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Preparation of Polyboronphenylsiloxanes by Mechanochemical Activation

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Abstract—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 in molar ratio 1 : 1 was shown to lead to the formation of polyboronphenylsiloxane with the given Si/B ratio. The products are characterized by gel chromatography, IR, NMR spectroscopy, elemental analysis, and X-ray phase analysis. 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. The mechanism of the reaction is suggested.

Keywords: polyboronphenylsiloxane, polyphenylsilsesquioxane, boron difluoride acetylacetonate, mechanochemical activation

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Synthesis of organoelemental polysiloxanes is traditionally performed in organic solvents [1]. With the goal to elaborate environmentally safe solvent-free methods of the synthesis of polyorganometalsiloxanes we have studied the synthesis of these compounds under the conditions of mechanochemical activation [2–6]. Typically, the reaction of heterofunctional polycondensation was used proceeding with elimination of sodium chloride. Its removal by water treatment results in partial hydrolysis and removal of metal from the polymer chain. In [6], we have first studied the splitting of the siloxane bond by metal oxides under the conditions of mechanochemical activation. However, we failed to reach the given Si/Me ratio.

In continuation of these studies in the present work we have investigated the synthesis of polyboronphenylsiloxanes by mechanochemical activation using the earlier unknown reaction of polyphenylsilsesquioxane with boron difluoride acetylacetonate. As a variable parameter the starting ratio Si/B was chosen.

Boron difluoride acetylacetonate and polyphenylsilsesquioxane taken in the Si/B molar ratios of 1 : 1 (synthesis *a*), 2 : 1 (synthesis *b*), and 3 : 1 (synthesis *c*) were activated in a planetary ball mill (see Experimental). In all syntheses the activation time was 3 min. Apparently, the reaction proceeds according to Eq. (1):

$$x(\mathrm{PhSiO_{1.5}})_n + n\mathrm{F_2B(acac)} + n/2\mathrm{H_2O} \rightarrow [(\mathrm{PhSiO_{1.5}})_{x-1}(\mathrm{PhSiFO})\mathrm{BO(acac)}]_n + n\mathrm{HF}, \quad (1)$$

$$x = 1\ (a),\ 2\ (b),\ 3\ (c).$$

The obtained products are viscous substances of yellowish (synthesis *a*), brown (synthesis *b*) or light-brown color (synthesis 3). No insoluble fractions remained after extraction of the products with toluene in the Soxhlet apparatus.

From the data of gel chromatography, the dispersity of the products is increased with the decrease of the fraction of the starting boron difluoride acetylacetonate. Thus, the molecular mass M_r of the product from synthesis *a* (Si : B = 1 : 1) is ≥ 5000 (Fig. 1). The product from synthesis *b* (Si : B = 2 : 1) is a mixture of compounds with $M_r \geq 5000$ and $M_r \approx 1200$ (Fig. 1). The product from synthesis *c* (Si : B = 3 : 1) apart from high-molecular compounds contains a low-molecular compound with $M_r \approx 400$ (Fig. 1).

All products were treated by fractional precipitation in toluene–hexane. Then two fractions were formed from the products of syntheses *b* and *c* and one fraction from synthesis *a*.

The elemental analysis of the product from synthesis *a* corresponds to the taken composition (compound **I**, table). Its high viscosity (81.6 mL/g) determined by the method of viscometry and the elemental composition are indicative of the linear structure of the polymer and its rather high molecular mass. Therefore, compound **I** is polyboronphenylsiloxane with the fluorine atom at silicon and the acetylacetonate group at boron, $[(PhSiFO)OB(acac)]_n$. Its structure was proved by the IR and NMR spectroscopy data. The IR spectra of all products contain absorption bands at 1430 and 1135 cm^{-1} corresponding to the Si–Ph bond vibrations in siloxanes and silsesquioxanes, respectively. The =B–O vibration bands in the B–O–Si fragment are observed at 1360 and 1380 cm^{-1}. Besides, the IR spectra contain a doublet signal corresponding to the stretching vibrations of the C=O bond at 1555 cm^{-1}.

In the ^{19}F and ^{11}B NMR spectra of compound **I** intense signals appear at 27 and 0 ppm, respectively. The chemical shift of 0 ppm in the ^{11}B NMR spectrum is indicative of the presence of three oxygen atoms in the surrounding of the boron atom similar to anion BO_3^{3-}. The quadrupole moment of the boron atom does not allow obtaining a high resolution spectrum. The only ^{19}F NMR signal at 27 ppm points to the presence of the fluorine atom at silicon.

The X-ray diffraction pattern of compound **I** (Fig. 2) apart from amorphous galo ($d_1 = 11.18$ and $d_2 = 4.69$) contains the signals corresponding to the crystalline phase. The intensity of these peaks reaches 5000, which is indicative of a high degree of crystallinity of the compound. With lowering the temperature of measurements the intensity of the peaks of the crystalline forms drops to 160.

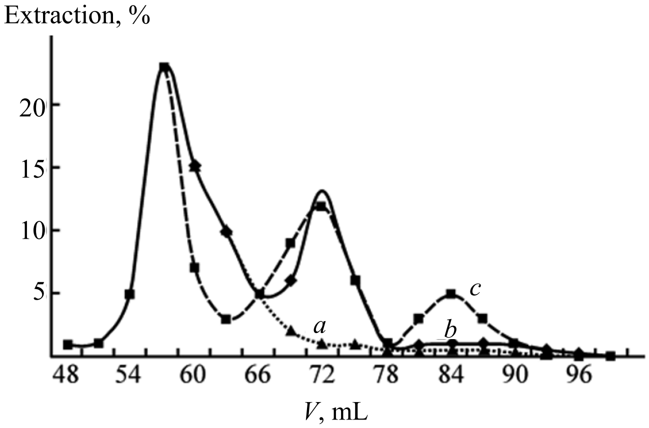
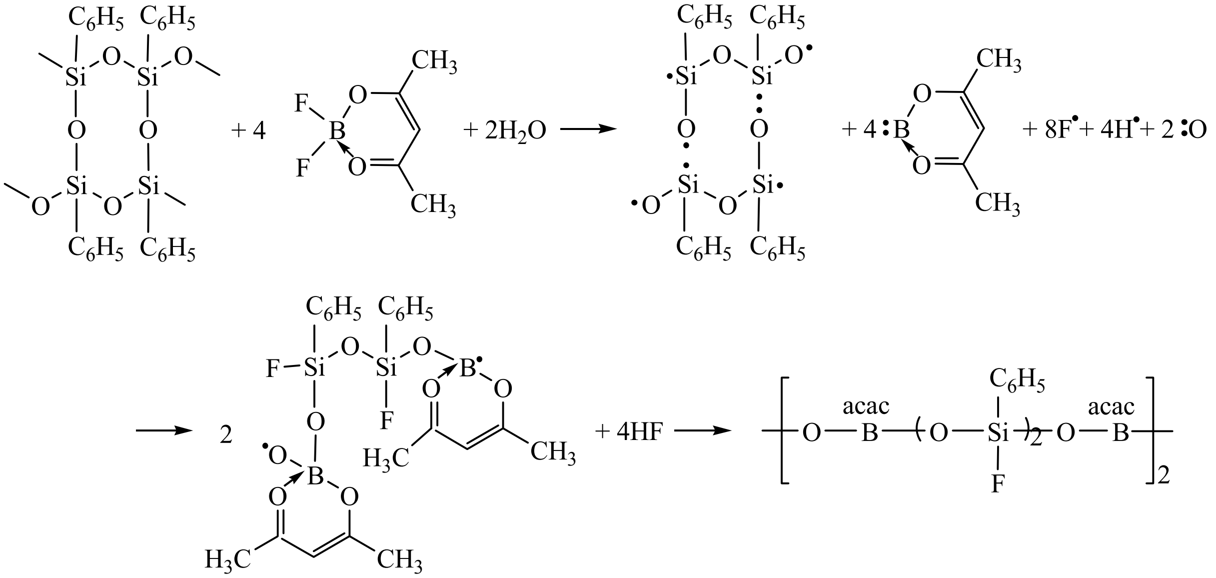


Fig. 1. Gel permeation chromatography of the products of syntheses *a–c*.

According to [7], the intensity of separate reflections may increase with temperature when the increase is followed by structural changes, that is, phase transitions or recrystallization. Phase changes of compound **I** are observed visually: It becomes more dense at storage. The color is also changed to more light. The mechanism of transformations may be suggested with Scheme 1.

The possibility of the rupture of the Si–O–Si bond by the radical mechanism at the mechanochemical activation is in agreement with the literature data [8] and was proved by the results of the mass-spectro-

Scheme 1.



Elemental composition of polyboronphenylsiloxanes

Comp. no.	Si/B	Found, %					Calculated, %			
		C	Si	B	F	Si/B	C	Si	B	F
I	1 : 1	50.3	10.3	3.5	7.3	1.1 : 1	$[(PhSiFO)OB(acac)]_n$			
							49.7	10.5	4.1	7.1
IIa	2 : 1	53.3	11.3	4.3	0.2	1 : 1	$[(PhSiO_{1.5})_{0.98}(PhSiFO)_{0.02}OB(acac)]_n$			
							51.8	11.0	4.2	0.2
IIb	2 : 1	48.9	20.8	1.1	1.7	7.3 : 1	$\{(PhSiO_{1.5})_{5.8}(SiO_2)_{1.5}[OB(acac)]_{0.6}\}_n{\cdot}0.4n[BF_2(acac)]$			
							48.9	20.9	1.1	1.6
IIIa	3 : 1	53.0	14.1	1.7	6.1	3.2 : 1	$[(PhSiO_{1.5})_{1.2}(PhSiFO)_2OB(acac){\cdot}0.6C_6H_5CH_3]_n$			
							55.4	14.5	1.7	6.1
IIIb	3 : 1	51.2	14.1	2.5	9.2	2.2 : 1	$(PhSiFO_{1.5})_2B(acac)$			
							50.3	13.8	2.7	9.4

metry study of ionization using the MALDI method. Fragmentation of compound **I** leads to the formation of fragments of composition $[(PhSiFO)BO(acac)]_n$ and $PhSiFO[(PhSiFO)BO(acac)]_n$, where n = 4–9.

The increase of the starting Si : B ratio to 2 : 1 (synthesis *b*) or 3 : 1 (synthesis *c*) results in the formation of fractions with the Si : B ratio different from the originally given.

Fraction **IIa** (compound **IIa**) is polyboronphenylsiloxane with the Si/B ratio equal to 1, $[(PhSiO_{1.5})_{0.98}{\cdot}(PhSiFO)_{0.02}OB(acac)]_n$. The mass fraction of it is less than in the synthesis *a*.

Fraction **IIb**, from the data of chromatomass spectrometry and column chromatography is a mixture of products of the composition $\{(PhSiO_{1.5})_{5.8}(SiO_2)_{1.5}{\cdot}[OB(acac)\}_{0.6}]_n{\cdot}0.4n[BF_2(acac)\}$, which is indicative of

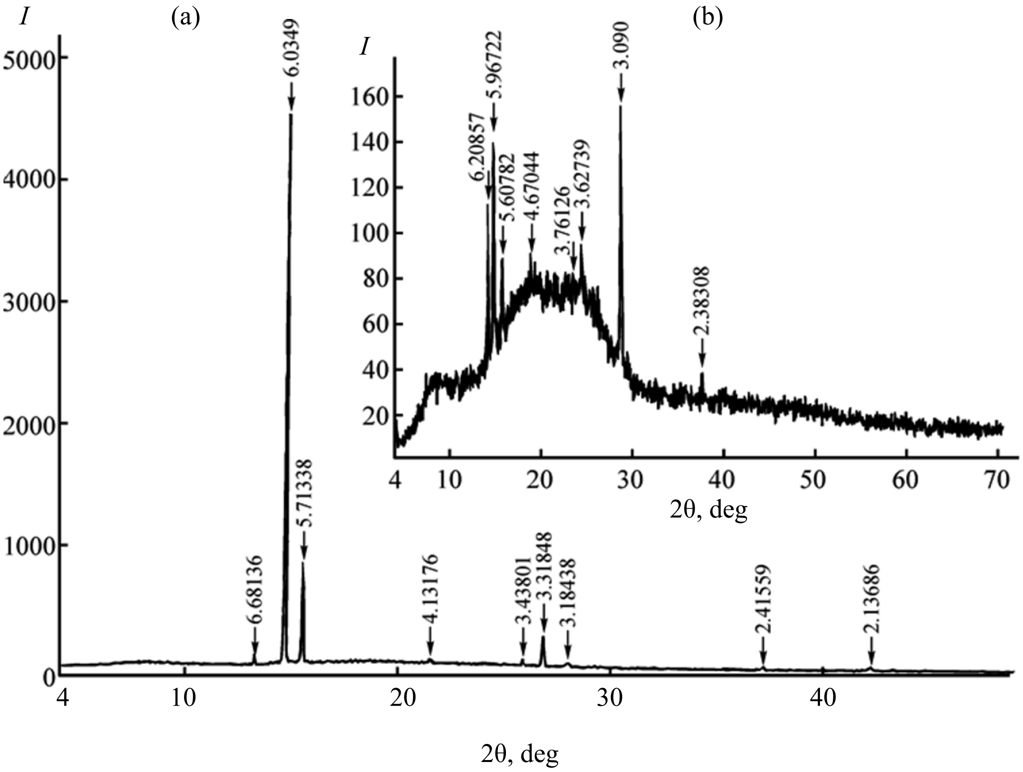


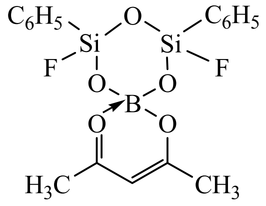
Fig. 2. X-Ray diffraction pattern of compound **I** at (a) 25°C and (b) –150°C.

a partial elimination of the phenyl radical. Apparently, in this case the processes of decomposition of the siloxane chain under mechanochemical activation proceed more actively than in the synthesis *a*.

The products of synthesis **III** (with the starting ratio Si : B = 3 : 1) are as follows: fraction **IIIa** is $[(PhSiO_{1.5})_{1.2}(PhSiFO)_2OB(acac)\cdot 0.6C_6H_5CH_3]_n$ and fraction **IIIb** is $(PhSiFO_{1.5})_2B(acac)$.

The Si : B ratio in the high-molecular fraction **IIIa** ($M_r \geq 5000$) is close to that in the charge. Its mass fraction is less than that of the similar fractions in syntheses *a* and *b*. Apparently, this is due to the decrease of the fluorine content in the reaction mixture. Besides, this proves the assumption that the increase in the starting ratio Si/B leads to the increase in the processes of decomposition of the siloxane chain under the action of mechanochemical activation.

Fraction **IIIb**, from the elemental analysis and gel chromatography data ($M_r \approx 400$) is a cyclic product:



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In the IR spectrum of this compound the absorption bands in the region 3600–3200 cm^{-1} are lacking that proves this assumption. Our attempt to isolate the compound by distillation failed because of its polymerization.

On the X-ray diffraction pattern of the product of synthesis *b* (Fig. 3) the intensity of the peaks corresponding to the crystalline phase is lower, about 400, and remains practically constant with temperature. This is suggestive of a lower crystallinity of the products of synthesis *b*.

The decrease in the degree of crystallinity with the decrease in the boron content and increase in the temperature (in the case of compound **I**) can be due to the presence of the –O→B coordination bonds in the structure. The number of these bonds is decreased with temperature and with the decrease of the boron content.

To conclude, the mechanochemical activation of polyphenylsilsesquioxane and boron difluoride acetylacetonate in the ratio of 1 : 1 results in the formation of soluble products with the desired Si/B ratio and proceeds by Eq. (1). The increase in the starting ratio Si/B leads to more complex processes due to the decomposition of the siloxane chain during mechanochemical activation.

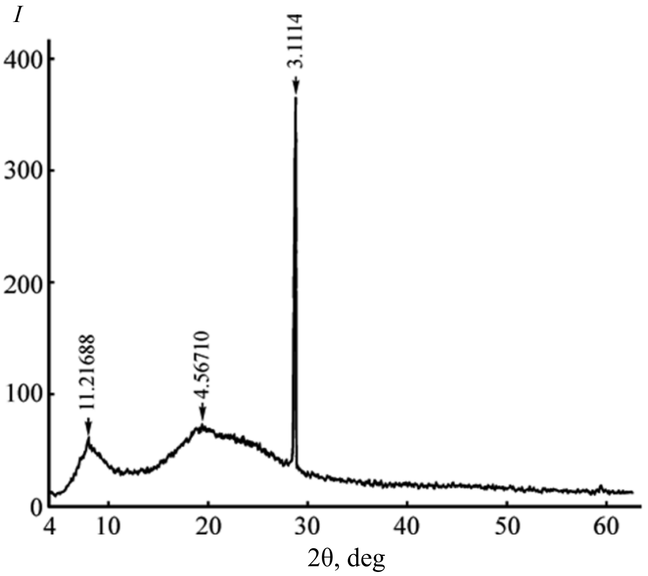

Fig. 3. X-Ray diffraction pattern of compound **IIa**.

EXPERIMENTAL

IR spectra were recorded on a Hewlett Packard Series 1110 MSD spectrometer in KBr pellets. X-Ray phase analysis was performed on a Bruker AXS D8 Advanced instrument. ^{11}B, ^{19}F NMR spectra were registered on a spectrometer Avance 400 (Bruker). Gel chromatography was performed on a column of 980 mm length and 12 mm diameter filled with copolymer of polystyrene and 4% of divinyl benzene. Diameter of grains 1 mm, eluent – toluene, flow rate 1 mL/min, the weight of the specimen was ~ 0.2 g. The detection was performed by weighing the dry residue in the fractions. The specimen was dissolved in 2 mL of toluene and passed through the column. Fractions of 3 mL were collected, the solvent removed in a drying box till constant mass.

Matrix-assisted laser desorption/ionization (MALDI) mass spectra were taken on a MALDI mass spectrometer ULTRA FLEX III (Bruker, Germany). The solution of the polymer in chloroform with concentration of 0.01 mg/mL was prepared. 1 μL of the solution was placed on the target. As a matrix, 1 μL of dihydrobenzoic acid was used.

Boron difluoride acetylacetonate was prepared by the known procedure [9]. Yield 85.2 %. Found, %: C 41.0; B 7.4; F 25.3. $C_5H_7O_2BF_2$. Calculated, %: C 40.6; B 7.3; F 25.7.

Synthesis *a*. A planetary ball mill “Pulverisette 6” with stainless still balls was charged with 0.05 mol of polyphenylsiloxane and the equivalent amount of boron difluoride acetylacetonate. The ratio of the mass of the charged material to the mass of balls equals 1.8. The time of activation was 3 min at 600 rpm (10 Hz). The product was isolated by extraction with toluene in the Soxhlet apparatus. The solvent was removed first at atmospheric pressure and then under a vacuum of a water pump. No insolable fractions remained. Compound **I** was obtained by fractional crystallization in toluene–hexane mixture (see table). The yield with respect to boron was 78.8 %, to silicon, 89.4%.

Synthesis *b*. Similar to synthesis *a*; 0.1 mol of polyphenylsiloxane and 0.05 mol of boron difluoride acetylacetonate were charged in the reactor. The Si/B ratio was 2 : 1. Fractional precipitation from toluene–hexane gave products **IIa** and **IIb** (see table). Fraction **IIa**: yield with respect to boron 94.2 %, yield with respect to silicon – 48.6%. Fraction **IIb**: yield with respect to boron 5.7 %, yield with respect to silicon, 21.5%.

Synthesis *c*. Similar to synthesis *a*; 0.06 mol of polyphenylsiloxane and 0.02 mol of boron difluoride acetylacetonate were charged in the reactor. The Si/B ratio was 2 : 1. Fractional precipitation from toluene–hexane gave products **IIIa** and **IIIb** (see table). Fraction **IIIa**: yield with respect to boron 45.4 %, yield with respect to silicon 49.3%. Fraction **IIIb**: yield with respect to boron 54.4 %, yield with respect to silicon 40.2%.

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