

Hydrolytic condensation of trialkoxysilanes in the presence of alkali metal and copper(II) ions. Influence of the reaction conditions on the structure of Cu/M organosiloxanes*

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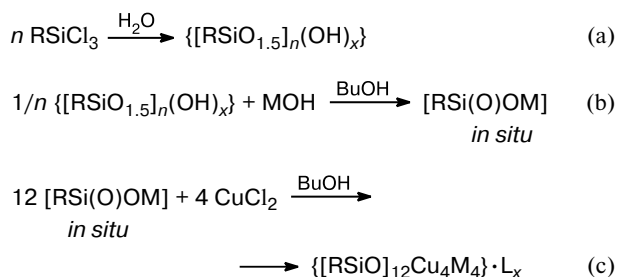
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The formation of polyhedral copper/sodium(potassium) organosiloxanes was examined as a result of hydrolytic condensation of organotrialkoxysilanes in the presence of copper(II) and sodium or potassium ions. High selectivity of the synthesis of copper/sodium(potassium) organosiloxanes having desired structures can be achieved by choosing the reaction conditions.

Key words: hydrolytic condensation, organotrialkoxysilanes, alkali metal organosiloxanates, polyhedral organometallasiloxanes, stereoregular organocyclosiloxanes, trimethylsilylation.

Earlier, a series of new crystalline copper-containing organosiloxanes have been synthesized and characterized.^{1–5} These compounds were prepared according to two procedures. One procedure, which was traditionally used for the synthesis of various metallasiloxanes, involved three steps (Scheme 1): (a) hydrolysis of organotrichlorosilane giving rise to low-molecular-weight organosilsesquioxane resin, (b) alkaline cleavage of organosilsesquioxane resin with sodium or potassium hydroxide in an alcoholic medium (Si/M = 1), and (c) the reaction of alkali metal organosiloxanolate formed *in situ* with CuCl₂.^{**}

Scheme 1



L = BuOH, H₂O; M = Na, K

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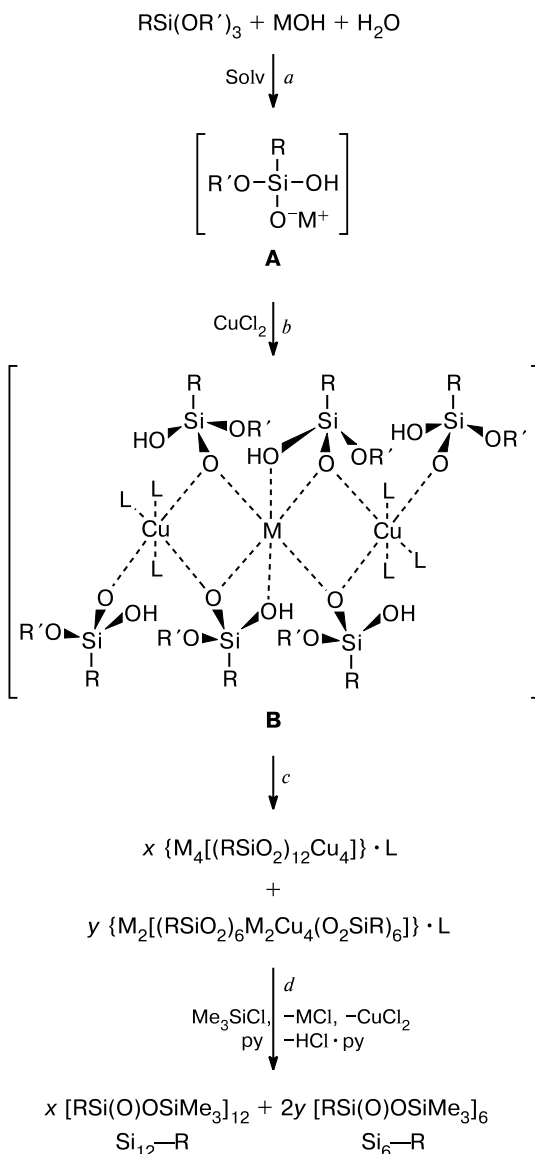
** In the present study, we examined copper-containing organosiloxanes, which were prepared by the partial replacement of alkali metal ions in organosiloxanolate that formed with copper(II) ions (Si/Cu = 3).

This scheme was used for the preparation of polyhedral Cu/M organosiloxanes with different molecular structures, *viz.*, copper/sodium phenylsiloxane {Na₄[(PhSiO₂)₁₂Cu₄]·8(BuOH) (**1**), copper/potassium vinylsiloxane {K₄[(ViSiO₂)₁₂Cu₄]·6(BuOH) (Vi = CH=CH₂) (**2**),¹ copper/potassium ethylsiloxane {K₂[(EtSiO₂)₆K₂Cu₄(O₂SiEt)₆]·4(BuOH) (**3**),² and copper/sodium methylsiloxane {Na₄[(EtSiO₂)₁₂Cu₄]·4(BuOH) (**4**).³

Based on the data published in the literature⁶ and the results of our studies, we have later developed a new procedure for the synthesis of organometallasiloxanes^{4,7,8} (Scheme 2, reactions *a–c*). This method involves alkaline hydrolysis of organotrialkoxysilane (Si/MOH = 1) in an alcoholic medium (step *a*) followed by the exchange reaction of the assumed^{4,7b} alkaline intermediate (**A**) formed *in situ* with chlorides of another metal (in the case under consideration, with CuCl₂; Si/Cu = 3) (step *b*). In our opinion, this process is accompanied by association of metal-containing intermediates to form aggregates (**B**). In the latter, the ionic "lattice," which includes also alcohol and water molecules is enclosed by organosilicon fragments containing functional groups. Under particular reaction conditions, these functional groups are involved in condensation to form organosiloxanolate rings on a "metallic matrix," *i.e.*, Cu/M-organosiloxane molecules (step *c*).

The new method not only made it possible to reproduce the syntheses of structures **1–4** but also allowed us to isolate new compounds, which have not been prepared earlier. In particular, copper/sodium vinylsiloxane {Na₄[(ViSiO₂)₁₂Cu₄]·4(BuOH) (**5**),⁵ copper/po-

Scheme 2*



R = Ph, Vi, Me; R' = Me, Et, Bu; L = ROH, H₂O; M = Na, K
Solv is solvent

tassium phenylsiloxane {K₂[(PhSiO₂)₆K₂Cu₄(O₂SiPh)₆]} · 8(BuOH) (**6**),⁵ and copper/sodium methylsiloxane {Na₄[(MeSiO₂)₁₂Cu₄]} · 4(EtOH) · 4(MeOH) (**7**)⁹ were synthesized.

Studies of compounds **1**–**7** by X-ray diffraction analysis demonstrated that this process (see Scheme 2) gave rise to Cu/M-containing organosiloxane molecules of two structural types, viz., sandwich and globular.

* Hereinafter, the number of the [–Si(R)(OSiMe₃)O–] units in cyclosiloxane and the organic substituent R at the Si atom are given in the notations.

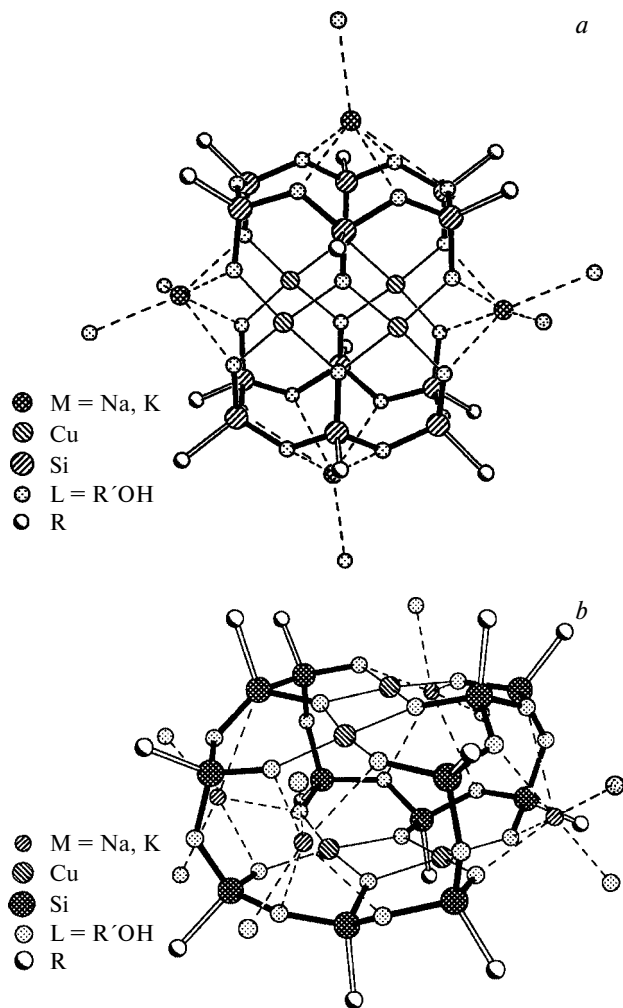


Fig. 1. Molecular structures of Cu/M organosiloxanes: sandwich (a) and globular (b).

For example, compounds **3** and **6** have a sandwich structure (Fig. 1, a), in which two cyclohexasiloxanolate ligands [RSi(O)O[–]]₆ (R = Ph or Et) adopting a *cis* configuration are linked to each other via a layer consisting of four Cu^{II} ions. The overall electroneutrality of the molecule is provided by four K⁺ ions, each ion being coordinated by O atoms from the outside of the framework.

The molecules of Cu/M organosiloxanes **1**, **2**, **4**, **5**, and **7** have a globular structure (see Fig. 1, b). This structure contains the twelve-membered organosiloxanolate ligand [RSi(O)O[–]]₁₂ (R = Ph, Vi, or Et) in the tris-*cis*-tris-*trans* configuration as the major element. The saddle conformation of this ligand is fixed by four Cu^{II} ions. Electroneutrality of the molecule is provided by four external Na⁺ or K⁺ cations.

Taking into account a combination of the stereochemical characteristics of Cu^{II} (see Ref. 10) and the specific features of the siloxane bond (its nature, properties, and transformations),¹¹ one would expect the formation of a

large number of various copper-containing organosiloxanes. However, the available data are indicative of the structural selectivity of the processes under consideration. The factors responsible for this selectivity of copper-containing organocyclosiloxanes have attracted considerable attention because these compounds serve as the only source of a new class of stereoregular cyclosiloxanes.⁸ The distinguishing feature of these compounds is the violated up-and-down symmetry, *i.e.*, the presence of two types of "surrounding" on opposite sides of the ring, which differ radically in character from intermolecular interactions. The latter fact is reflected in the specific physical properties of cyclosiloxanes.¹²

In the present study, we examined hydrolytic condensation of a series of organotrialkoxysilanes in the presence of alkali metal (Na^+ and K^+) and copper(II) ions. Our study was aimed at developing a procedure for the controlled synthesis of polyhedral Cu/M organosiloxanes with a strictly defined structure. Particular attention was given to the influence of such factors as the nature of alkali metal and the organic substituent at the Si atom, the reactivity of the alkoxy group, the amount of water, and the nature of the solvent on the homogeneity of the composition and the structure of the final copper-containing organosiloxane.

Results and Discussion

Hydrolytic condensation of phenyl- and vinyltri-alkoxysilanes $\text{RSi}(\text{OR}')_3$ ($\text{R} = \text{Ph}$ or Vi ; $\text{R}' = \text{Me}$, Et , or Bu) in the presence of the Na^+ (K^+) and Cu^{II} ions as well as of methyltriethoxysilane in the presence of Na^+ and Cu^{II} ions at $\text{Si}/\text{M} = 1$ and $\text{Si}/\text{Cu} = 3$ has been studied in most detail. Alcohols corresponding to the alkoxy group (MeOH , EtOH , or BuOH) were used as the solvent. The polarity of the medium was changed by adding aromatic solvents (toluene or benzene). The amount of water in the reaction was varied from one to nine H_2O molecules per Si atom.

In the solid state, all Cu/M-containing organosiloxanes under consideration occur as powders varying in color from pale to dark blue. In most of experiments, the exchange reactions (see Scheme 2, reaction *c*) afforded both crystalline and amorphous Cu/M-containing organosiloxanes. With the aim of examining the possibilities of separation of crystalline and amorphous copper-containing siloxanes as well as of crystals of different structural types, all reaction mixtures were fractionated as follows: 1) crystallization (or the formation of an amorphous precipitate) from the reaction mixture upon cooling after the completion of the reaction, 2) crystallization (or the formation of an amorphous precipitate) upon concentration of the solution, 3) complete removal of the solvent from the mother liquor.

In the next step, we studied the structures of the products isolated. One cannot use only elemental analysis data because the molecular formulas for the sandwich and globular structures are identical. X-ray diffraction method is also inadequate to solve this problem, because the structure of one crystal is not proof that the entire crystalline material is structurally homogeneous. In addition, it is sometimes impossible to prepare single crystals suitable for X-ray diffraction study. Therefore, in addition to the above-mentioned physical methods, we also used the well-known approach applied in the organosilicon chemistry, which consists in preparing trimethylsilyl derivatives of the functional systems under study and which we have optimized for the treatment of organometallasiloxanes.¹³ As a result, we isolated cyclic siloxane fragments of the starting organometallasiloxanes with retention of the size and configuration of the ring as a trimethylsiloxy derivative (TMS derivative) (see Scheme 2, step *d*). Therefore, trimethylsilylation of the copper-containing siloxane globular structure afforded the only cyclododecasiloxane $\text{Si}_{12}-\text{R}$, whereas two cyclohexasiloxanes Si_6-R were derived from the copper-containing siloxane with a sandwich structure. The earlier studies of TMS derivatives of Cu/M phenylsiloxanes by gel permeation chromatography (GPC)¹⁴ and NMR spectroscopy⁸ demonstrated that a combination of these methods allows one to reasonably justify the composition of the starting Cu/M organosiloxanes in the case of partial separation of the different-size siloxane rings by GPC.

The results of these studies are presented in Figs. 2–6, which give the conditions of the synthesis of Cu/M organosiloxanes (organotrialkoxysilane, alkali metal hydroxide, and the solvent or a mixture of solvents) and present the chromatograms of TMS derivatives of the precipitated products. Generally, the yield of Cu/M organosiloxanes summed over all fractions (precipitate + product prepared by the complete removal of the solvent from the mother liquor) was ~95% because of loss of the compound upon separation from MCl and fractionation. In most cases, crystallization under the synthesis conditions did not lead to complete isolation of crystalline Cu/M organosiloxanes from the reaction mixture due to which the mother liquors contained amorphous products with a certain percentage of crystalline products. However, the latter can be isolated by additional recrystallization. Precipitates of the products consisting of amorphous and crystalline Cu/M organosiloxanes can be separated analogously.

Synthesis and composition of Cu/M siloxanes with the phenyl substituent at the Si atom. *Synthesis and composition of Cu/M phenylsiloxanes prepared from $\text{PhSi}(\text{OMe})_3$ (see Fig. 2).* Hydrolytic condensation of phenyltrimethoxysilane in the presence of Na^+ and Cu^{II} ions in MeOH afforded a mixture of amorphous (according to the

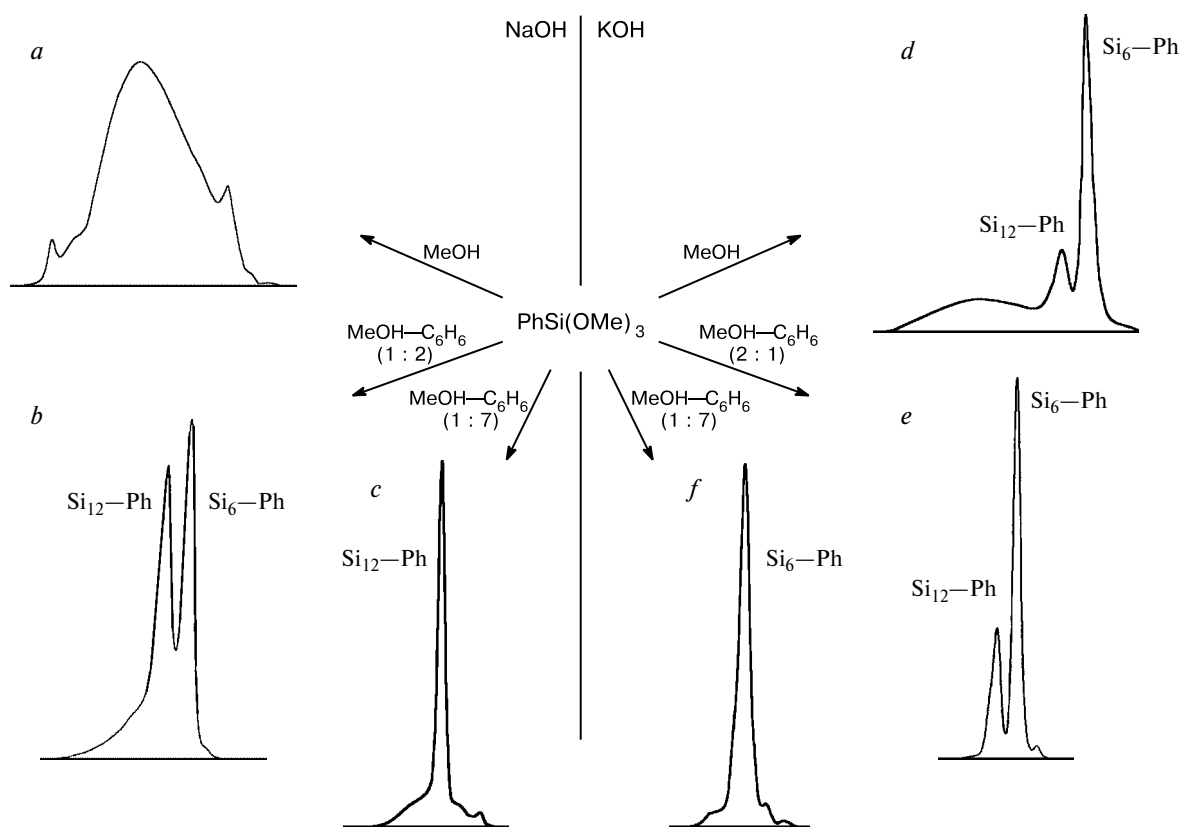


Fig. 2. Chromatograms of TMS derivatives of Cu/M phenylsiloxanes prepared from $\text{PhSi}(\text{OMe})_3$ under different reaction conditions (a–f); M = Na (a–c), K (d–f).

powder X-ray diffraction data) Cu/Na phenylsiloxanes (Table 1, run 1).

Trimethylsiloxy derivatives of these products occur as mixtures of polydispersed oligomeric phenylsiloxanes containing trimethylsiloxy groups (see Fig. 2, a), which are analogous in their molecular-weight characteristics to oligomeric phenylsilsesquioxanes formed by hydrolysis of phenyltrichlorosilane.

Under analogous conditions, the use of K^+ ions instead of Na^+ ions led to a substantial decrease in the percentage of an amorphous product and the formation of crystalline products (43.5%) (see Table 1, run 2). The latter consisted predominantly of molecules of the sandwich type and crystallized from the reaction mixture simultaneously with the precipitation of a portion of an amorphous product. The chromatogram of the TMS derivative of the Cu/K-containing phenylsiloxane fraction that precipitated has a broad peak in the high-molecular-weight region (oligomeric products) and a peak of six-membered cyclosiloxane ($\text{Si}_6\text{—Ph}$, ~50%) (see Fig. 2, d).

The addition of aromatic solvents (both benzene and toluene) to the reaction mixture led to a substantial increase in the percentage of crystalline copper-containing siloxanes in the reaction products (see Table 1, runs 3–6). As a result, the chromatograms have peaks corresponding

to $\text{Si}_6\text{—Ph}$ and $\text{Si}_{12}\text{—Ph}$ (see Fig. 2, b, c, d, and f). At a high concentration of benzene ($\text{MeOH}/\text{C}_6\text{H}_6 = 7/1$), trimethylsilylation afforded $\text{Si}_{12}\text{—Ph}$ and $\text{Si}_6\text{—Ph}$ as the major products in the case of NaOH (see Fig. 2, c) and KOH (see Fig. 2, f and Table 2), respectively, which is indicative of the selective formation of copper-containing siloxane exclusively with a globular (see Table 1, run 5) or sandwich (see Table 1, run 6) structure. The reaction with the use of toluene instead of benzene afforded crystalline Cu/M phenylsiloxanes in the highest yields (up to 95%) (see Table 1, runs 7 and 8). However, these products are mixtures of molecules with sandwich and globular structures regardless of the $\text{MeOH}/\text{MeC}_6\text{H}_5$ ratio.

Synthesis and composition of Cu/M phenylsiloxanes prepared from $\text{PhSi}(\text{OEt})_3$ (see Fig. 3). The composition of TMS derivatives of Cu/M phenylsiloxanes prepared by hydrolytic condensation of $\text{PhSi}(\text{OEt})_3$ in the presence of Na^+ (K^+) and Cu^{II} ions also depends on the nature of alkali metal and solvents.

The synthesis of Cu/Na phenylsiloxane in EtOH, unlike the analogous synthesis in MeOH (see Fig. 2, a), gave rise to crystalline products, although in low yields (25%). This process afforded predominantly crystals with a sandwich structure (see Table 1, run 10). The TMS derivative consists of a mixture of $\text{Si}_6\text{—Ph}$ and $\text{Si}_{12}\text{—Ph}$ along with

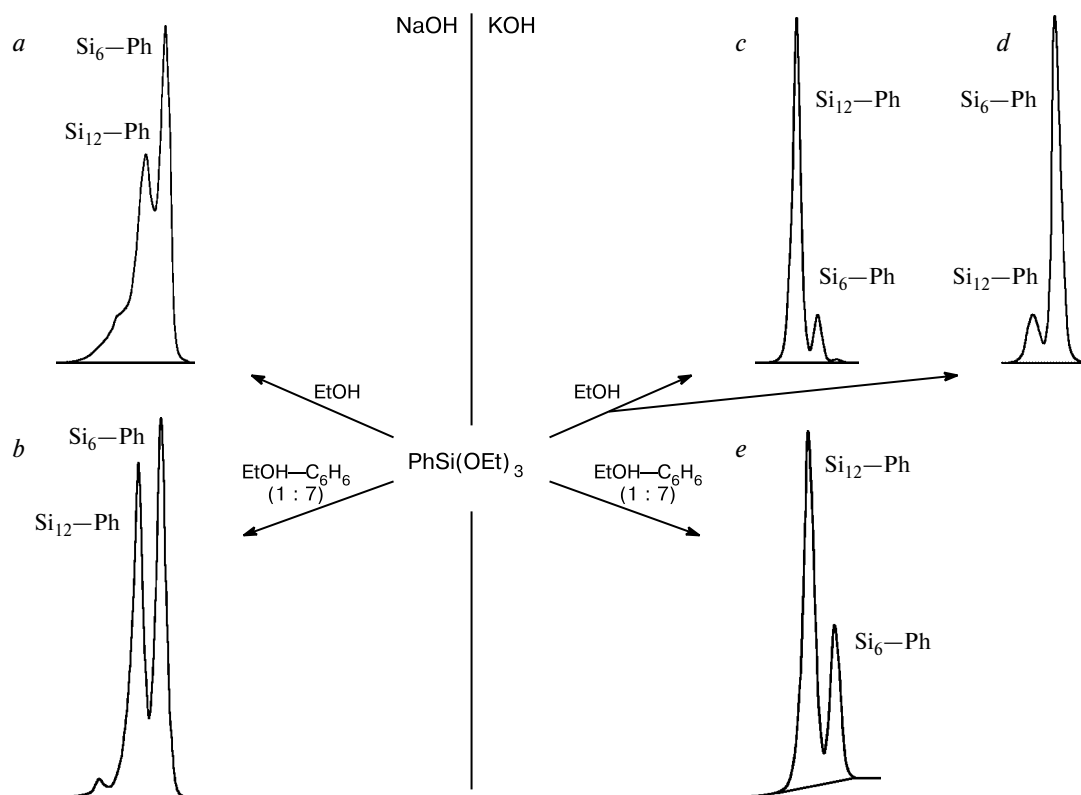


Fig. 3. Chromatograms of TMS derivatives of Cu/M phenylsiloxanes prepared from $\text{PhSi}(\text{OEt})_3$ under different reaction conditions (a–e); M = Na (a, b), K (c–e).

a substantial amount of unidentified oligomers (see Fig. 2, a).

Crystallization of Cu/K phenylsiloxane from the reaction mixture prepared in EtOH (see Table 1, run 10) is characterized by the following feature. The rates of crystallization of the products having different molecular structures (globular and sandwich) differ to an extent that the first fraction of crystals (see Table 1, run 10, a) (approximately one-half of the crystalline product) precipitates simultaneously with KCl immediately after the addition of CuCl_2 (see Scheme 2, b), whereas the second fraction (see Table 1, run 10, b) slowly crystallizes from the mother liquor. The TMS derivatives of the first crystalline fraction consist predominantly of the $\text{Si}_{12}-\text{Ph}$ molecules with a small impurity of Si_6-Ph (see Fig. 3, c), whereas the TMS derivatives of the second crystalline fraction consist predominantly of Si_6-Ph with an impurity of $\text{Si}_{12}-\text{Ph}$ (see Fig. 3, d). Under these conditions, unlike the analogous synthesis in the presence of Na^+ ions, crystalline Cu/K phenylsiloxane was obtained in a rather high total yield (81.7%).

The addition of an aromatic solvent to the reaction mixture led to the formation and isolation of a mixture of crystalline Cu/M phenylsiloxanes of both types (see Fig. 3, b, e, Table 1). In the case of NaOH, their yield depends on the $\text{C}_6\text{H}_6(\text{MeC}_6\text{H}_5)/\text{EtOH}$ ratio (66–88%),

whereas the yield in the reaction with the use of KOH is high (~90%) independently of this ratio (see Table 1, runs 11–16).

Synthesis and composition of Cu/M phenylsiloxanes prepared from $\text{PhSi}(\text{OBu})_3$ (see Fig. 4). The use of phenyltri-alkoxysilane containing the less reactive butoxy groups as the starting reagent is favorable for the formation of crystalline Cu/M phenylsiloxanes (90%) characterized by the maximum percentage of the molecules with a globular structure (80 and 67% for Cu/Na and Cu/K phenylsiloxanes, respectively) and selective crystallization of the products of this structural type (see Table 1, runs 17 and 18). According to the results of GPC and NMR spectroscopy (^1H and ^{29}Si), their TMS derivatives are pure $\text{Si}_{12}-\text{Ph}$ (see Fig. 4 and the Experimental section).

Synthesis and composition of Cu/M siloxanes with the vinyl substituent at the Si atom (see Fig. 5). Hydrolytic condensation of vinyltrimethoxy-, vinyltriethoxy-, and vinyltributoxysilanes in the corresponding alcohols (MeOH, EtOH, or BuOH) in the presence of Na^+ and Cu^{II} ions afforded Cu/Na vinylsiloxane with a globular structure as the only crystalline product. Its yield depends on the reactivity of the alkoxy group in the starting silane and increases in the series $\text{OMe} < \text{OEt} < \text{OBu}$ (see Table 1, runs 19–21). The results of GPC and NMR spectroscopy provide evidence that TMS derivatives of these Cu/Na

Table 1. Synthesis of Cu/M phenylsiloxanes (1–18) and Cu/M vinylsiloxanes (19–24)^a

Run	RSi(OR') ₃	MOH	Solvent (v/v)	Characteristic of crystalline Cu/M organosiloxane	
				Yield (% of theoretical)	Ratio between globular (G) and sandwich (S) structures: G/S
1	PhSi(OMe) ₃	NaOH	MeOH	— ^b	—
2	PhSi(OMe) ₃	KOH	MeOH	43.5	1/4
3	PhSi(OMe) ₃	NaOH	MeOH/C ₆ H ₆ (1/2)	73.5	1/2
4	PhSi(OMe) ₃	KOH	MeOH/C ₆ H ₆ (2/1)	70.0	1/2
5	PhSi(OMe) ₃	NaOH	MeOH/C ₆ H ₆ (1/7)	53.0	1/—
6	PhSi(OMe) ₃	KOH	MeOH/C ₆ H ₆ (1/7)	54.0	—/1
7	PhSi(OMe) ₃	NaOH	MeOH/MeC ₆ H ₅ (1/2)	90.0	1/1
8	PhSi(OMe) ₃	KOH	MeOH/MeC ₆ H ₅ (1/5)	95.0	1/1
9	PhSi(OEt) ₃	NaOH	EtOH	25.0	1/4
10	PhSi(OEt) ₃	KOH	EtOH	a) 37.2 ^c ; b) 44.5 ^d	1/1
11	PhSi(OEt) ₃	NaOH	EtOH/C ₆ H ₆ (1/7)	66.0	1/2
12	PhSi(OEt) ₃	KOH	EtOH/C ₆ H ₆ (1/7)	90.0	1/1
13	PhSi(OEt) ₃	NaOH	EtOH/C ₆ H ₆ (1/2)	88.0	1/1
14	PhSi(OEt) ₃	NaOH	EtOH/MeC ₆ H ₅ (1/2)	84.0	1/2
15	PhSi(OEt) ₃	KOH	EtOH/C ₆ H ₆ (1/7)	90.0	1/1
16	PhSi(OEt) ₃	KOH	EtOH/MeC ₆ H ₅ (1/7)	91.0	1/2
17	PhSi(Obu) ₃	NaOH	BuOH	90.0	4/1
18	PhSi(Obu) ₃	KOH	BuOH	90.0	2/1
19	ViSi(OMe) ₃	NaOH	MeOH	38.0	1/—
20	ViSi(OEt) ₃	NaOH	EtOH	82.0	1/—
21	ViSi(Obu) ₃	NaOH	BuOH	90.0	1/—
22	ViSi(OMe) ₃	KOH	MeOH	49.0	1/20
23	ViSi(OEt) ₃	KOH	EtOH	a) 35.0 ^c ; b) 35.5 ^d	1/1
24	ViSi(Obu) ₃	KOH	BuOH	95.0	1/—

^a Reaction conditions: RSi(OR')₃/MOH = 1, RSi(OR')₃/H₂O = 1, RSi(OR')₃/CuCl₂ = 3, c = 0.5 mol L⁻¹.^b Only an amorphous product.^c The yield of the first fraction of crystals (globular molecular structure).^d The yield of the second fraction of crystals (sandwich molecular structure).

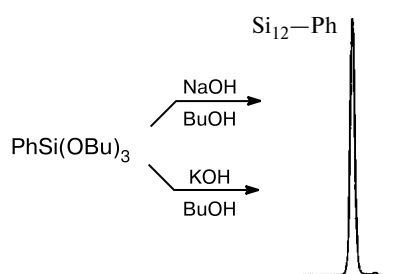
vinylsiloxanes are the individual twelve-membered siloxane rings Si₁₂—Vi (see Fig. 5, a).

In the presence of K⁺ ions instead of Na⁺, the reactivity of the alkoxy group (in the above-mentioned series) in the starting silane influences both the yield and composition of the final crystalline Cu/K vinylsiloxane. For example, hydrolysis of ViSi(OMe)₃ in MeOH in the presence of K⁺ and Cu^{II} ions afforded predominantly molecules with a sandwich structure, the yield of the crystalline product being relatively low (49%) (see Table 1,

run 22). The chromatogram of the TMS derivative of this product has two peaks corresponding to the six- and twelve-membered siloxane rings with the Si₆—Vi content of 95% (see Fig. 5, b). The use of ViSi(OEt)₃ as the starting reagent and EtOH as the reaction medium led to an increase in the percentage of crystalline Cu/K vinylsiloxane (70.5%) in the reaction products (see Table 1,

Table 2. Synthesis of Cu/Na methylsiloxanes from MeSi(OEt)₃^a

Run	Molar ratio H ₂ O/MeSi(OEt) ₃	Solvent (v/v)	Yield ^b (%)
1	≤3	EtOH	24.0
2	9	EtOH	91.0
3	3	EtOH/MeC ₆ H ₅ (5/1)	29.5
4	3	EtOH/C ₆ H ₆ (3/2)	86.5
5	3	EtOH/C ₆ H ₆ (1/4)	87.5
6	11	BuOH	95.0

^a Reaction conditions: MeSi(OEt)₃/NaOH = 1, MeSi(OEt)₃/CuCl₂ = 3, c = 0.5 mol L⁻¹.^b The yield of crystalline Cu/Na methylsiloxane as a percentage of the theoretical yield.**Fig. 4.** Chromatogram of TMS derivatives of Cu/M phenylsiloxanes prepared from PhSi(Obu)₃ in BuOH (M = Na or K).

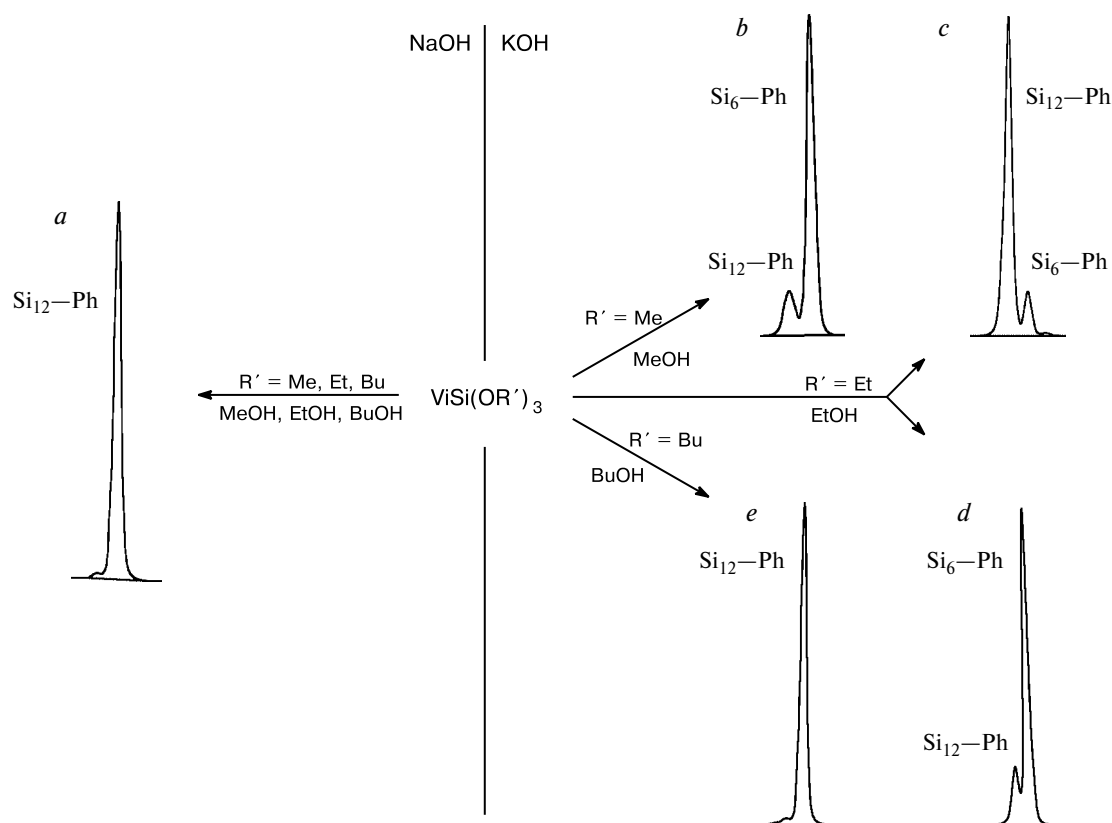


Fig. 5. Chromatograms of TMS derivatives of Cu/M vinylsiloxanes prepared from $\text{ViSi}(\text{OR}')_3$ under different reaction conditions (a–e); M = Na (a), K (b–e).

run 23). This process, like the synthesis of Cu/K siloxane containing the phenyl substituent at the Si atom in EtOH (see Fig. 3, c, d), was accompanied by spontaneous fractionation of crystalline products: a fraction of the product containing predominantly globular molecules precipitated simultaneously with KCl (see Fig. 5, c, Table 1, run 23, a) followed by precipitation of the second fraction containing predominantly molecules with a sandwich structure (see Fig. 5, d, Table 1, run 23, b).

The use of the starting silane containing butoxy groups led to the selective formation of crystalline Cu/K vinylsiloxane with a globular structure as the only reaction product (see Fig. 5, e; Table 1, run 24).

Synthesis and composition of Cu/Na siloxanes with the methyl substituent at the Si atom (see Fig. 6). The structural composition of Cu/Na methylsiloxanes prepared by hydrolytic condensation of $\text{MeSi}(\text{OEt})_3$ in the presence of Na^+ and Cu^{II} ions appeared to be most sensitive to changes in the reaction conditions. It was found that the composition of the products depends not only on the nature of the alkoxy groups and the solvent (like in the above-described cases) but also on the $\text{H}_2\text{O}/\text{Si}$ ratio.

For example, the reaction in EtOH at the ratio $\text{H}_2\text{O}/\text{Si} \leq 3$ afforded crystalline Cu/Na methylsiloxane in low yield (24%) (see Table 2). This product consists of

molecules with globular and sandwich structures in a ratio of ~1/1 (see Fig. 6, a).

An increase in the $\text{H}_2\text{O}/\text{Si}$ ratio to 9 (see Table 2, run 2) is favorable for the formation of molecules with a globular structure (up to 90%) (see Fig. 6, b), the total yield of crystalline Cu/Na methylsiloxane being substantially increased (91%). The addition of a small amount of toluene ($\text{EtOH}/\text{MeC}_6\text{H}_5 = 5/1$) to the reaction mixture at the ratio $\text{H}_2\text{O}/\text{Si} = 3$ (see Table 2, run 3) also led to an increase in the yield of products with a globular structure, but the total yield of the crystals decreased (~30%).

In the presence of a larger amount of toluene, trimethylsiloxy derivatives of Cu/Na methylsiloxanes were prepared as mixtures of oligomers.

The compositions of TMS derivatives of Cu/Na methylsiloxanes isolated from mixtures of EtOH and benzene are of interest. For example, the chromatogram of the TMS derivatives of crystalline Cu/Na methylsiloxane prepared in 86.5% yield (see Table 2, run 4) at the ratios $\text{H}_2\text{O}/\text{Si} = 3/1$ and $\text{EtOH}/\text{C}_6\text{H}_6 = 3/2$ has three partially separated peaks with an area ratio of ~2 : 1 : 1 (see Fig. 6, c). The left- and rightmost peaks correspond to $\text{Si}_{12}\text{-Me}$ and $\text{Si}_6\text{-Me}$, and the central peak was presumably identified as $\text{Si}_8\text{-Me}$ based on the calibration dependence $\log M - t_R$ (M is the molecular weight of the product, t_R is

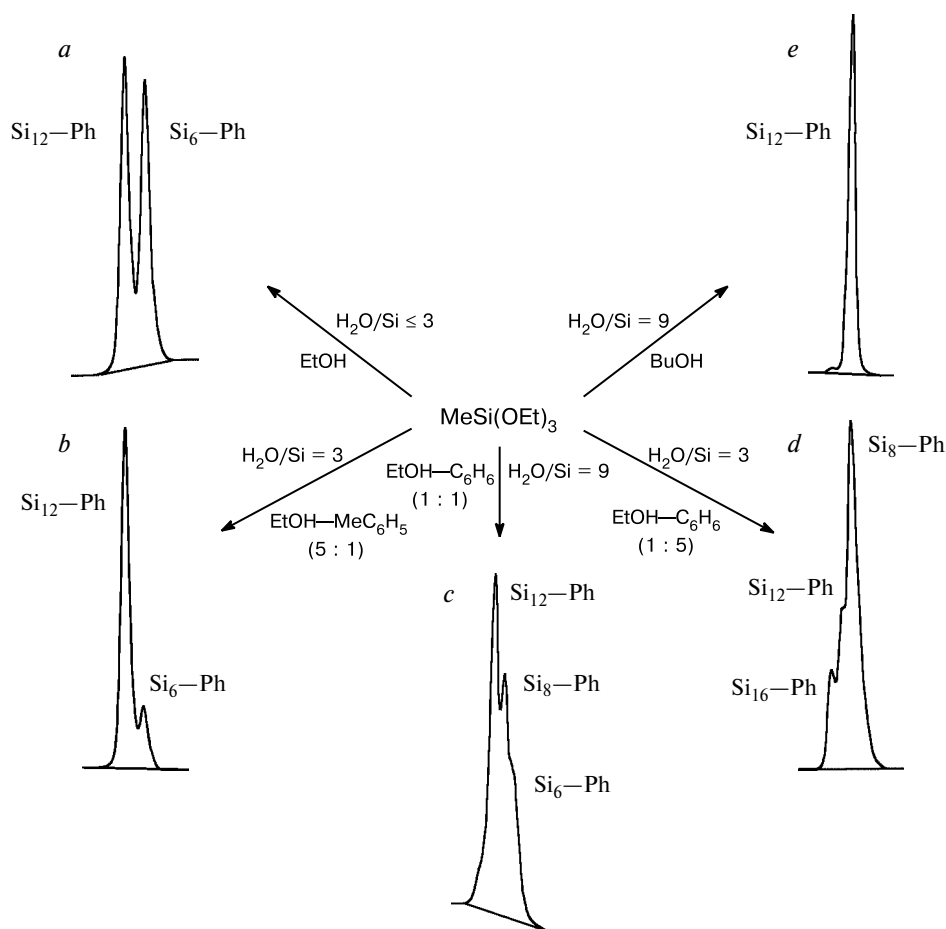


Fig. 6. Chromatograms of TMS derivatives of Cu/Na methylsiloxanes prepared from $\text{MeSi}(\text{OEt})_3$ under different reaction conditions (a–e).

the retention time). Hydrolytic condensation in an $\text{EtOH}-\text{C}_6\text{H}_6$ medium (1 : 4) (see Table 2, run 5) also afforded crystals in high yield (87.5%). In an analogous way, $\text{Si}_{16}-\text{Me}$ and Si_8-Me were presumably identified along with the known $\text{Si}_{12}-\text{Me}$ in the trimethylsilylation products (see Fig. 6, d). The ratio between the peak areas corresponding to $\text{Si}_{16}-\text{Me}$, $\text{Si}_{12}-\text{Me}$, and Si_8-Me was ~1 : 2 : 2.

The molecular structures of Cu/Na-methylsiloxanes based on the six-, eight-, and sixteen-membered methylsiloxanolate rings were not unambiguously established, because we failed to prepare single crystals suitable for X-ray diffraction study. Based on the organization of metallasiloxanes, which we have described earlier,^{2,5,13} we assumed that Cu/Na methylsiloxanes containing the six- and eight-membered siloxanolate rings as the major fragments have a sandwich structure analogous to that shown in Fig. 1, a. Recently, we have isolated and characterized Cu-containing methylsiloxane with a sandwich structure devoid of alkali metal ions, in which two eight-membered siloxanolate rings $[\text{RSi}(\text{O})\text{O}]_8$ coordinate eight copper ions,¹⁵ which is indirect evidence of the

possible formation of Cu/Na methylsiloxane with a sandwich structure.

Hydrolysis of $\text{MeSi}(\text{OEt})_3$ in the presence of Na^+ and Cu^{II} ions in BuOH at the ratio $\text{H}_2\text{O}/\text{Si} = 9/1$ (see Table 2, run 6) selectively (95%) afforded crystalline Cu/Na-methylsiloxane. Its globular structure was established by X-ray diffraction analysis (detailed results of X-ray diffraction study will be published elsewhere). Study of the TMS derivative of Cu/Na methylsiloxane by GPC and NMR spectroscopy (^1H and ^{29}Si) demonstrated the presence only of twelve-membered methyl(trimethylsiloxy)cyclosiloxane. This fact confirmed the homogeneous composition of the starting metallasiloxane (see Fig. 5, e).

* * *

The study of hydrolytic condensation of various organotrialkoxysilanes $\text{RSi}(\text{OR}')_3$ ($\text{R} = \text{Me}, \text{Vi}, \text{or Ph}$; $\text{R}' = \text{Me}, \text{Et}, \text{or Bu}$) in the presence of Cu^{II} and Na^+ or K^+ ions showed that the yield and composition of crystalline Cu/M organosiloxanes depend on the nature of the

organic substituent and the alkoxy group at the Si atom in the starting alkoxy silane, the nature of alkali metal and solvents, and the amount of water.

The nature of the organic substituent at the Si atom is the major factor responsible for sensitivity of the system under consideration to changes in the reaction conditions influencing the structures of the final Cu/M-organosiloxanes.

We found the conditions for the selective formation of Cu/Na-containing phenylsiloxane, Cu/Na(K)-containing vinylsiloxane, and Cu/Na-containing methylsiloxane with a globular structure as well as of Cu/K-containing phenylsiloxane with a sandwich structure.

Experimental

Trimethylsiloxy derivatives of Cu/M organosiloxanes were analyzed by GPC on a Waters instrument equipped with an M484 UV detector (for Cu/M phenylsiloxanes) and an M410 refractive index (RI) detector (for Cu/M vinylsiloxanes and Cu/M methylsiloxanes) and U-Styrigel 500 and 1000 Å columns (30000 theoretical plates) using a Maxima system for data processing; CHCl_3 (for Cu/M phenylsiloxanes) and toluene (for Cu/M vinylsiloxanes and Cu/M methylsiloxanes) were used as the eluent. The flow rate was 1 mL min^{-1} . The direct calibration on the $\log M - t_R$ coordinates was carried out using phenyl(trimethylsiloxy)cyclosiloxanes $[\text{PhSi}(\text{O})\text{OSiMe}_3]_4$,⁷ $[\text{PhSi}(\text{O})\text{OSiMe}_3]_6$, and $[\text{PhSi}(\text{O})\text{OSiMe}_3]_{12}$,¹³ which have been characterized and purified by additional recrystallization earlier, as well as with the use of $[\text{MeSi}(\text{O})\text{OSiMe}_3]_{12}$, $[\text{ViSi}(\text{O})\text{OSiMe}_3]_{12}$, and $[\text{ViSi}(\text{O})\text{OSiMe}_3]_6$, which were isolated and characterized in the present study.

Earlier, it has been demonstrated¹⁴ that the behavior of TMS derivatives of organocyclosiloxanes corresponds to the exclusion mechanism of separation, and the retention times are described by the linear equation $\log M = A - Bt_R$. It appeared that the retention times of phenyl-, vinyl-, and methyl(trimethylsiloxy)cyclosiloxanes containing the rings of the same sizes are equal to each other within the reproducibility of the method ($\pm 0.12\%$), *i.e.*, the retention time of the rings containing the bulky trimethylsilyl substituents is determined by the size of the ring and is virtually independent of the organic substituent (Ph, Vi, or Me) at the Si atom.

The ^1H and ^{29}Si NMR spectra were measured on a Bruker AMX spectrometer (^1H , 400.13 MHz; ^{29}Si , 79.495 MHz) at 20°C in CDCl_3 .

Powder X-ray diffraction studies were carried out on a DRON-3M diffractometer (Cu- $K\alpha$ radiation) at -20°C .

Organotrialkoxysilanes and trimethylchlorosilane were purchased from Aldrich; NaOH and KOH of analytical grade were used. Anhydrous CuCl_2 was prepared by heating its crystal hydrate at 120°C to a constant weight. The solvents were prepared according to known procedures.¹⁶

Synthesis of Cu/M organosiloxanes (general procedure). Organotrialkoxysilane and the solvent were placed in a three-neck flask equipped with a stirrer and a reflux condenser with a calcium chloride guard tube. Then alkali metal hydroxide and a calculated amount of water were added with stirring. After ho-

mogenization, the reaction mixture was brought to reflux, and an alcoholic solution of anhydrous CuCl_2 was added. The reaction mixture was refluxed for 15 min and filtered off from the precipitate of alkali metal chloride. The product that precipitated from the filtrate was separated by filtration, the residual solvent was removed on a rotary evaporator (10 Torr, 90°C), and the product was dried *in vacuo* (1 Torr, 90°C). The next fraction, which precipitated from the concentrated filtrate, and the residue, which was obtained after removal of the solvent from the mother liquor, were treated analogously.

Elemental analysis of all Cu/M organosiloxanes demonstrated that the Si : Cu : M ratio is equal to the theoretical value (3 : 1 : 1). As an example, we report the results of elemental analysis of copper/sodium phenylsiloxane prepared from phenyltrimethoxysilane. Found (%): C, 40.17; H, 3.86; Si, 14.88; Cu, 11.92; Na, 4.10. Calculated for $\{\text{Na}_4[\text{PhSi}(\text{O})\text{O}]_{12}\text{Cu}_4\} \cdot 3\text{MeOH} \cdot 6\text{H}_2\text{O}$, $\text{C}_{75}\text{H}_{84}\text{Si}_{12}\text{Cu}_4\text{Na}_4\text{O}_{33}$ (%): C, 41.00; H, 3.85; Si, 15.34; Cu, 11.57; Na, 4.19. Calculated for $\{\text{Na}_4[\text{PhSi}(\text{O})\text{O}]_{12}\text{Cu}_4\}$, $\text{C}_{72}\text{H}_{60}\text{Si}_{12}\text{Cu}_4\text{Na}_4\text{O}_{24}$ (%): C, 43.40; H, 3.04; Si, 16.92; Cu, 12.76; Na, 4.61. The difference between the theoretical and calculated percentage compositions is attributed to the presence of the coordinated solvent molecules in all samples and varies depending on the type of the solvent.

Trimethylsilylation of Cu/M organosiloxanes was carried out according to a procedure published earlier.¹³

Dodecaphenyldodeca(trimethylsiloxy)cyclododecasiloxane ($\text{Si}_{12}-\text{Ph}$). ^1H NMR, δ : two singlets -0.10 (9 H, OSiMe_3 , *cis/cis*) and -0.33 (9 H, OSiMe_3 , *cis/trans*) with the integral intensity ratio of 1 : 2; $6.50-7.50$ (m, 5 H, O_3SiPh); the integral intensity ratio of the signals of the protons of Me and Ph is 9 : 5. ^{29}Si NMR, δ : 8.81 (s, OSiMe_3 , *cis/cis*); 9.80 (s, OSiMe_3 , *cis/trans*); -80.69 (s, O_3SiPh , *cis/cis*). GPC (t_R/min): 15.92 (UV); 18.68 (RI).

Hexaphenylhexa(trimethylsiloxy)cyclohexasiloxane (Si_6-Ph). ^1H NMR, δ : 0.15 (s, 9 H, SiMe_3); $6.51-6.93$ (m, 5 H, Ph); the integral intensity ratio of the signals of the protons of Me and Ph is 9 : 5. ^{29}Si NMR, δ : 9.77 (s, OSiMe_3); -80.97 (s, O_3SiPh). GPC (t_R/min): 16.71 (UV); 19.33 (RI).

Dodecavinylidodeca(trimethylsiloxy)cyclododecasiloxane ($\text{Si}_{12}-\text{Vi}$). ^1H NMR, δ : 0.10 (s, 9 H, OSiMe_3); $5.86-5.98$ (m, 3 H, O_3SiVi); the integral intensity ratio of the signals of the protons of Me and Vi is 3 : 1. ^{29}Si NMR, δ : 8.76 (s, OSiMe_3 , *cis/cis*); 8.61 (s, OSiMe_3 , *cis/trans*); -81.80 (s, O_3SiVi , *cis/trans*); -81.88 (s, O_3SiVi , *cis/cis*). GPC (t_R/min): 18.68 (RI).

Hexavinylhexa(trimethylsiloxy)cyclohexasiloxane (Si_6-Vi). ^1H NMR, δ : 0.16 (s, 9 H, OSiMe_3); $5.81-5.93$ (m, 3 H, O_3SiVi); the integral intensity ratio of the signals of the protons of Me and Vi is 3 : 1. ^{29}Si NMR, δ : 9.21 (s, OSiMe_3); -82.28 (s, O_3SiVi). GPC (t_R/min): 19.36 (RI).

Dodecamethylidodeca(trimethylsiloxy)cyclododecasiloxane ($\text{Si}_{12}-\text{Me}$). ^1H NMR, δ : 0.13 (s, 9 H, OSiMe_3) and 0.10 (s, 3 H, O_3SiMe); the integral intensity ratio is 3 : 1. ^{29}Si NMR, δ : 7.67 (s, OSiMe_3 , *cis/cis*); 7.61 (s, OSiMe_3 , *cis/trans*); -67.21 (s, O_3SiMe , *cis/trans*); -67.48 (s, O_3SiMe , *cis/cis*). GPC (t_R/min): 18.68 (RI).

Hexamethylhexa(trimethylsiloxy)cyclohexasiloxane (Si_6-Me). ^1H NMR, δ : 0.12 (s, 9 H, OSiMe_3); 0.03 (s, 3 H, O_3SiMe). ^{29}Si NMR, δ : 8.50 (s, OSiMe_3 , *cis/cis*); -68.18 (s, OSiMe_3). GPC (t_R/min): 19.33 (RI).

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