Synthesis of alkoxybenzylmethylsilanes and polybenzylmethylsiloxane polymers on their basis

S. A. Milenin,[a]★ A. A. Kalinina,[a] V. V. Gorodov,[a] N. G. Vasilenko,[a] M. I. Buzin,[b] and A. M. Muzafarov[a,b]★

[a]*N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation.
Fax: +7 (495) 335 9000
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085. E-mail: aziz@ispm.ru

An efficient solvent-free procedure for the preparation of alkoxybenzylmethylsilanes by organomagnesium synthesis was developed. The reaction conditions gave the high yields of the target products. A number of benzylmethylsiloxane polymers was synthesized by polycondensation of alkoxybenzylmethylsilanes in anhydrous acetic acid. The products obtained can become a good alternative to phenylsiloxanes in some practical applications.

Key words: organoalkoxysilanes, organomagnesium synthesis, alkoxybenzylmethylsilanes, polycondensation, polybenzylmethylsiloxanes.

The introduction of aromatic fragments into the composition of polyorganosiloxanes increases their oxidation, thermal, and thermooxidation stability.[1] The most studied phenyl-substituted polyorganosiloxanes are already widely used in practice. It was found that phenyl groups in polymethylphenylsiloxane also stabilize the methylsiloxane fragments. The presence of phenyl substituents leads to the improvement of physical and mechanical properties of siloxane polymers. Polybenzylmethylsiloxanes are another type of organosilicon polymers containing an aromatic group. They are studied poorly and yet have no practical application, while the benzylsiloxane products of oligomeric and cyclic structure were obtained by S. Kipping using a hydrolytic polycondensation of dibenzylchlorosilane and benzyldichloroethylsilane just at the beginning of 20th century.[2] The chemical stability of the benzyl group at the silicon atom as compared to the phenyl substituent was also studied at that time. An increased stability of benzyl siloxane polymers to strong acids as compared to the phenyl analogues is the most attractive property from the practical point of view. Thus, the phenyl group can be substituted by the hydroxy one with the cleavage of benzene upon treatment with concentrated sulfuric acid at the temperature below 100 °C, whereas the benzyl group under the same conditions remains at the silicon atom. Conversely, in the alkaline medium the Si—Ph bond is stable under very drastic conditions, while the $Si—CH_2—Ph$ fragment disintegrates relatively easy with the liberation of toluene. Both substituents (phenyl and benzyl) eliminate from the silicon atom upon treatment with aluminum chloride at the temperature considerably below 100 °C. The benzyl group also can be removed upon treatment with sodium metal.[3,4] Therefore, in the cases when a latent functionality at the silicon atom is required, for example, a stable protecting group, the use of the benzyl group has clear advantages. However, since the first S. Kipping's works there are practically no publications dealing with the synthesis and studies of properties of the benzyl-containing siloxane products, except of several works in which, however, no efficient procedures for the preparation of such polymers were suggested.[5—8] At the same time, the new approaches to the synthesis of alkoxy functional benzylmethylsilanes and polybenzylmethylsiloxanes on their basis open a possibility of various applications for these compounds.

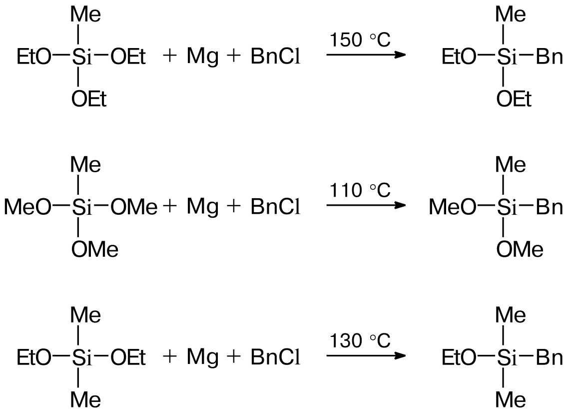
Results and Discussion

Synthesis of alkoxybenzylsilanes. One of the reason for the lack of studies of benzyl-containing siloxanes is the shortage of efficient methods for the preparation of the starting compounds, functional benzylsilanes. Since the polycondensation of organoalkoxysilanes was shown to be the most acceptable method for the preparation of polyorganosiloxanes from both technological and environmental points of view, we developed the synthesis of alkoxy functional benzylsilanes. Organometallic synthesis which uses the Grignard reaction is the most convenient method for the preparation of aryl-containing functional silanes. This method was used in the preparation of benzylchlo-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2498—2504, October, 2015.

rosilanes in the laboratory practice.[2,9—11] Alkoxybenzylsilanes were generally obtained by esterification of chlorosilanes, except the works,[12,13] in which a possibility of organometallic synthesis of such monomers was demonstrated based on tri- and tetraalkoxysilane, but the yield of the target products was below 10%. We carried out a search for the optimal conditions for the organomagnesium synthesis of benzylethoxymethylsilanes in high yield of the target products and the minimal technological risks. Industrially available $MeSi(OEt)_3$ and $Me_2Si(OEt)_2$ were used as the starting compounds (Scheme 1).

Scheme 1



The process was carried out in the absence of organic solvents in the excess of alkoxysilane.[14] To optimize the synthesis, we varied the ratio of reagents involved in the process and found the ratio providing the highest yield of the target product (Table 1).

The data obtained showed that the excesses of magnesium and triethoxymethylsilane have a noticeable influence on the result of the reaction. The maximal yield of the target product (70%) was reached at the molar ratio $MeSi(OEt)_3 : BnCl : Mg = 2.5 : 1.0 : 1.5$ (see Table 1, entry *3*). A further increase in the content of these reagents relative to the amount of BnCl practically did not lead to the change in the yield of the target product.

Table 1. The yield of $BnMeSi(OEt)_2$ depending on the ratio of reagents

Entry	Ratio of reagents/mol			Yield (%)
	$MeSi(OEt)_3$	BnCl	Mg	
1	1.6	1.0	0.8	16.1
2	2.0	1.0	1.5	46.5
3	2.5	1.0	1.5	70.0
4	3.0	1.0	1.1	37.2
5	3.0	1.0	2.0	71.0

Silane $BnMe_2SiOEt$ was obtained according to a similar procedure with a two-fold excess of diethoxydimethylsilane and magnesium relative to benzyl chloride. The highest yield of the target product was 65%.

To sum up, the optimization of the reaction conditions allowed us to obtain the target compounds in high yield, whereas the absence of diethyl ether in the reaction medium considerably increased the processability of the method.

Specific feature of organomagnesium synthesis of benzylethoxymethylsilanes is that there is no need to activate the reaction by standard activators such as dibromoethane, iodine, or phenyl bromide used in similar reactions for the preparation of ethoxymethylphenylsilanes. This is explained by the high enough activity of benzyl chloride as compared to phenyl chloride in the Grignard reaction. The process is activated spontaneously with an extensive evolution of heat upon addition of reagents.

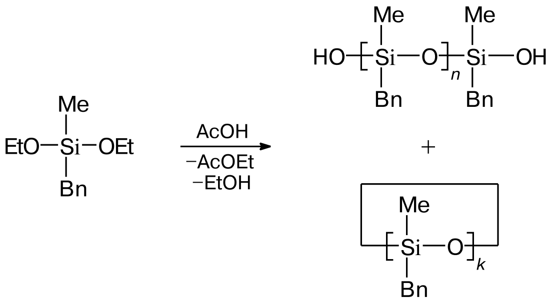
Another advantage of the suggested synthesis of benzyl-substituted silanes is a possibility of preparation of $BnMeSi(OMe)_2$, whereas the synthesis of phenyl-substituted methoxysilanes is not feasible. The yield of $BnMeSi(OMe)_2$ at the ratio of the starting reagents $BnCl : MeSi(OMe)_3 : Mg$ equal to 1.0 : 2.5 : 1.5 was 67%.

In conclusion, the studies of the synthesis of $BnMeSi(OEt)_2$, $BnMeSi(OMe)_2$, and $BnMe_2SiOEt$ in nonetherial medium showed that the preparation of these compounds has a number of advantages as compared to the processes of preparation of their phenyl analogues. The reaction with benzyl chloride does not require activation of the reaction mixture, the reaction begins spontaneously upon reflux, is accompanied by evolution of heat, which maintains the reflux of the reaction mixtures. In the process of preparation of benzylethoxysilanes, a small amount of a side product bibenzyl was obtained, which was formed by the mechanism of Wurtz reaction. It is not toxic, in contrast to biphenyl formed in the similar process of preparation of ethoxyphenylsilanes. The yield of alkoxybenzylsilanes was ~70%, that is higher than the yield of the methylphenyl analogues.

Synthesis of polybenzylmethylsiloxanes. Nowadays, the most promising method for the preparation of polyorganosiloxanes based on organoalkoxysilanes is the polycondensation in the "active medium", anhydrous acetic acid, which plays the role of both the reagent and the solvent. It was shown earlier that this process is a complex of the cascade interrelated reactions proceeding with participation of water formed in the course of esterification reaction between acetic acid and alcohol. The alcohol, in turn, is formed in the acetoxylation of alkoxysilane.[15] The formed water *in situ* is consumed in the hydrolysis reaction of acetoxysilyl groups. Then, the heterofunctional condensation of silanols with acetoxysilyl groups results in the formation of the siloxane bond. The acetic acid formed at this stage returns back to the reaction cycle. This mechanism explains a number of specificities and advantages of this procedure: the process in all the stages proceeds in the homogeneous medium, is well controlled, and makes it possible to prepare polymeric product with a required structure.

The polycondensation of $BnMeSi(OEt)_2$ in the excess of anhydrous acetic acid led to the formation of a mixture of linear oligomers with terminal hydroxy groups and cyclic compounds (Scheme 2), which is typical of the processes of polycondensation of difunctional organosilicon monomers.

Scheme 2



The reaction was monitored by the changes in the intensity of signals of the protons of the ethoxysilyl groups in the ^1H NMR spectrum of the reaction mixture samples at the 100% conversion of the Si—OEt groups. The reaction product was also analyzed by GPC and IR spectroscopy.

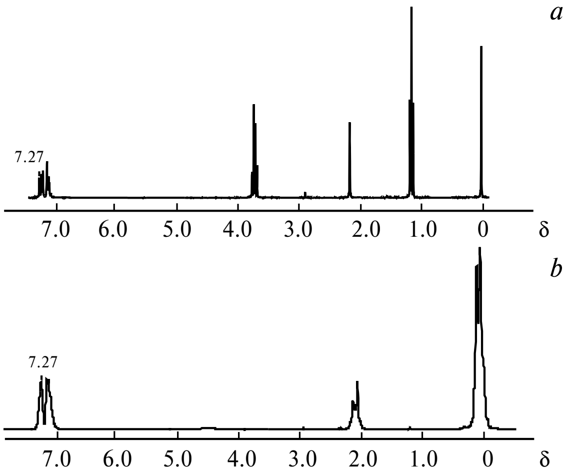


Fig. 1. ^1H NMR spectra of the starting benzylmethyldiethoxysilane (*a*) and the condensation product (*b*).

To determine the amount of terminal hydroxy groups, we carried out the blocking of obtained oligobenzylmethylsiloxanes with chlorotrimethylsilane (Scheme 3) under conditions allowing to retain the composition of the starting products (GPC data), but with a full conversion of the hydroxy groups, which was confirmed by the absence in the IR spectra of the blocked samples of the absorption band in the region of 3100—3600 cm^{-1} characteristic of the SiOH groups.

When the polycondensation was carried out simply by mixing the reagents, the reaction product was a ~50% mixture of linear and cyclic oligomers with ~20 mol.% content of terminal hydroxy groups. We studied a possibility of increasing the process selectivity. As it was mentioned above, in the polycondensation of organoalkoxysilanes in anhydrous acetic acid the water necessary for the hydrolysis is generated in the esterification reaction, the rate determining step of the process. It was shown earlier that the composition of the reaction products can be controlled varying the rate of water generation in the condensation process. Slowing the rate of the liberation of water in the system leads to a predominant formation of linear oligomers, whereas an increase in the rate favors formation of cyclic oligomers.[16]

Cyclic benzylmethylsiloxanes can be of interest as monomers for preparation of polybenzylmethylsiloxanes by polymerization. For their selective formation in the process of polycondensation of $BnMeSi(OEt)_2$ in acetic acid, it is necessary to increase the rate of liberation of water, which, as it was shown earlier, can be reached by the addition of an alcohol into the reaction mixture. The addition of ethanol during polycondensation of $BnMeSi(OEt)_2$ in the active medium allowed us to increase the content of cyclic components to 75% with the fairly high content of valuable cyclotrisiloxane (Table 2).

To increase the content of linear oligomers in the product, the synthesis was carried out by a gradual addition of $BnMeSi(OEt)_2$ to the refluxing acetic acid in order to decrease the rate of the formation of ethanol and, therefore, water in the reaction mixture (Table 3) as compared to the experiment with the simultaneous mixing of reagents. However, the expected effect of the increase in the selectivity of the process (the growth of the amount of

Scheme 3

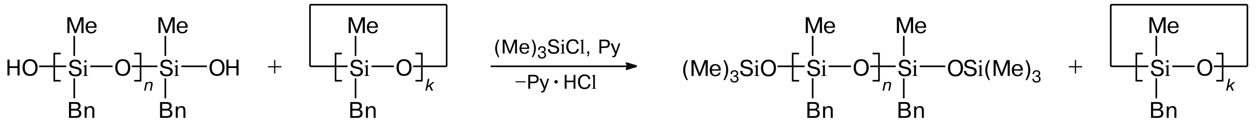


Table 2. The influence of the reaction conditions of polycondensation of $BnMeSi(OEt)_2$ in acetic acid with additives of ethanol on the yield of cyclosiloxanes

Entry	Ratio of reagents /mol			Yield of cyclosiloxanes (%)	Content in the product* (%)	
	$BnMeSi(OEt)_2$	AcOH	EtOH		$[BnMeSiO]_3$	$[BnMeSiO]_4$
1	1	3	0.5	51	39	12
2	1	3	5	76	58	18
3	1	10	0.5	38	28	10
4	1	10	5	74	50	24

*GPC data.

Table 3. The condensation of benzylmethyldiethoxysilane in acetic acid

Reaction conditions	Yield (%)	
	Linear oligomer	Cyclic oligomer
Simultaneous mixing of reagents	50	50
Slow addition of alkoxysilane	66	34

linear products by ~10%) was considerably smaller than in the case of methylphenyl oligomers (~40%).[16]

The linear oligomers with terminal hydroxy groups are promising starting compounds for both the development of different polymeric compositions and the preparation of high-molecular-weight polymers. It is known that the molecular weight of linear polycondensation oligomeric products can be increased by the homocondensation of terminal hydroxysilyl groups. The process of high-temperature condensation in the temperature range 50—160 °C (*in vacuo* and in the absence of catalysts) did not lead to a noticeable effect: the GPC data showed that the content of both the cyclic components and the linear oligomers remained the same (Fig. 2, curves *1—4*). The use of a catalytic amount of potassium acetate resulted in the considerable increase in the molecular weight of the polymer (see Fig. 2, curve *5*). The polybenzylmethylsiloxane was obtained with the molecular mass of 7000 a.m.u. The process was not accompanied by the unwanted depolymerization, the content of cyclic products in the mixture did not increase.

To sum up, the polycondensation of dialkoxybenzylmethylsilane in the active medium makes it possible to obtain cyclic and linear benzylmethylsiloxanes. The alternation of the reaction conditions allows one to change the ratio of cyclic and linear oligomers in the reaction product. The catalytic homocondensation of hydroxy functional linear oligomers leads to the formation of high-molecular-weight benzylmethylsiloxanes.

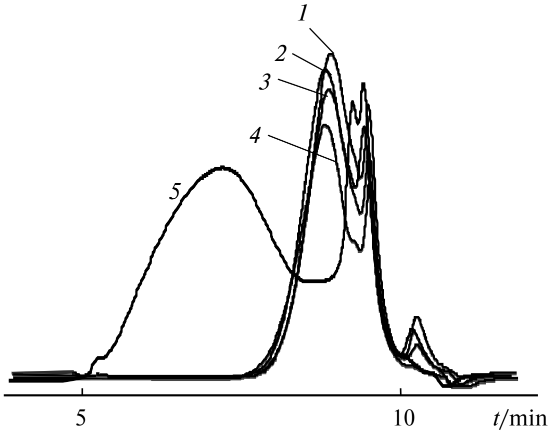


Fig. 2. The GPC curve of the starting oligomer (*1*), the products of homocondensation of the starting oligomer at 50 (*2*), 10 (*3*), 160 °C (*4*), and the product of catalytic condensation of the starting oligomer in the presence of potassium acetate (*5*).

The new organosilicon aryl-containing polymer, *viz.*, the linear polybenzylmethylsiloxane, has the physicochemical properties practically similar to those of its known analogue polymethylphenylsiloxane. The introduction of the methylene spacer between the phenyl group and the silicon atom did not noticeably change the thermal properties of the polymer. The glass transition temperatures of polymethylphenylsiloxane and polybenzylmethylsiloxane of close molecular masses (MM ~ 30000 a.m.u.) are practically the same: –22 °C for polymethylphenylsiloxane[17] and ~–(20—22) °C for polybenzylmethylsiloxane (DSC data) (Fig. 3).

The new aryl-containing polymer is characterized by the high thermal stability: the thermal decomposition of the polymer starts at 370 °C (Fig. 4). The mass loss upon heating of polymethylphenylsiloxane begins at the same temperatures.[17] The processes of thermooxidation destruction in both cases begin in the region of 250 °C. The TGA curves of the benzylmethyl polymers (both in air and in an inert gas) has a shoulder at ~400 °C attributed, apparently, to the cross-linking process of the polymeric chains through the hydrocarbon bridges upon the loss of phenyl

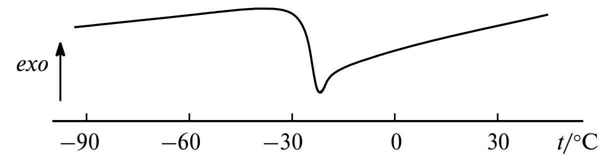


Fig. 3. The DSC thermogramm of polybenzylmethylsiloxane.

substituents. However, the general picture of thermal stability is not affected by this process. It can be concluded that he thermal stability of polybenzylmethylsiloxane is not inferior to that of known methylphenylsiloxane analogues.

It is known that even a small amount of phenyl substituents in the composition of methylsiloxane copolymers determines a number of valuable characteristics and, first of all, extends the temperature range of the efficient exploitation of the material, for example, as organosilicon liquids. The efficiency of the effect of aromatic substituents depends not only on their amount, but also on their distribution in macromolecule. It was shown earlier that the polycondensation of organoalkoxysilanes in anhydrous acetic acid is the optimal method for the preparation of copolymeric products, which provide the absence of homofunctional impurities, the uniformity of the copolymer chain structure, and a full agreement between the amount of comonomers taken for the reaction and the corresponding unlike units in the final product.[18] This procedure was used to synthesize a benzyl-containing organosilicon copolymer. To compare the properties, the ratio of methyl and benzyl substituents and the amount of branching methylsilsesquioxane units were chosen the same as in the industrial methylphenyl product (Scheme 4).

To decrease the amount of low-molecular-weight cyclic products, the reaction was carried out by a slow addition of a solution of monomers in acetic acid to the refluxing acetic acid. The GPC data indicate that the polycondensation product is characterized by a bimodal distribution of molecular masses, with the content of the oligomeric part being 80% (M_{pica} 1100 a.m.u.). The IR spectra of the obtained oligomer exhibits the bands attributed to the residual hydroxy groups, the amount of which assessed from the ^{1}H NMR spectrum of the sample blocked with chlorotrimethylsilane is 1.6% (Fig. 5).

The presence of hydroxy groups was used for the increase of the copolymer molecular mass. In the absence of catalysts, the process was not successful. Therefore, we carried out a catalyzed post-condensation of the hydroxy groups. It was interesting to conduct this reaction in the presence of acidic catalysts, which cannot be used in the case of copolymers with phenyl substituents because of the instability of phenylsiloxane bond in acidic media. The use of sulfuric acid as the catalyst allowed us to increase the molecular mass of the product to 3500 a.m.u.

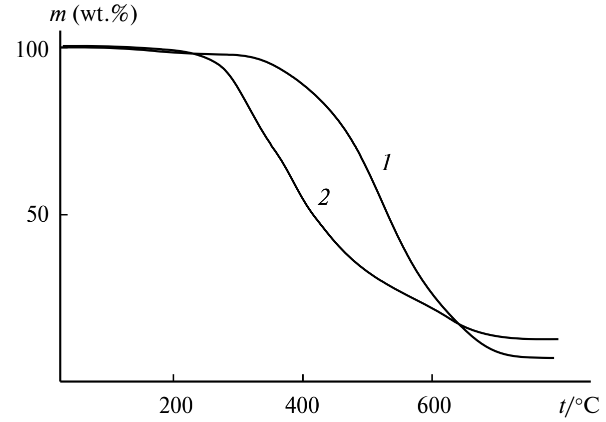


Fig. 4. The TGA curves of polybenzylmethylsiloxane in air (*1*) and in an inert gas (*2*).

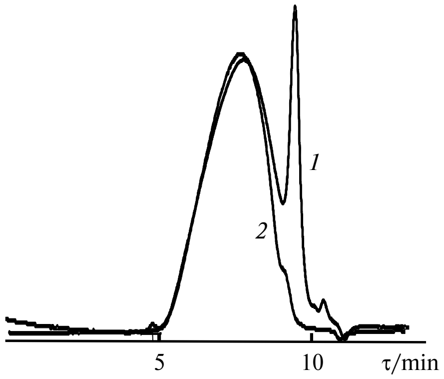
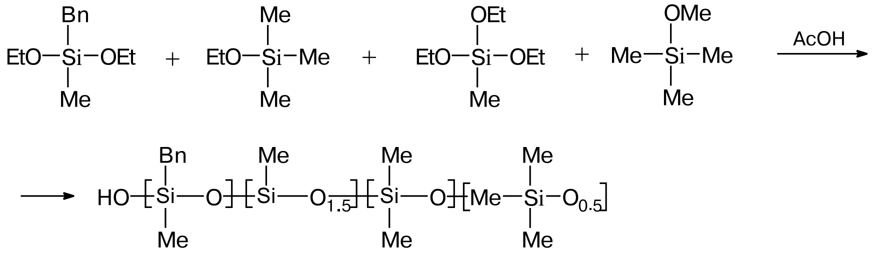


Fig. 5. The GPC curves of copolycondensation product after reaction (*1*) and after evacuation (*2*).

Scheme 4



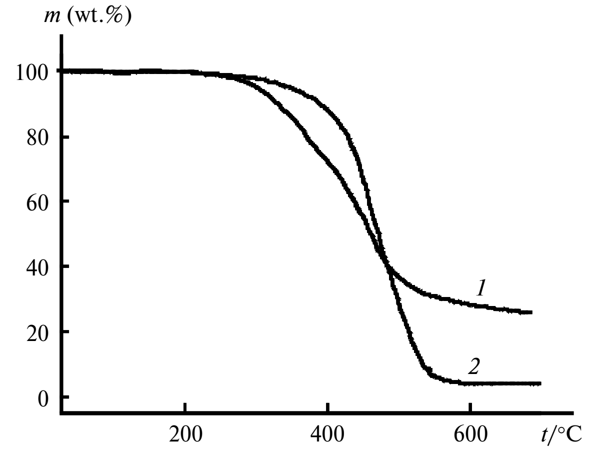


Fig. 6. The TGA curves of benzylmethylsiloxane copolymer in air (*1*) and in an inert gas (*2*).

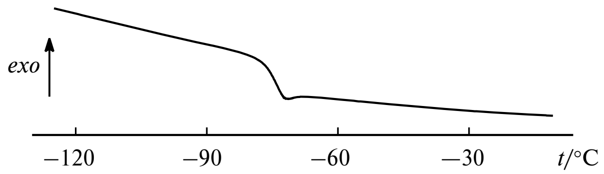


Fig. 7. The DSC thermogramms of benzylmethylsiloxane copolymer.

The TGA (Fig. 6) and DSC results (Fig. 7) indicate a good thermal stability of the synthesized benzylmethylsiloxane copolymer. Its thermal properties are similar to those of the phenyl-containing copolymer.[18]

In conclusion, the introduction of the benzyl substituent in the composition of siloxane polymers of both the homo- and the copolymeric structure leads to the formation of compounds whose thermal characteristics are not inferior to those of methylphenylsiloxane compounds and possessing an increased stability to acidic media. A practical possibility for the preparation of such compounds is determined by feasible synthesis of dialkoxybenzylmethylsilane developed by us.

Experimental

Starting reagents. Methylalkoxysilanes, chlorotrimethylsilane, toluene, THF, hexane, ethanol were purified according to the general procedures.[19] Acetic acid was dried by distillation over P_2O_5.

^{1}H NMR spectra were recorded on a BrukerWP-250 SY spectrometer in $CDCl_3$, using the ACD LABS program. GLC analysis was carried out on a Khromatek Analitik 5000 instrument (Russia) with katharometer as a detector, carrier gas helium, 2 m×3 mm columns, stationary phase SE-30 (5%) deposited on Chromaton-H-AW, the Khromatek Analitik program (Russia). GPC analysis was carried out on a chromatographic system comprising a STAIER high pressure pump (Akvilon, Russia), a SmarTBLine RI 2300 refractometer (KNAUER, Germany), and a JETSTREAM 2 PLUS thermostat (KNAUER, Germany). T.p. 40 °C (+/–0.1 °C). Eluent THF, the flow rate 1.0 mL min^{-1}, 300×7.8 mm columns, sorbent Phenogel (Phenomenex, USA), 5 μm, pore size from 10^3 to 10^5 Å. IR spectra were recorded on a Bruker Equinox 55/S spectrometer.

DSC analysis of the samples was carried out on a MetTBLer-822e differential scanning calorimeter, the rate of heating 10 deg min^{-1}. TGA analysis of the samples was carried out on a Derivatograf-K instrument (MOM, Hungary), the rate of heating 5 deg min^{-1}.

Benzylmethyldiethoxysilane. A mixture of $MeSi(OEt)_3$ (445 g, 2.5 mol) and BnCl (126.5 g, 1 mol) was added to Mg (36 g, 1.5 mol) with reflux and stirred for 6 h at 150 °C. After addition of toluene (600 mL), the mixture was filtered, toluene and $MeSi(OEt)_3$ were evaporated. The product was isolated by distillation *in vacuo*. B.p. = 120—122 °C (14 mBar). The yield was 70%. ^{1}H NMR ($CDCl_3$), δ: 0.05 (s, 3 H, $SiCH_3$); 2.19 (s, 2 H, $SiC\underline{H}_2C_6H_5$); 7.21—7.09 (m, 5 H, $SiCH_2C_6\underline{H}_5$); 3.78—3.70 (m, 4 H, $Si(OC\underline{H}_2CH_3)$, J = 6.71 Hz), 1.19 (t, 6 H, $Si(OCH_2C\underline{H}_3)$, J = = 6.71 Hz).

Benzylmethyldimethoxysilane was obtained and isolated according to a similar procedure based on $MeSi(OMe)_3$. B.p. = = 95—96 °C (14 mBar). The yield was 67%. ^{1}H NMR ($CDCl_3$), δ: 0.08 (s, 3 H, $SiCH_3$); 2.22 (s, 2 H, $SiC\underline{H}_2C_6H_5$); 7.27—7.08 (m, 5 H, $SiCH_2C_6\underline{H}_5$); 3.51 (s, 9 H, $Si(OCH_3)_3$).

Benzyldimethylethoxysilane was obtained and isolated according to a similar procedure based on $Me_2Si(OEt)_2$. The yield was 65%. ^{1}H NMR ($CDCl_3$), δ: 0.08 (s, 6 H, $SiCH_3$); 2.18 (s, 2 H, $SiC\underline{H}_2C_6H_5$); 7.21—7.04 (m, 5 H, $SiCH_2C_6\underline{H}_5$); 3.69—3.60 (m, 2 H, $Si(OC\underline{H}_2CH_3)$, J = 7.33 Hz); 1.17 (t, 3 H, $Si(OCH_2C\underline{H}_3)$, J = 6.71 Hz).

Polycondensation of $BnMeSi(OEt)_2$ in anhydrous AcOH. A mixture of $BnMeSi(OEt)_2$ (19.1 g, 0.086 mol) and AcOH (51.6 g, 0.86 mol) was refluxed until the signals for the protons of the ethoxy group completely disappeared from the ^{1}H NMR spectra of the reaction mixture samples. Then, toluene was added to the reaction mixture, which was washed with water until neutrality. The resulting solution was dried with sodium sulfate and filtered, the solvent was evaporated. Oligobenzylmethylsiloxane was obtained in quantitative yield. ^{1}H NMR ($CDCl_3$), δ: 0.16—0.39 (m, 3 H, $(C\underline{H}_3)(C_6H_5CH_2)Si$); 2.16—2.40 (m, 2 H, $(CH_3)(C_6H_5C\underline{H}_2)Si$); 7.25—7.66 (m, 5 H, $(CH_3)(C_6\underline{H}_5CH_2)Si$). IR ($CCl_4$), ν/cm^{-1}: 3100—3600 (SiOH). The amount of the OH groups 1.8% (the data from the ^{1}H NMR spectra of the samples blocked with chlorotrimethylsilane). GPC: MM_{pica} = 900 a.m.u. (58%), 500 a.m.u. (42%).

The condensation of $BnMeSi(OEt)_2$ in anhydrous AcOH with a slow addition of $BnMeSi(OEt)_2$ was carried out according to a similar procedure, using a dosing unit for the addition of $BnMeSi(OEt)_2$. ^{1}H NMR ($CDCl_3$), δ: 0.16—0.40 (m, 3 H, $(C\underline{H}_3)(C_6H_5CH_2)Si$); 2.16—2.39 (m, 2 H, $(CH_3)(C_6H_5C\underline{H}_2)Si$); 7.24—7.68 (m, 5 H, $(CH_3)(C_6\underline{H}_5CH_2)Si$). IR ($CCl_4$), ν/cm^{-1}: 3100—3600 (SiOH). The amount of the OH groups 1.9% (the data from the ^{1}H NMR spectra of the samples blocked with chlorotrimethylsilane). GPC: MM_{pica} = 900 a.m.u. (66%), 500 a.m.u. (34%).

The condensation of $BnMeSi(OEt)_2$ in anhydrous AcOH with EtOH was carried out according to a similar procedure with the addition of anhydrous ethanol to the reaction mixture. Oligobenzylmethylsiloxane was obtained in quantitative yield. ^{1}H NMR ($CDCl_3$), δ: 0.15—0.38 (m, 3 H, $(C\underline{H}_3)(C_6H_5CH_2)Si$);

2.17—2.50 (m, 2 H, $(CH_3)(C_6H_5C\underline{H}_2)Si$); 7.26—7.65 (m, 5 H, $(CH_3)(C_6\underline{H}_5CH_2)Si$).

Blocking of terminal hydroxy groups of oligobenzylmethylsiloxanes. A 20% solution of oligobenzylmethylsiloxane (0.54 g, 0.004 mol) in anhydrous toluene was added dropwise to a mixture of chlorotrimethylsilane (0.82 g, 0.007 mol) and pyridine (0.59 g, 0.007 mol) in toluene (10 mL). The mixture was refluxed with stirring for 4 h. The product was washed with water until neutrality, dried with sodium sulfate, and evacuated at 50 °C. ^1H NMR ($CDCl_3$), δ: 0.15—0.39 (m, 9 H, $(C\underline{H}_3)_3Si$); 0.15—0.39 (m, 3 H, $(C\underline{H}_3)(C_6H_5CH_2)Si$); 2.16—2.40 (m, 2 H, $(CH_3)(C_6H_5C\underline{H}_2)Si$); 7.25—7.66 (m, 5 H, $(CH_3)(C_6\underline{H}_5CH_2)Si$). IR ($CCl_4$), ν/cm^{-1}: the signals of the SiOH groups in the region of 3300 cm^{-1} are absent.

Synthesis of linear high-molecular-weight polybenzylmethylsiloxane. A mixture of oligobenzylmethylsiloxane (1 g, 0.007 mol) and AcOK (1 wt.%) in acetic acid was stirred for 5 h *in vacuo* (1 Torr) at 180 °C. The product was dissolved in toluene, washed with DI water, and dried with sodium sulfate. The solvent was evaporated *in vacuo* (1 Torr) at 50 °C. The yield of the product was 0.88 g (88%). IR (CCl_4), ν/cm^{-1}: the signals in the region of 3100—3600 cm^{-1} (SiOH) are absent. GPC: MM_{pica} = 6000 a.m.u. (72%), 500 a.m.u. (28%). ^1H NMR ($CDCl_3$), δ: 0.16—0.40 (m, 3 H, $(C\underline{H}_3)(C_6H_5CH_2)Si$); 2.16—2.39 (m, 2 H, $(CH_3)(C_6H_5C\underline{H}_2)Si$); 7.24—7.68 (m, 5 H, $(CH_3)(C_6\underline{H}_5CH_2)Si$).

Copolycondensation of diethoxydimethylsilane, benzylmethyldiethoxysilane, trimethylmethoxysilane, and triethoxymethylsilane in acetic acid. A mixture of diethoxydimethylsilane (144.3 g, 0.97 mol), benzylmethyldiethoxysilane (150.6 g, 0.67 mol), triethoxymethylsilane (12 g, 0.067 mol), trimethylmethoxysilane (14 g, 0.134 mol), and anhydrous acetic acid (543.6 g, 7.25 mol) was slowly added dropwise to anhydrous acetic acid (543.6 g, 7.25 mol) with stirring and reflux. IR (CCl_4), ν/cm^{-1}: the signals in the region of 3100—3600 cm^{-1} (SiOH) are present. The amount of the OH groups 1.6% (the data from the ^1H NMR spectrum of the blocked sample). The volatile products were removed *in vacuo* at 120 °C. The yield was 95%. GPC: MM_{pica} = = 1400 a.m.u. (72%), 600 a.m.u. (28%). ^1H NMR ($CDCl_3$), δ: 7.05—7.33 (m, 5 H, $(C_6\underline{H}_5CH_2)(CH_3)_2Si$); 1.98—2.23 (m, 2 H, $(C_6H_5C\underline{H}_2)(CH)_3Si$),); (m, 6 H, $(CH_3)_2Si$); 0.1—0.12 (m, 9 H, $(CH_3)_3Si$).

Catalytic post-condensation at the OH groups of copolymer. The reaction was carried out by the addition of concentrated sulfuric acid (1.36 g, 0.0139 mol) to the copolymer (136 g, 0.37 mol). The reaction mixture was stirred for 2 h, then diluted with toluene until complete dissolution of the content, washed with water to pH 7, and dried with sodium sulfate. After filtration, the volatile products were removed *in vacuo* at 300 °C. The yield was 75%. ^1H NMR ($CDCl_3$), δ: 7.04—7.18 (m, 5 H, $(C_6\underline{H}_5CH_2)(CH_3)_2Si$); 1.97—2.09 (m, 2 H, $(C_6H_5C\underline{H}_2)(CH)_2Si$),); (m, 6 H, $(CH_3)_2Si$); −0.04—0.01 (m, 9 H, $(CH_3)_3Si$). GPC: MM_{pica} = 3600 a.m.u., n_d^{20} = 1.4825.

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Received December 26, 2014