Condensation of methylphenylalkoxysilanes in an active medium as a selective method for synthesis of cyclic or linear methylphenylsiloxanes*

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Polycondensation of methylphenyldialkoxysilane was studied under the conditions of an active medium, namely, an acetic acid excess, being simultaneously a reactant, catalyst, and solvent. This method was shown to be universal for the synthesis of a wide range of polymethylphenylsiloxanes of diverse structure. The conditions that allow one to synthesize both linear and cyclic methylphenylsiloxanes by this method were found. The possibility to prepare linear polymethylphenylsiloxanes with the molecular weight up to 34000 amu was shown.

Key words: polycondensation, active medium, organoalkoxysilanes, polymethylphenylsiloxanes, methylphenylcyclosiloxanes.

Polymethylphenylsiloxanes represent a wide class of organosilicon compounds used for the production of rubbers and liquids. Presently, the whole range of methylphenylsiloxane products is prepared in several stages using polycondensation and polymerization processes. As a rule, hydrolysis of methylphenyldichlorosilane occurs at the first stage.[1] The hydrolysis products are a mixture of linear and cyclic components. Possibilities of controlling their composition are fairly restricted, first of all, because the process that occurs is heterogeneous.[2] Therefore, the thermocatalytic rearrangement (TCR) of the hydrolytic polycondensation (HPC) products is carried out at the second stage. As a result, the yield of 1,3,5-trimethyltriphenylcyclotrisiloxane increases due to the shift of equilibrium between cyclosiloxanes with various sizes of cycles upon its removal from the reaction mixture by distillation.[1] Thus obtained 1,3,5-trimethyltriphenylcyclotrisiloxane is used in processes of polymerization and copolymerization for syntheses of high-molecular-weight polymethylphenylsiloxanes.

As can be seen from the description presented above, the used approach to the synthesis of methylphenylsiloxane polymers is energy consuming and is accompanied by a large amount of waste to be utilized.[1,3]

There is a recent tendency for using organoalkoxysilanes instead of organochlorosilanes as the starting reactants.[4—6] It is necessary to use a new raw materials, because, first of all, requirements for ecological safety of manufacturing have been increased. However, the new starting compounds demand the development of new technological approaches to the preparation of polymer products and, therefore, the study of possibilities of directed synthesis of polyorganosiloxanes using organoalkoxysilanes is an urgent task.

A recently developed concept of condensation of organoalkoxysilanes in an active medium,[6] being simultaneously the reactant and solvent, whose essence is the use of an excess of anhydrous carboxylic, particularly, acetic acid, can be promising and universal method for the synthesis of polyorganosiloxanes. The principal advantage of alkoxysilane condensation in an active medium is that, unlike HPC of organochlorosilanes, it occurs under homogeneous conditions. The study of the process showed that this is a classic cascade process consisting of a series of consecutive steps: acidolysis of alkoxy groups, esterification of the evolved alcohol, hydrolysis of acetoxysilyl groups with water evolved in the esterification, and heterofunctional condensation of silanols with acetoxysilyl groups to form the siloxane bond. Acetic acid evolved in this process returns to the reaction cycle. The efficiency of HPC of organoalkoxysilanes in the active medium was confirmed by an example of synthesis of polymethylsiloxanes from methylalkoxysilanes.[6]

The purpose of this work is the study of condensation of methylphenyldialkoxysilanes in an active medium

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* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 80th birthday.

as a selective method for synthesis of linear or cyclic products.

Results and Discussion

Condensation of methylphenyldialkoxysilane was carried out at reflux in an acetic acid excess. The reaction course was monitored by sampling the reaction mixture and analyzing the samples by ^{1}H NMR spectroscopy. The completion of the process was concluded by the disappearance of signals from protons of the alkoxysilyl groups. The reaction products obtained after the end of the process, *i.e.*, the products of complete conversion of the Si—OR groups, were characterized by GPC and IR and ^{1}H NMR spectroscopy. An analysis of the obtained data showed that the reaction products represented a mixture of cyclic and linear oligomers containing no alkoxysilyl groups but having residual hydroxysilyl groups (Scheme 1).

Scheme 1
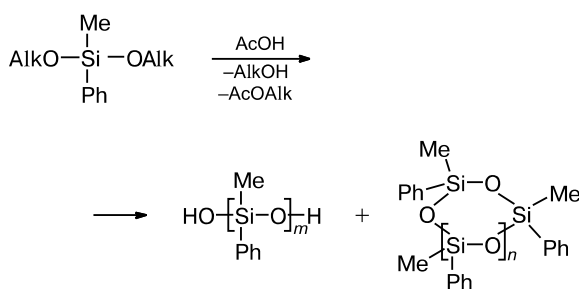
n = 1, 2, 3.

To determine the number of terminal hydroxysilyl groups, the obtained oligomethylphenylsiloxanes were blocked with trimethylchlorosilanes under the conditions providing the complete conversion of the hydroxysilyl groups and the absence of the side reaction of their homocondensation that violates the initial composition of the reaction products (Scheme 2).

Scheme 2
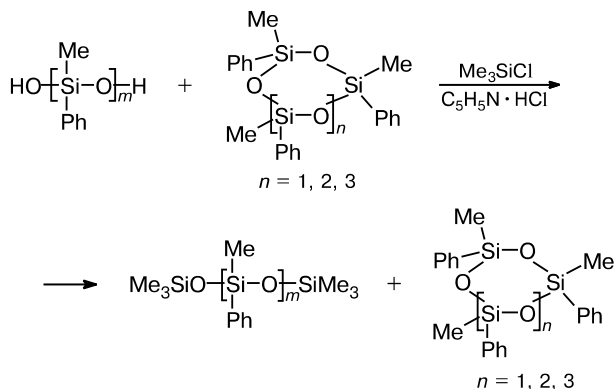
The absence of a change in the molecular weight distribution of oligomethylphenylsiloxanes during blocking was indicated by the identical GPC curves before and after blocking of the terminal hydroxysilyl groups (Fig. 1).

The complete conversion of hydroxysilyl groups was confirmed by IR spectroscopy from the absence of the absorption band in the region of 3100—3600 cm^{-1} characteristic of hydroxysilyl groups. The number of introduced trimethylsilyl groups and, correspondingly, the number of terminal hydroxysilyl groups of the product were determined from the ratio of integral intensities of signals from the protons of the trimethylsilyl blocking groups and protons of the phenyl substituent at the silicon atom in the ^{1}H NMR spectra of the blocked samples.

The change in the type of the alkoxy group of the initial organoalkoxysilane exerted no appreciable effect on the composition of the final product, as in the case of the condensation of dimethyldialkoxysilanes.[6] Condensation in an active medium of both methoxy- and ethoxysilanes on reflux resulted in obtaining oligomethylphenylsiloxanes with almost identical GPC curves. In the both cases, the products were a mixture of cyclic and linear oligomethylphenylsiloxanes with an insignificantly differed amount of the cyclic fraction at the same degree of polymerization of linear oligomers (Fig. 2).

The obtained mixture of linear and cyclic products is entirely suitable for the preparation of methylphenylcyclosiloxanes by the TCR method. A mixture of methylphenylcyclosiloxanes was obtained in a yield of more than 90% by the TCR method from a mixture of oligomethylphenylsiloxanes synthesized at the previous stage. According to the GLC data, the mixture contained 56 and 44% methylphenylcyclotri- and tetrasiloxanes, respectively. Lithium hydroxide known as an efficient catalyst of TCR of oligomethylphenylsiloxanes[1] was used as a catalytic additive.

Thus, it was shown that methylphenylcyclosiloxanes can be obtained using methylphenyldialkoxysilanes. An important advantage of the use of organoalkoxysilanes in-
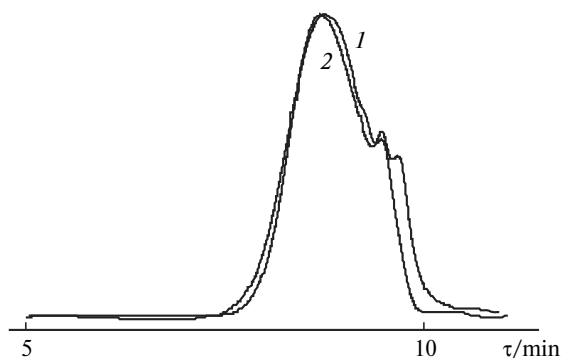
Fig. 1. GPC curves (75 kDa) for oligomethylphenylsiloxanes before (*1*) and after (*2*) blocking of terminal groups with trimethylchlorosilane.
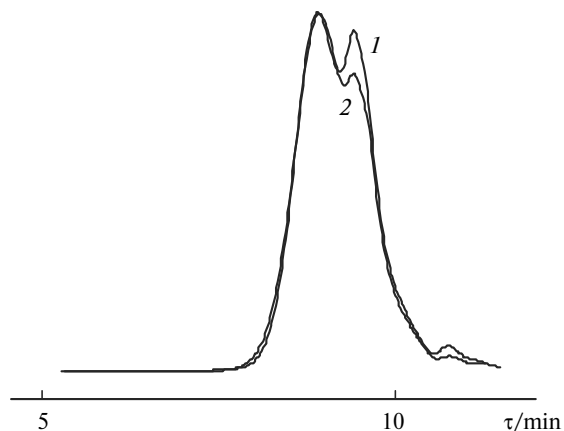
Fig. 2. GPC curves (75 kDa) for oligomethylphenylsiloxanes synthesized by the condensation of MePhSi(OMe)$_2$ (*1*) and MePhSi(OEt)$_2$ (*2*) in the active medium.

stead of organochlorosilanes was confirmed: a large amount of waste as hydrochloric acid and precipitates of calcium salts used for neutralization of the products of hydrolysis of organochlorosilanes can be excluded from the production cycle.

As has been shown above, the condensation of methylphenyldialkoxysilane in anhydrous acetic acid afforded a mixture of linear and cyclic products, which is typical, as a whole, of polycondensation processes of bifunctional organosilicon monomers. However, the purpose of the work implied an increase in the selectivity of the process, since a very energy-consuming and low-conductivity TCR process can be rejected in the case of selective formation of cyclic products directly during the condensation of methylphenyldialkoxysilane. It was also very interesting to study the selective direction of condensation in the active medium towards the formation of linear functional oligomers that are promising starting compounds for the whole series of polymer compositions.

Specificity of the polycondensation of organoalkoxysilanes in the active medium is that the water necessary for hydrolysis is formed at the slowest stage of the cascade process and is immediately consumed in faster reactions of hydrolysis of acetoxysilyl groups. Thus, monitoring of the structure of the reaction products can be reduced to the control of the rate of water generation during condensation. The formation of water during condensation of organoalkoxysilanes in acetic acid occurs in esterification (Scheme 3).

Scheme 3

AcOH + AlkOH $\rightleftharpoons$ AcOAlk + HOH
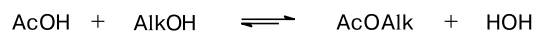
Therefore, the rate of water generation depends on the amount of alcohol, which is generated in turn in the sys-

tem when the starting diorganodialkoxysilane is acetoxylated (Scheme 4).

Scheme 4

$$Me_2Si(OAlk)_2 + AcOH \rightleftharpoons Me_2Si{\overset{OAlk}{\underset{OAc}{\big\langle}}} + AlkOH$$

To increase the amount of water formed in the reaction system, methylphenyldiethoxysilane was refluxed in acetic acid with the addition of anhydrous ethanol. The method was quite efficient, and an analysis of the reaction products by GPC and ^{1}H NMR spectroscopy showed that the obtained oligomethylphenylsiloxanes contained more than 80% of cyclic components. The data of GPC analysis of the condensation products of methylphenyldiethoxysilane in acetic acid with the addition of anhydrous ethanol are shown in Fig. 3.

As follows from Fig. 3, an increase in the amount of alcohol introduced into the reaction mixture increases the yield of the fraction of cyclic oligomethylphenylsiloxanes. In particular, the addition of 0.75 mole of ethanol per 1 mole of methylphenyldiethoxysilane affords a mixture of oligomethylphenylsiloxanes containing 50% of cyclic components, whereas an increase in the amount of introduced alcohol to 3.25 moles per 1 mole of alkoxysilane results in the formation of more than 80% of cyclic oligomethylphenylsiloxanes.

It was reasonable to assume that the backward process, *i.e.*, retardation of the rate of water formation in the system, would result in the predominant formation of linear oligomethylphenylsiloxanes. In order to decrease the rate of water generation, methylphenyldimethoxysilane was introduced into boiling acetic acid gradually, thus ensur-
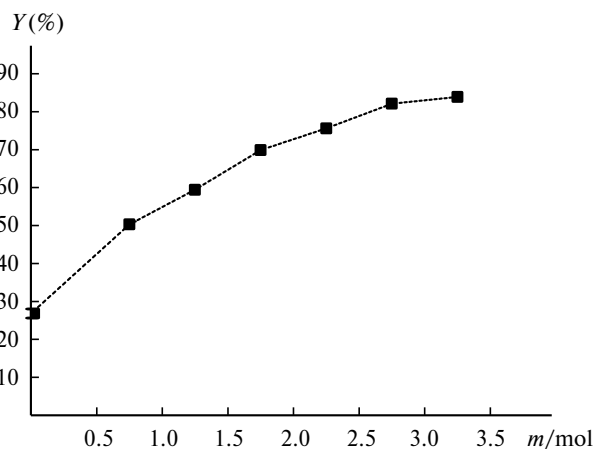

Fig. 3. Dependence of the yield of cyclic oligomethylphenylsiloxanes (*Y*) on the amount of anhydrous methanol (m/mol^{-1} per 1 mole of methylphenyldiethoxysilane) introduced into the reaction mixture.

ing the slow formation of alcohol in the reaction mixture. In this case, an analysis of the product by GPC and ^{1}H NMR showed that the yield of linear oligomethylphenylsiloxanes exceeded 80%. The molecular weight of the obtained oligomers was ~1600 amu.

Thus, management of the rate of water generation in the reaction mixture is an efficient tool of controlling the selectivity of the process towards the predominant formation of linear and cyclic structure. The formation of linear functional oligomethylphenylsiloxanes provide wide possibilities of their use in various reaction, particularly, for the synthesis of polymer systems of complex architecture.[7−11] However, the main promising application of the obtained linear oligomethylphenylsiloxanes with terminal functional groups is the synthesis of linear methylphenylsiloxanes with high molecular weight.

The molecular weight of the polycondensation linear products was increased by the homocondensation of the terminal hydroxysilyl groups. The homocondensation of the terminal hydroxysilyl groups of methylphenylsiloxane oligomers in the absence of catalytic additive even *in vacuo* at elevated temperature did not result in any noticeable increase in the molecular weight of the oligomers (Table 1, entries *1—3*). Therefore, the influence of a series of additives catalyzing the condensation of terminal Si—OH groups was studied. As should be expected,[12,13] the introduction of cesium fluoride turned out to be efficient.

The GPC analysis of the condensation products showed a considerable increase in the molecular weight of the starting oligomethylphenylsiloxane (by ~20 times) at the nearly unchanged content of the cyclic components (see Table 1, entry *4*; Fig. 4, curve *2*). Based on the chromatogram, one may assume that cesium fluoride selectively catalyzes the homocondensation of linear oligomers and does not catalyze the depolymerization reaction. However, the model experiment, being the heating of linear methylphenylsiloxane purified from cyclic products (see Fig. 4, curve *3*) in the presence of CsF, showed that the content
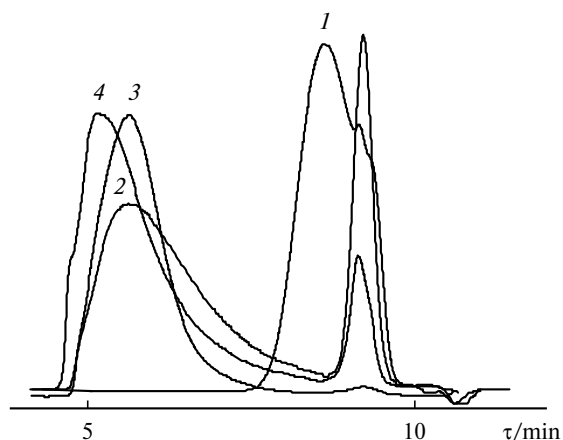

Fig. 4. GPC curves (75 kDa) of the initial oligomethylphenylsiloxane (*1*) and the product of its condensation (*2*) in the presence of cesium fluoride, (*3*) linear fraction isolated from product *2*, and (*4*) condensation product of product *3* in the presence of cesium fluoride.

of the cyclic component increased considerably, by 10% (see Fig. 4, curve *4*, Table 1; entry *5*). Thus, it was unambiguously shown that the introduction of this catalytic additive accelerated the homocondensation of hydroxysilyl groups and also depolymerized the polymer siloxane chain to form a volatile cyclic component.

Then the catalytic homocondensation of linear oligomethylphenylsiloxanes with terminal hydroxysilyl groups in the presence of potassium acetate as a catalyst was considered. This process gave polymethylphenylsiloxane with a molecular weight of 19 000 amu (see Table 1, entry *6*) but was not accompanied by undesirable depolymerization. The complete absence of depolymerization was demonstrated for the model experiment of condensation of oligomers containing almost no cyclic fraction. The GPC curves of polymethylphenylsiloxane before and after condensation are presented in Fig. 5 (curves *1* and *2*, respectively).

Table 1. Conditions of condensation of oligomethylphenylsiloxanes *in vacuo* and characterization of the products

| Entry | Condensation conditions of oligomethylphenylsiloxane | | Characterization of olifomethylphenylsiloxane | | | |
| | | | before condensation | | after condensation | |
	Catalyst	T^a/°C	MW$_{peak}$ in GPC (75 kDa, PSS^b)	Content of cycles (%)	MW$_{peak}$ in GPC (75 kDa, PSS^b)	Content of cycles (%)
1	—	20	1700	25	1700	25
2	—	150	1700	25	1700	25
3	—	180	1700	25	1700	25
4	CsF	180	1700	25	32000	33
5	CsF	180	32000	2	34000	12
6	AcOK	180	2500	2	19000	2

^{a} Condensation temperature.
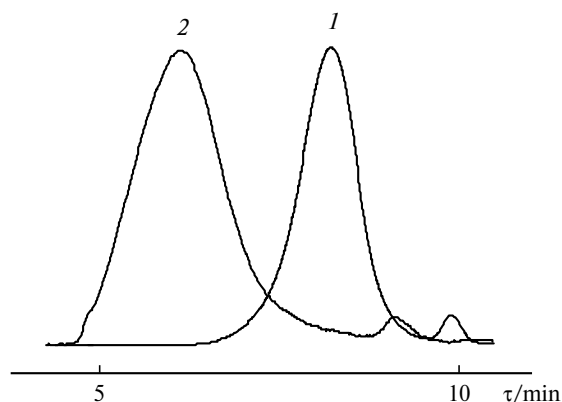^{b} PSS is polystyrene standard.

Fig. 5. GPC curves (75 kDa) of the initial polymethylphenyl-siloxane (*1*) and the product of its condensation (*2*) in the presence of potassium acetate (*2*).

Thus, the polycondensation of methylphenyldialkoxy-silane in an active medium is a universal method providing the selective formation of methylphenylsiloxanes of both cyclic and linear structure. The possibility of controlling the structure of the final product is an important advan-

tage of the method compared to the HPC of organochloro-silanes.

Experimental

Methylphenyldimethoxysilane and methylphenyldiethoxy-silane were distilled prior to use; acetic acid, ethanol, toluene, and potassium acetate were pre-dried using known procedures.[14] Cesium fluoride, *o*-xylene, and an aqueous solution of lithium hydroxide (Aldrich) were used without additional purification. ^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer (250.13 MHz) using Me$_4$Si as an internal standard.

GLC analysis was carried out on a Khromatek-Analitik-5000 chromatograph (Russia) using a katharometer as a detector and helium as a carried gas (columns 2 m × 3 mm, stationary phase SE-30 (5%) supported on Chromaton-H-AW).

GPC analysis was carried out on a Staier liquid chromatograph (Akvilon, Russia) in toluene or THF on columns Pheno-gel-75 KD, 500 KD (particle size 7.5 μm). The molecualr weight was determined by the ratio to linear polystyrene standards. A RIDK 102 differential refractometer was used as a detector.

IR spectra were recorded on a Bruker Equinox 55/S IR spectrometer. Liquid cells with KBr glasses and CCl$_4$ as a solvent were used for measurements.

Table 2. Conditions of condensation of methylphenyldialkoxysilanes in the active medium and characterization of the product

Alk[a]	Condensation conditions		Characterization of product					
	EtOH /mol[b]	Order of introduction of reactants	^{1}H NMR		GPC (75 kDa, PSS) of OMPS[d]			
					linear		cyclic (%)	
			N (%)[c]	MW[c]	MW$_{peak}$	C (%)[f]	Formula of cycle[e]	C (%)[f]
Me	—	Mixing	13.7	2000	1600	57.4	A3	10.5
							A4	32.1
Et	—	Mixing	15.1	1800	1600	73.1	A3	10.6
							A4	16.3
Me	—	Introduction of MePhSi(OMe)$_2$ into AcOH for 10 h	15.1	1800	1600	83.6	A3	9.7
							A4	6.7
Et	0.75	Mixing	10.9	2500	1400	49.6	A4	18.6
							A5	31.8
Et	1.25	Mixing	9.1	3000	1300	40.5	A4	23.5
							A5	36.0
Et	1.75	Mixing	7.8	3500	1300	30.1	A4	26.3
							A5	43.6
Et	2.25	Mixing	7.4	3700	1100	24.3	A4	28.8
							A5	46.9
Et	2.75	Mixing	6.8	4000	1300	17.8	A4	27.1
							A5	55.1
Et	3.25	Mixing	6.7	4100	1300	16.0	A4	24.7
							A5	59.3

[a] The Alk group of the initial MePhSi(OAlk)$_2$.
[b] The amount of added alcohol per 1 mole of MePhSi(OAlk)$_2$.
[c] The number of terminal OH groups (*N*) and the molecular weights (MW) calculated from the ^{1}H NMR spectra of the condensation products blocked by trimethylchlorosilane.
[d] OMPS is oligomethylphenylsiloxane.
[e] A3, A4, and A5 designate [MePhSiO]$_3$, [MePhSiO]$_4$, and [MePhSiO]$_5$, respectively.
[f] *C* is the content of OMPS.

All reactions were carried out in an inert atmosphere.

Condensation of dialkoxy(methyl)phenylsilane in acetic acid at the mole ratio 1 : 10 (general procedure). A mixture of reactants was refluxed with vigorous stirring until the signals from protons of the alkoxy groups in the ^{1}H NMR spectra of reaction mixture samples disappeared completely. Then volatile components were removed at 20—25 °C (1 Torr). The yield of the product was 98—99%. ^{1}H NMR (CDCl$_3$), δ: 0.1—0.65 (m, 3 H, (C$\underline{H}_3$)(C$_6$H$_5$)Si); 7.1—7.8 (m, 5 H, (CH$_3$)(C$_6\underline{H}_5$)Si). IR (CCl$_4$), ν/cm^{-1}: 3300(OH) w. The number of the terminal hydroxysilyl groups of the obtained oligomethylphenylsiloxane was determined by the ^{1}H NMR spectra of the samples blocked with trimethylchlorosilane.

Blocking of terminal hydroxyl groups of oligomethylphenylsiloxane (general procedure). A 20% solution of oligomethylphenylsiloxane (10.0 g, 0.07 mol) in anhydrous toluene was added dropwise to trimethylchlorosilane (16.7 g, 0.15 mol) and pyridine (12.2 g, 0.15 mol) in toluene (30 mL). The mixture was refluxed with stirring for 4 h. The obtained product was washed off with distilled water to neutral pH, dried over sodium sulfate, and evacuated on heating to 50 °C. ^{1}H NMR (CDCl$_3$), δ: 7.1—7.8 (m, 5 H, (C$_6$H$_5$)(CH$_3$)Si); 0.1—0.65 (m, 9 H, (C$\underline{H}_3$)$_3$Si); 0.1—0.65 (m, 3 H, (C$_6$H$_5$)(C$\underline{H}_3$)Si). IR (CCl$_4$), ν/cm^{-1}: no signals of the OH groups at 3300 cm^{-1}.

The conditions of condensation of diethoxy(methyl)phenylsilane in the active medium and characterization of the products blocked with trimethylchlorosilane are presented in Table 2.

Thermocatalytic depolymerization of oligomethylphenylsiloxanes. Oligomethylphenylsiloxane (68.58 g, 0.5 mol, 4.23 mol L^{-1}) and an aqueous solution of lithium hydroxide (0.8 mL) and *o*-xylene (54.32 mL) were heated for 1 h followed by the distillation of water and *o*-xylene *in vacuo* (14 Torr). Then fractional distillation of methylphenylcyclosiloxanes was carried out (195—210 °C, 3—4 Torr). A mixture of methylphenylcyclosiloxanes was obtained in a yield of 63.58 g (93%). According to the GLC data, 56% methylphenylcyclotrisiloxane and 44% methylphenylcyclotetrasiloxane were obtained.

Synthesis of linear high-molecular-weight polymethylphenylsiloxane (general procedure). Oligomethylphenylsiloxane and 1 wt.% of the corresponding catalyst were stirred *in vacuo* (1 Torr) on heating for 5 h. The yield of the product was quantitative. The molecular weight of the product and the content of the cyclic fraction were estimated by GPC. The conditions for condensation of oligomethylphenylsiloxane and the GPC data are given in Table 1. In entries *5* and *6* (see Table 1), the initial linear oligomethylphenylsiloxane was preliminarily isolated by fractional precipitation from a 10% solution of a mixture of linear and cyclic components in toluene with hexane at room temperature and was further used for the catalytic condensation.

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