallium tris-acetylacetonate as the starting compound, a polymer product with a given Si/Ga ratio is obtained; however, its yield is not high (less than 26%).

A comparison of the results of syntheses based on aluminum and gallium acetylacetonates shows that an increase in the basicity of the heteroatom leads to a decrease in the mass fraction of polyelementorganosiloxanes; however, the Si/M ratio is closer to the specified one.

As a result of the mechanochemical activation of PPSSO and bis(acetylacetonate) tin dichloride (initial ratio Si/Sn = 1:1), three fractions are distinguished. The toluene-insoluble fraction is tin and silicon oxides, as well as the unreacted starting components. Fraction 2, obtained by precipitation of hexane from a toluene-soluble fraction, is a polymer product. The resulting ratio of Si/Sn differs from the set and is 1.96:1:



The third fraction is a monomeric compound corresponding to the following structural formula:



6. Conclusions

1. By the mechanochemical activation, low and high molecular weight element-toorganosiloxanes containing atoms of boron, aluminum, gallium, and tin can be synthesized. As starting materials, boron oxide, boric acid, boron difluoride acetylacetonate, aluminum and gallium acetylacetonates, and bis(acetylacetonate) tin dichloride can be used.
2. The composition and structure of the products obtained depend on the conditions of mechanochemical activation, as well as the initial ratio of the reacting substances.
3. An increase in the activation time and the ratio of the mass of the nozzle to the mass of the payload leads to the breaking of the siloxane bond and the removal of the heteroatom from the polymer chain by increasing the impact force from the grinding bodies.
4. During the mechanochemical activation of polyphenylsilsesquioxane and element oxides, the incorporation of the *p*-element heteroatom into the siloxane chain decreases in the series $B > Al > Ga$ with an increase in the basic properties of the oxide, an increase in the ionicity and strength of the crystal lattice, and the *s*-element heteroatom in the series $Ca > Mg > Be$ with a decrease in its radius and an increase in the strength of the crystal lattice of heteroatom oxide.
5. During the mechanochemical activation of polyphenylsilsesquioxane and organic derivatives of *s*- and *p*-elements, a heteropolycondensation reaction occurs, the result of which depends on the polarity of the $M-O-C$ bond: when alkaline earth metal acetylacetonates are used as the starting compounds, the polycondensation ability increases with the size of the atom included in the corresponding metal acetylacetonate and, accordingly, bond polarity: $Ca(AcAc)_2 > Mg(AcAc)_2 > Be(AcAc)_2$.
6. The course of the mechanochemical process, as well as the composition and structure of the reaction products, depends on the functionality of the starting compounds:
 - a. A decrease in the functionality of the organoboron derivative results in compounds with a lower Si/B ratio.
 - b. - A decrease in the functionality of the organosilicon derivative leads to its lower reactivity and the formation of low molecular weight reaction products.
7. The presence of hydroxyl groups and crystallization water affects the course of mechanochemical activation.

8. When using bifunctional halogen-containing organic derivatives of p-elements, the products of mechanochemical activation have a linear structure. Products of both polymer and monomeric nature are formed.

Conflict of interest

The authors declare no conflict of interest.

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