Russian Chemical Bulletin, Vol. 43, No. 6, June, 1994

Application of size exclusion chromatography to the structural study of polyorganometallosiloxanes

I. V. Blagodatskikh, O. I. Shchegolikhina, Yu. A. Pozdnyakova, Yu. A. Molodtsova, and A. A. Zhdanov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Size exclusion chromatography was employed to elucidate the structure of the organosiloxane moiety in trimethylsiloxy derivatives of organometallosiloxanes containing Na, K, Ni, Mn, Cu, and Fe. An efficient technique of trimethylsilylation of organometallosiloxanes was developed to minimize alterations in their structure. The TMS derivatives of organometallosiloxanes were found to exist mostly as a more or less polydisperse mixture of cyclic poly[phenyltrimethylsiloxy siloxane]s. The preferred size of the cycles depends primarily on the nature of the metal in organometallosiloxane.

Key words: polyorganometallosiloxanes; size exclusion chromatography; cyclic poly(phenyltrimethylsiloxy)siloxanes.

Recently[1–4], a series of organometallosiloxanes (OMS) was synthesized by the reaction of sodium phenylsilanolate with the chlorides of transition metals (Ni, Mn, Co, Cu). The structure of these compounds was determined by X-ray diffraction analysis. They were named framework organometallosiloxanes, because their structure is characterized by the presence of organosiloxane layers having a cyclic structure and bound with the metal atoms in the inner layer of a sandwich.

However, the investigation of the composition and structure of the amorphous part of OMS is a challenging problem. To solve this problem, a method was developed[5] that comprises decomposition of OMS with trimethylchlorosilane (TMCS) in mild conditions. The crystalline cyclic poly(phenyltrimethylsiloxy)siloxanes (CPPTS) were isolated from the products of trimethylsilylation. The structure of these compounds was confirmed by X-ray diffraction and NMR spectroscopy. Nevertheless, the full composition of the polyorganometallosiloxanes and their TMS-derivatives remained unknown.

The objective of this work was to analyze the TMS derivatives of various OMS with the method of high performance size-exclusion chromatography (SEC). This method was selected because the results of the analysis for mixtures of oligomers are very easy to interpret, as the molecules are separated on the basis of a single parameter, namely, their dimensions.

Experimental

Synthesis of organometallosiloxanes and their derivatives. The methods for the synthesis of sodium phenylsilanolate (SPS) and also phenylnickel- and phenylmanganese siloxanes have been disclosed earlier[11]. Potassium phenylsilanolate was produced similarly to SPS, by replacing NaOH with KOH and without the addition of metallic potassium.

Phenylcopper siloxane was synthesized according to the procedure reported in Refs. 5, 9.

The method for the preparation of TMS derivatives. An amount of pyridine equivalent to the amount of metal in OMS was added to SPS or another OMS placed in a flask. Then a solution of TMCS in toluene was introduced. The mild conditions of the reaction were characterized by the fact that the amount of TMCS added to the solution was equivalent to the metal content in OMS. The optimum procedure of trimethylsilylation is characterized by a twofold excess of TMCS with respect to the metal of OMS. This excess is necessary to neutralize impurities present in metallosiloxanes (water, butanol, *etc.*).

Synthesis of poly[phenyliron(III) siloxane]. NaOH (2 g; 0.05 mol) was added to a solution of polyphenylsiloxane (12.9 g, 0.1 mol) in 200 mL of butanol. The mixture was boiled until complete dissolution of alkali and then sodium (5.41 g, 0.33 mol) was introduced. Then the reaction mixture was boiled for an additional two hours, and treated with freshly sublimated $FeCl_3$ dissolved in butanol (60 mL). The boiling was continued for 1 h, the precipitated NaCl was separated, and then the solvent was distilled off the filtrate to leave 14.1 g of poly[phenyliron(III) siloxane] (90.1 % of theoretical yield). Found (%): C, 48.25; H, 4.54; Si, 14.64; Fe, 9.78. Calculated values for $(C_6H_5SiO_{1.5})12(FeO_{1.5})_4(C_4H_{10}O)_5(O_{0.5}H)_4$: C, 47.99; H, 4.76; Si, 15.30; Fe, 10.14.

Size-exclusion chromatography. The analysis of the TMS derivatives of OMS was performed on an installation (Waters) comprising an M 600 pump, M 484 UV detector (λ = 254 nm), U-Styragel 500 and 1000 Å columns (32 000 theoretical plates), and a Maxima data processing system. Chloroform was the eluent (25 °C). The calibration of the logM vs. τ (molecular mass—retention time) plot was performed with samples of CPPTS of the general formula $[PhSiO(OSiMe_3)]_x$ that were

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1057—1062, June, 1994.

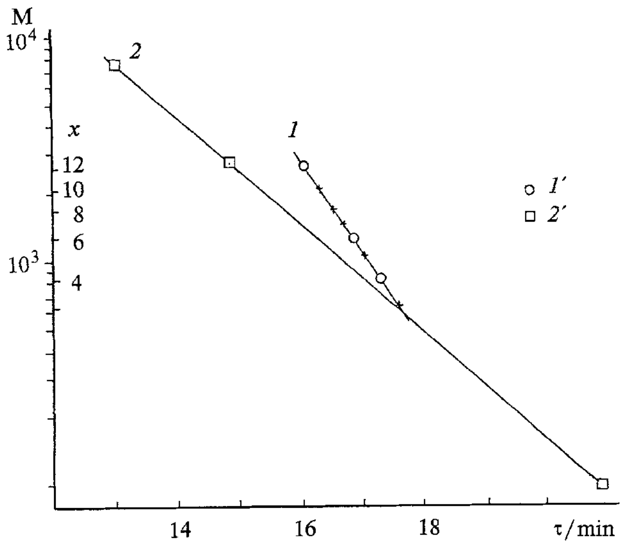


Fig. 1. The calibration curves for: CPPTS (*1*) and for polystyrene (*2*) (*1′* corresponds to experimental and *2′* to calculated values).

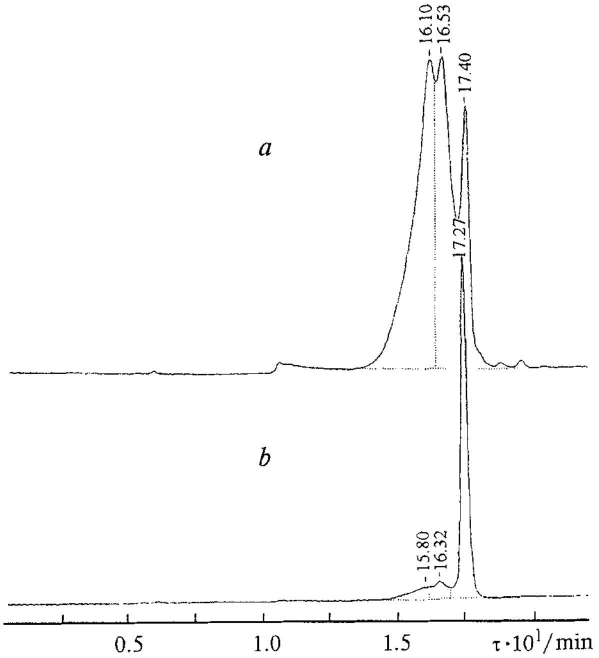


Fig. 2. The chromatograms of TMS derivatives of SPS: (*a*) SPS trimethylsilylated under mild conditions, (*b*) the same under the optimum conditions.

purified by additional recrystallization. These cyclic oligomers were isolated from the products of the trimethylsilylation of crystalline OMS containing sodium (x = 4), nickel (x = 6), and copper (x = 12). The structure of these cyclic compounds was determined using X-ray diffraction and NMR spectroscopy. The calibration curve is presented in Fig. 1 with the respective curve for polystyrene. Shown in the figure are also the points that correspond to the retention times calculated for the cycles having $x = 3\div10$ according to the equation $\log M = A + B\cdot\tau$. It will be shown below that the chromatograms of the TMS derivatives of OMS show peaks corresponding to some of these points. Using the calibration dependence for CPPTS and the universal Benoit calibration[6] we calculated efficient parameters of the Mark—Howink equation for these cycles

$$[\eta] = 5.79\cdot10^{-3}\cdot M^{0.065}$$

In this calculation we invoked the dependence of intrinsic viscosity on molecular mass for polystyrene

$$[\eta] = 7.16\cdot10^{-5}\cdot M^{0.76}$$

The fact that the exponent in the equation for CPPTS is close to zero implies that these cyclic compounds in solution behave like rigid ellipsoidal particles that grow in size as the number of repeat units increases but retain their shape[7].

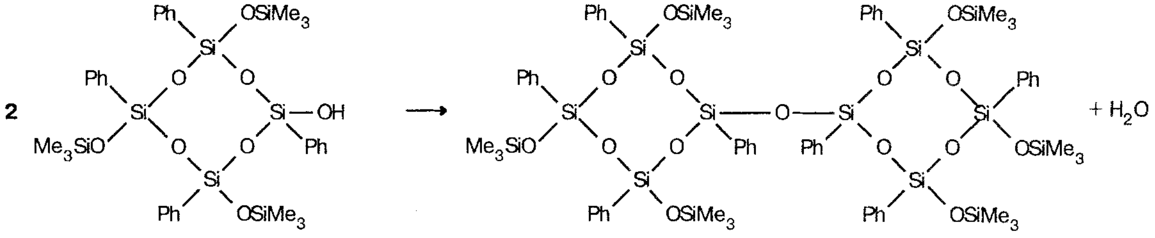
The weak dependence of the hydrodynamic volume of molecules on molecular mass results in reduced selectivity of oligomer separation in size-exclusion chromatography. For this reason, the chromatograms of oligomer mixtures usually do not resolve into separate peaks corresponding to particular homologs or they comprise partially resolved peaks. The usual methods for processing the data of size-exclusion chromatography for polymers[8] can be employed for these chromatograms; one can determine average molecular masses $\overline{M}_n$ and $\overline{M}_w$ and polydispersity $\overline{M}_w/\overline{M}_n$ using the calibration curve.

Results and Discussion

In order to use the data on the TMS derivatives to characterize the structure of the initial OMS, we had to develop an efficient technique of trimethylsilylation that would make it possible to isolate the organosiloxane fragments of OMS in the form of their respective TMS derivatives without any substantial disturbance in the composition and structure of the organosiloxane fragment. This problem was solved using sodium phenylsilanolate as an example. Figure 2 shows the dependence of the composition of TMS derivatives of one and the same sample of SPS on the particular method of trimethylsilylation. A comparison of the chromatograms (Figs. 2, *a* and 2, *b*) shows that the reaction under mild conditions (*i.e.*, without excess TMCS) yields a number of products. In addition to the main product, cyclotetra(phenyltrimethylsiloxy siloxane) (τ = 17.27), the reaction mixture contains the products of its decomposition and a substantial amount of higher molecular mass products. Supposedly, these products are di- and trimeric products of the condensation of cycles connected by Si—O—Si bonds that form from partially trimethylsilylated cycles according to Scheme 1.

Silanol groups can form by hydrolysis, because SPS always contains some residual water. The condensation

Scheme 1



reaction presented in Scheme 1 is possible when TMCS is deficient in the reaction system. This assumption is confirmed by the data of ^{1}H NMR spectroscopy. In theory, the products of trimethylsilylation should contain 9 methyl protons and 5 phenyl protons, whereas the TMS derivatives presented in Fig. 2, *a* have the ratio of methyl protons to phenyl protons of 3.35 : 5, and for those presented in Fig. 2, *b*, this ratio is 9.3 : 5. This means that a twofold excess of TMCS with respect to sodium at an equimolar concentration of pyridine (what we called the optimum technique) make it possible to substantially suppress the undesirable side reactions. This is also confirmed by the chromatogram shown in Fig. 2, *b*. Nevertheless, this chromatogram also reveals small peaks corresponding to di- and trimers that either formed in the course of trimethylsilylation or were already present in the initial SPS. The retention times of these peaks (16.32 and 15.80) are close to those of cycles with double and triple the number of siloxane units, yet do not coincide with them. Using recrystallization we isolated pure cyclotetrasiloxane from the produced mixture of trimethylsilylation products. This compound was used as a standard for calibration. The characteristics of the TMS derivative of SPS obtained by means of the above described technique are presented in Table 1. Thus, we determined the optimum method for trimethylsilylation of OMS, which consists of using a twofold excess of TMCS and an equimolar pyridine concentration. However, even under optimum conditions, one should allow for the possible formation of connected cycles due to their condensation.

In this work we analyzed TMS derivatives of organometallosiloxanes containing Na, K, Ni, Mn, Cu, and Fe. Trimethylsilylations were performed using either crude reaction masses formed in reactions of SPS with metal chlorides and freed of the solvent by evaporation, or the crystalline products isolated from these reaction masses.

Figure 3 presents the chromatogram of the TMS derivative of potassium phenylsilanolate. Unlike the monofractional TMS derivative of sodium organosiloxane, the trimethylsilylated potassium phenylsilanolate is a polydisperse mixture of cycles. The chromatogram shows well resolved peaks corresponding to the cyclic tri- and tetramers. The maximum molecular mass distribution corresponds to the trimer. The parameter of polydisper-

Table 1. The results of chromatographic analysis of TMS derivatives of OMS

OMS sample	Main peak		The main peak area (%)
	Position of peak, x $[\mathrm{PhSiO(OMe_3)}]_x$	Polydispersity $\overline{M}_w/\overline{M}_n$	
Na	4.0	1.00	95
K	3.0	1.53	99
Ni (reaction mass)	5.9	1.17	94
Ni (crystals)	5.7	1.03	84
Mn (reaction mass)	5.2	1.27	99
Mn (crystals)	5.2	1.04	94
CuNa (crystals)	12.0	1.00	82
Fe (laboratory)	6.3	1.11	66
Fe (commercial)	6.2	1.08	41

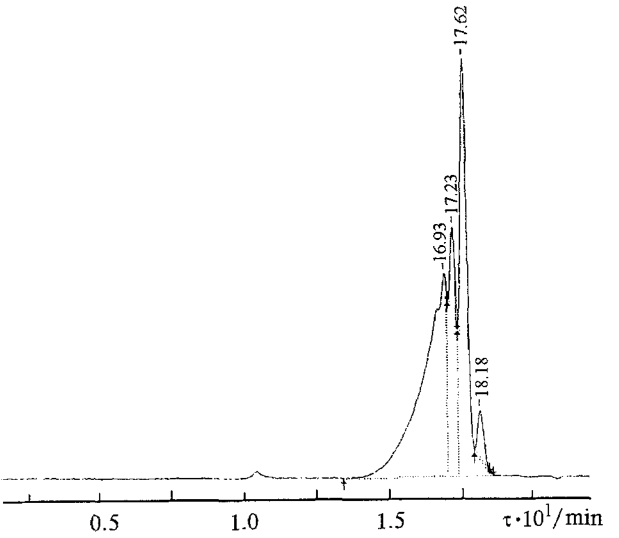


Fig. 3. The chromatograms of TMS derivatives of potassium phenylsilanolate.

sity is presented in Table 1. Apparently, it is this broad molecular mass distribution that makes isolation of crystalline potassium organosiloxane a difficult task.

Figures 4, *a* and 4, *b* present, respectively, the chromatograms of TMS derivatives of poly(phenylnickel siloxane) (crude reaction mass) and the crystals isolated from this mass (yield of crystalline product was 60—70 %). X-ray diffraction showed[4] that the structure of these crystals also incorporates two six-membered phenylsiloxane cycles, which frame the inner layer containing nickel atoms. The formula of this compound is $[PhSiO_{1.5}]_{12}(NiO)_6(NaCl)$. After trimethylsilylation, a regular cyclic hexamer was isolated from this crystalline sample[5]. The chromatograms of the TMS derivatives correspond to a mixture of CPPTS with a reasonably narrow distribution having the maximum close to $x = 6$. The parameters of polydispersity are presented in Table 1. The main peak in Fig. 5, *b* corresponds to a virtually monofractional cyclic hexamer. The small peaks (16.23 and 15.73) in chromatogram 4, *b* might, as in SPS, be related to the linked cycles formed in trimethylsilylation.

The TMS derivatives of poly(phenylmanganese siloxane)s show a picture analogous to the case of poly(phenylnickel siloxane)s. The characteristics of these compounds are also presented in Table 1.

Figure 5, *a*, *b* presents the results of analysis of the TMS derivatives of crystalline poly(phenylcoppersodium siloxane) (the yield of crystalline product is 67 %) and of the products of trimethylsilylation produced from the resin left after evaporating the mother liquor after separation of the crystals. According to X-ray diffraction data[9], the crystalline poly(organocoppersodium siloxane) has the formula $[PhSiO_{1.5}]_{12}(CuO)_4(NaO_{0.5})_4$ and the structure of its crystal incorporates a twelve-membered saddle-shaped organosiloxane cycle that frames the inner layer containing four sodium and four copper atoms. The chromatogram shows that the TMS derivative of crystalline copper-containing OMS is a mixture of twelve-membered (82 %) and six-membered cycles.

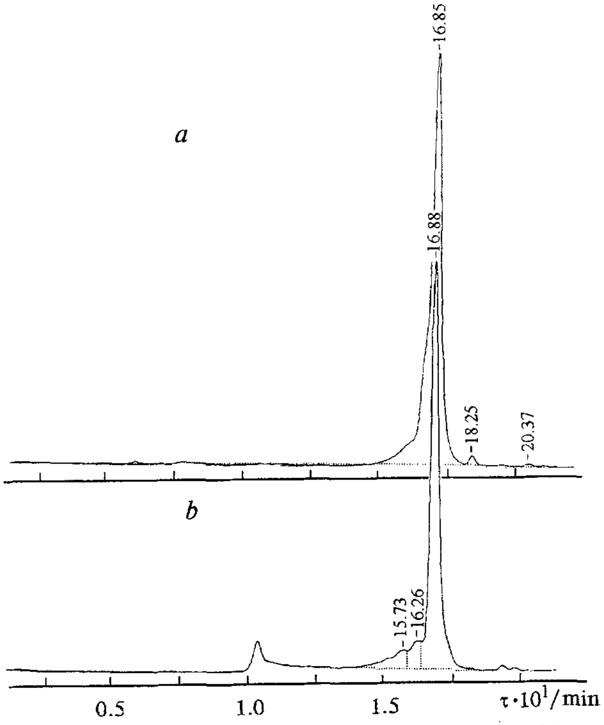


Fig. 4. The chromatograms of TMS derivatives of poly(phenylnickel siloxane)s: (*a*) those from the reaction mass of OMS and (*b*) from OMS crystals.

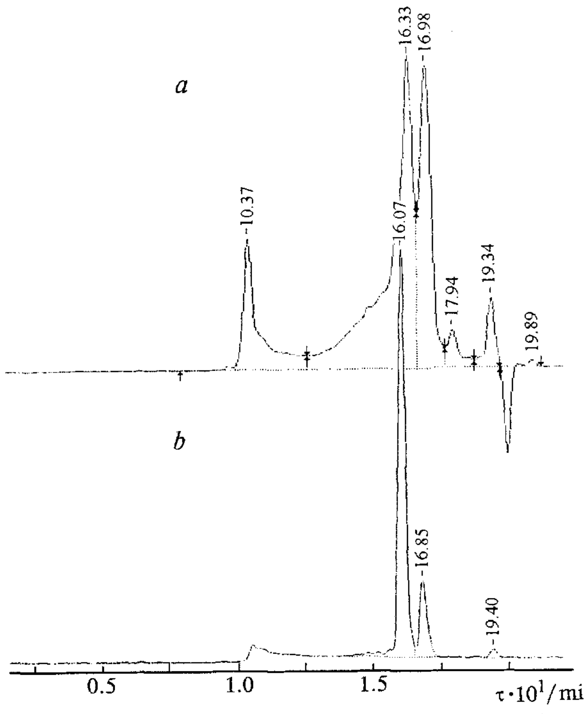


Fig. 5. The chromatograms of TMS derivatives of poly(phenylcoppersodium siloxane)s: (*a*) the residue of the mother liquor of OMS; (*b*) OMS crystals.

Table 2. Elemental analysis data for the samples of poly[phenyliron(III) siloxane]s and their TMS derivatives

OMS sample	TMS derivative			Initial OMS		
	% C	% Si	$(CH_3)_3SiO_{0.5}$: $C_6H_5SiO_{1.5}$ (molar)	% Fe	% Si	Fe : Si (molar)
1 laboratory	52.84	24.24	0.45 : 1	9.79	14.64	0.34 : 1
2 commercial	54.61	23.50	0.22 : 1	15.68	15.06	0.52 : 1

By means of recrystallization, we isolated from this mixture a pure dodecamer that was further used as a standard reference. The structure of this regular cycle was determined by X-ray diffraction and NMR spectroscopy. The product formed upon trimethylsilylation of the residue of the mother liquor (Fig. 5, *a*) is a bimodal mixture of cycles with distribution maxima at $x = 10$ and $x = 5 \div 6$. This indicates that the organosiloxane part of the initial organocoppersodium siloxane formed in the reaction of SPS with copper(II) chloride is a mixture of two cyclic fractions. The maximum of the major fraction corresponds to a twelve-membered cycle, and that of the smaller fraction, to a six-membered ring. It should be noted that the crystals isolated from neutral organocopper siloxane, according to X-ray diffraction, incorporate a six-membered cyclic siloxane fragment[4]. Therefore, one can assume that the reaction of SPS with $CuCl_2$ proceeds *via* two alternative paths that lead to the formation of either dodecameric or hexameric siloxane fragments. Another possible reaction scheme is a successive transition from dodecameric to hexameric fragments upon complete replacement of sodium with copper.

The results of the chromatographic analysis of the TMS derivatives of poly[phenyliron(III) siloxane]s produced according to the above-described procedure and according to the technique reported in Ref. 9 are shown in Fig. 6 and Table 1. Both samples are characterized by bimodal chromatograms indicating the presence of two fractions. The first fraction comprises cyclic poly(phenyltrimethylsiloxy siloxane)s with the maximum approximately corresponding to a six-membered cycle (Table 1). The high-molecular fraction, apparently, comprises linked cycles (bi-cycles, ladder structures).

This inference is based on a comparison of the elemental analysis data for different samples of OMS (content of Fe and Si) and their TMS derivatives (content of C and Si) that are presented in Table 2. The theoretical molar ratio of Fe : Si corresponding to the total binding of iron to silicon *via* oxygen atom is 1 : 3. One can see in Table 2 that for laboratory sample 1 this ratio is approximately equal to the theoretical value, and for sample 2, far exceeds it. Simultaneously, complete bonding of iron to silicon *via* oxygen followed by complete trimethylsilylation of these bonds corresponds to the ratio $(CH_3)_3SiO_{0.5}$: $C_6H_5SiO_{1.5}$ = 1 : 1 for the reaction products. This ratio calculated on the basis of the silicon and carbon content in the TMS derivatives shows that the content of trimethylsilyl fragments in sample 1 is approximately two times lower than that of phenylsiloxane fragments. For sample 2 this ratio is even lower. This result indicates either that iron is not completely bound by Fe—O—Si bonds (this effect is more pronounced in commercial sample 2) or that trimethylsilylation of these compounds is incomplete. The data on ironsiloxanes, when compared to the results of trimethylsilylation of OMS containing other metals, indicates that when poly(phenyliron siloxane)s are prepared according to conventional methods, only a fraction of the iron atoms are regularly bound with silicon *via* oxygen (one iron per three silicon atoms). Better understanding of the formation of iron-containing polyorganosiloxanes requires further investigations.

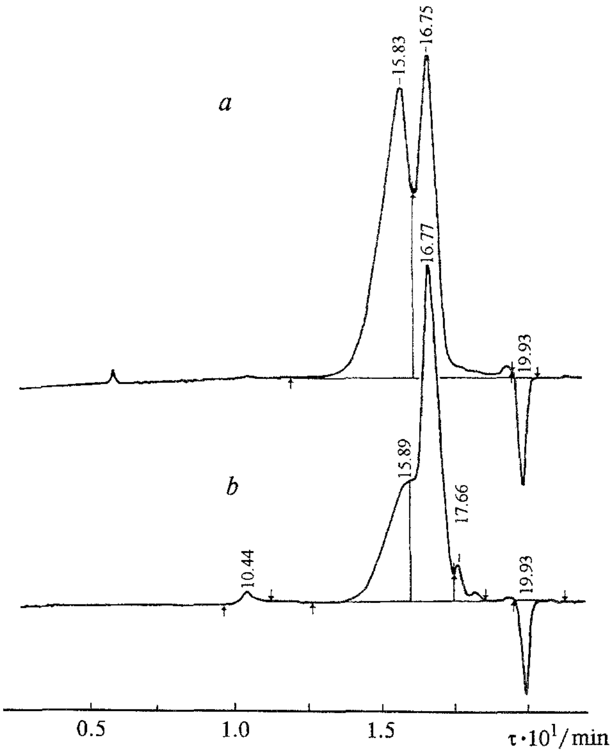


Fig. 6. The chromatograms of TMS derivatives of poly[phenyliron(III) siloxane]s: (*a*) that of OMS produced on a demonstrational apparatus and (*b*), synthesized in the laboratory.

Thus, the analysis of the TMS derivatives of Na-, K-, Ni-, Mn-, Cu-, and Fe-containing OMS allows us to conclude that the organosiloxane part of these OMS is a more or less polydisperse mixture of cycles of different lengths. The dimensions of the most favorable cyclic structure are determined primarily by the nature of the metal in the OMS.

This work was performed with the financial support of the Russian Foundation for Basic Research (Grant No. 93-03-18121).

References

1. O. I. Shchegolikhina, A. A. Zhdanov, V. A. Igonin, Yu. E. Ovchinnikov, V. E. Shklover, and Yu. T. Struchkov, *Metalloorg. Khim.*, 1991, **4**, 74 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
2. V. A. Igonin, S. V. Lindeman, K. A. Potekhin, V. E. Shklover, Yu. T. Struchkov, O. I. Shchegolikhina, A. A. Zhdanov, and I. V. Razumovskaya, *Metalloorg. Khim.*, 1991, **4**, 790 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
3. M. M. Levitsky, O. I. Shchegolikhina, A. A. Zhdanov, V. A. Igonin, Yu. E. Ovchinnikov, V. E. Shklover, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1991, **401**, 199.
4. V. A. Igonin, O. I. Shchegolikhina, S. V. Lindeman, M. M. Levitsky, Yu. T. Struchkov, and A. A. Zhdanov, *J. Organomet. Chem.*, 1992, **423**, 351.
5. O. I. Shchegolikhina, Yu. A. Molodtsova, Yu. A. Pozdnyakova, T. V. Strelkova, and A. A. Zhdanov, *Dokl. Akad. Nauk SSSR,* 1992, **325**, 1186 [*Dokl. Chem,* 1992, **325** (Engl. Transl.)].
6. H. Benoit, Z. Grubisic, P. Rempp, D. Decker, and J. G. Zillox, *J. Chem. Phys.*, 1966, **63**, 1507.
7. V. N. Tsvetkov, V. E. Eskin, and S. Ya. Frenkel, *Struktura makromolekul v rastvorakh* [*Structure of Macromolecules in Solutions*], Moscow, 1964 (in Russian).
8. B. G. Belen'kii and L. Z. Vilenchik, *Khromatografiya polimerov* [*Chromatography of Polymers*], Moscow, 1978 (in Russian).
9. V. A. Igonin, S. V. Lindeman, Yu. T. Struchkov, O. I. Shchegolikhina, A. A. Zhdanov, Yu. A. Molodtsova, and I. V. Razumovskaya, *Metalloorg. Khim.*, 1991, **4**, 1355 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
10. A. A. Zhdanov, K. A. Andrianov, and M. M. Levitskii, *Vysokomol. Soedin., Ser. A*, 1976, **18**, 2264 [*Polym. Sci. USSR*, 1976, **18** (Engl. Transl)].
11. A. A. Zhdanov, O. I. Shchegolikhina, and Yu. A. Molodtsova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 957 [*Russ. Chem. Bull,* 1993, **42**, 917 (Engl. Transl.)].

Received November 15, 1993