Synthesis of dimethylcyclosiloxanes in the active medium*

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The process of condensation of dimethyldiethoxysilane in the active medium in a presence of acetyl chloride, trifluoroacetic acid, and sulfocationites has been investigated. Their impact on the rate and selectivity of the process has been estimated. The prospects of the application of sulfocationites for the polycondensation of dimethyldiethoxysilane in anhydrous acetic acid with an 99% yield have been demonstrated.

Key words: polycondensation, alkoxysilane, cyclosiloxane, active medium.

The organocyclosiloxanes, primarily dimethylcyclosiloxanes are found an application in the industry as starting materials for the preparation of silicone rubbers through ionic polymerization. Synthesis and purification of these starting compounds are highly labor-consumptive processes, which in most cases do not have more affordable alternative. In this connection the task of the development of technologies for the production of these compounds, which satisfy modern requirements in terms of both cost and environmental characteristics, is very urgent. The main method of organocyclosiloxanes synthesis is hydrolytic polycondensation of diorganodichloro- and diethoxysilanes. General understanding of the mechanism of these reactions were formulated by K. A. Andrianov and N. N. Sokolov in the classical works.[1—3] Currently, an industrial process for the synthesis of cyclic and linear polyorganosiloxanes is hydrolytic polycondensation of diorganodichlorosilanes,[1—8] i.e. complex heterophase mass transfer process leading to the formation of a mixture of linear and cyclic products and accompanied by the formation of large amount of hydrogen chloride.[8] The hydrogen chloride catalyzes the condensation reaction, exerting a significant influence on the composition of the products. The phase separation in the reaction mixture complicates considerably the control and management of the process.[5] An im-plementation of the hydrolytic polycondensation of diorganodichlorosilanes under homogeneous conditions is almost impossible, since it requires large volumes of homogenizing solvent, which significantly reduces the reaction rate.[5,8] All these shortcomings of the process, as well as modern strict requirements for environmentally friendly industries determine the need for the transition to a chlorine-free "green" technology, using as the starting compounds alkoxy-functionalized silanes instead of chlorosilanes.

Hydrolytic polycondensation of diorganodialkoxysilanes also leads to the mixture of cyclic and linear products. However, a homogenization of the reaction mass in this case is easier to achieve as in the case of organochlorosilanes. Alcohol released during hydrolysis dissolves both water and the reaction products, but the total conversion of the alkoxy groups is possible only with the introduction of the additional quantities of solvent.[9—13]

Previously, it was shown that the ratio of cyclic and linear products depends greatly on the choice of the catalyst: by hydrolysis of diorganodialkoxysilanes in the presence of alkali catalysts linear siloxanes are predominantly formed,[14,15] and the addition of acid catalysts leads to formation of cyclic products.[16—21] However, this requires additionally a removal of operational catalysts and neutralizing of the reaction mass. Currently, the most successful approach is the implementation of organoalkoxysilanes polycondensation in the active medium, namely anhydrous acetic acid, which acts as reactant, solvent, and catalyst simultaneously (Scheme 1).[22—28]

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Scheme 1
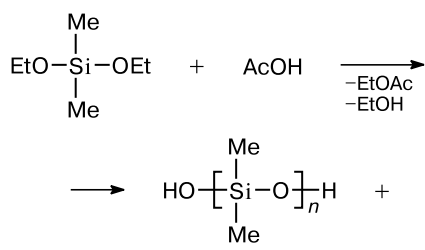
Due to the absence of chlorine-containing components in both the starting compounds and the waste, this process is ecological and meets the modern requirements for transition to a so-called "green chemistry".

Previously the prospects of the process for the preparation of various homopolymer and copolymer structures, from branched and polycyclic[22,23] to linear and cyclic organosiloxanes[24—28] have been demonstrated. However, a high level of selectivity of the process of cyclosiloxanes formation has not been achieved. This determined that this study aimed at finding the ways to increase the yield of cyclic products.

The specifics and the main advantage of the polycondensation of the organoalkoxysilanes in the active medium, undergoing through a number of concerted steps (Scheme 2), is the generation of water in the esterification reaction (see Scheme 2, the Eq. (2)) and its immediate consumption during hydrolysis of acetoxysilyl derivatives of silicon (see Scheme 2, the Eq. (3)). It determines the homogeneous state of the reaction mixture during the synthesis.
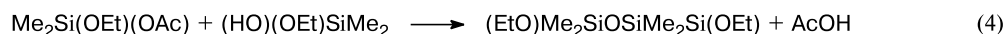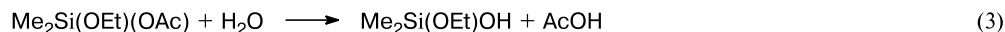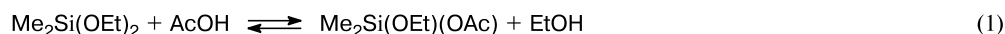
This feature of the process yields the number of technological advantages, including the ability to regulate

the direction of the selective formation of linear or cyclic products.[23,24] As it was demonstrated previously, the introduction of an additional amount of alcohol during polycondensation of dimethyldiethoxysilane (DMDES) in the active medium, which increases the rate of water generation, leads to an increase in yield of the dimethilcyclosiloxanes up to 80%. It means that the selectivity is only slightly lower than in the hydrolysis of dimethyldichlorosilane.[29—31] However, a disadvantage of this process is the need to maintain the reaction conditions until complete conversion of ethoxy groups for a long time, while the hydrolysis of dimethyldichlorosilane can be carried out continuously without heating. This fact makes it necessary to study the possibility of intensifying the process of DMDES condensation in the active media upon maintaining its high selectivity.

It is known from the literature, that the introduction of catalytic amounts of strong acid accelerates the hydrolysis of organoalkoxysilanes in acetic acid.[32—34] An introduction of the "dry" hydrogen chloride formed during the addition of acetyl chloride into the reaction mixture showed its effect for the intensification of the process in case of process of methylsiloxane binders fabrication.[21] And this process is a sequence of interrelated reactions (Scheme 3).

Despite the fact that the reactions of hydrolysis and the formation of siloxane bond are catalyzed by acid (see Scheme 3, Eqs (4) and (5)), achievement of complete conversion of alkoxy groups at room temperature requires unacceptably long time (more than 50 h). To accelerate the reaction a boiling of the reaction mixture is needed. In the process conducted at room temperature, the selectivi-
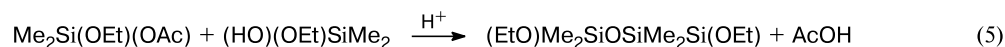
Scheme 2

$$Me_2Si(OEt)_2 + AcOH \rightleftharpoons Me_2Si(OEt)(OAc) + EtOH \qquad (1)$$

$$AcOH + EtOH \rightleftharpoons AcOEt + H_2O \qquad (2)$$

$$Me_2Si(OEt)(OAc) + H_2O \longrightarrow Me_2Si(OEt)OH + AcOH \qquad (3)$$

$$Me_2Si(OEt)(OAc) + (HO)(OEt)SiMe_2 \longrightarrow (EtO)Me_2SiOSiMe_2Si(OEt) + AcOH \qquad (4)$$

Scheme 3

$$Me_2Si(OEt)_2 + AcOH \rightleftharpoons Me_2Si(OEt)(OAc) + EtOH \qquad (1)$$

$$EtOH + AcCl \longrightarrow AcOEt + H_2O \qquad (2)$$

$$AcOH + EtOH \underset{}{\overset{H^+}{\rightleftharpoons}} AcOEt + H_2O \qquad (3)$$

$$Me_2Si(OEt)(OAc) + H_2O \overset{H^+}{\longrightarrow} Me_2Si(OEt)OH + AcOH \qquad (4)$$

$$Me_2Si(OEt)(OAc) + (HO)(OEt)SiMe_2 \overset{H^+}{\longrightarrow} (EtO)Me_2SiOSiMe_2Si(OEt) + AcOH \qquad (5)$$
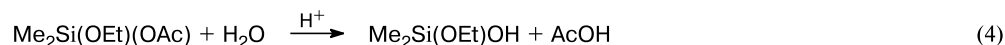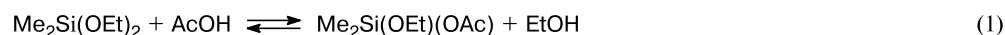
Table 1. The influence of AcCl on the polycondensation of DMDES in active media and on composition of the products

$T/°C$	τ^*/h	Product composition according to GC (%)			
		D_4	D_5	D_6	L_n
20	53	20	17	5	58
125	1	40	30	9	20

* Time of complete conversion of the ethoxy groups.

ty is absent in contrast to the process at boiling temperature (Table 1).

Thus, the introduction of catalytic amounts of acetyl chloride allows decreasing considerably the duration of the DMDES polycondensation process in the active medium upon maintaining high selectivity, but does not give a possibility to carry out the reaction at room temperature.

As it is shown previously,[22] the rate-limiting step in the process of alkoxysilanes polycondensation in the active medium is the esterification reaction of alcohol and acid (see Scheme 2, the Eq. (2)) with the formation of water required for hydrolysis. The alcohol is formed at acetoxylation (see Eq. (1)). The intensification of the process without raising the reaction temperature is possible in a presence of more active reagent, namely trifluoroacetic

Table 2. The influence of TFA on the polycondensation of dimethyldiethylsilane

Entry	Composition of the reaction mixture/mol			T	τ/h
	$Me_2Si(OEt)_2$	CF_3COOH	CD_3COOH		
1	1	3	0	20	4
2	1	1.5	0	20	48
3	1	0.5	2.5	20	>100

acid (TFA). The esterification of the TFA by the alcohol proceeds rapidly even at the temperatures close to room temperature.[35] DMDES polycondensation in the TFA was examined in two ways: using a TFA as the active medium at mole ratios DMDES : TFA equal to 1 : 3 and 1 : 1.5, and by using trifluoroacetic acid in admixture with acetic acid in molar ratios DMDES : TFA : AcOH equal to 1 : 0.5 : 2.5. To analyze the course of the reaction by ^{1}H NMR spectroscopy deuterated acetic acid has been used (Table 2).

^{1}H NMR spectra of samples of the reaction mixtures with different duration of the process are exhibited in the Fig. 1. The figure shows that the DMDES polycondensation in the TFA proceeds rapidly and goes through formation of di(trifluoroacetoxy) derivatives of silicon. As a result, the process can be represented by the reaction sequence (Scheme 4).
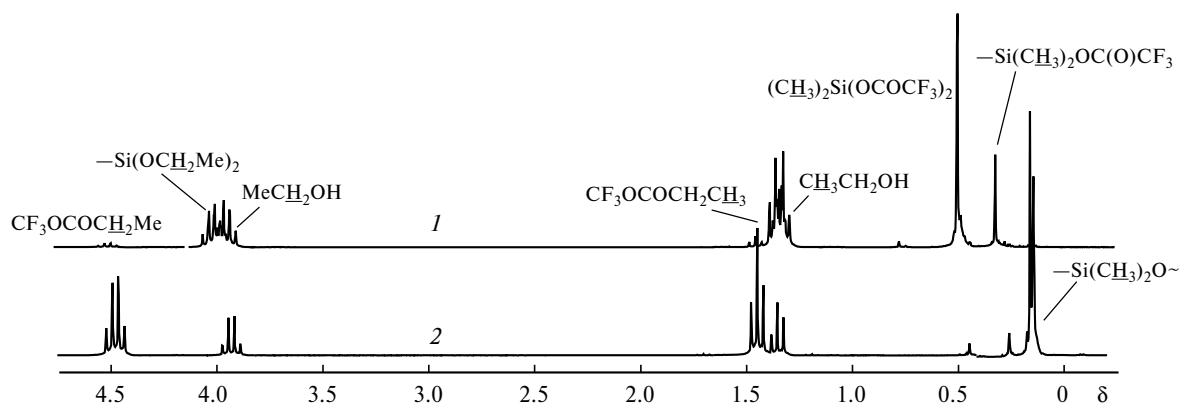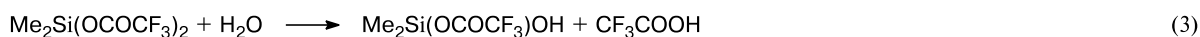
Scheme 4

$$Me_2Si(OEt)_2 + CF_3COOH \rightleftharpoons Me_2Si(OCOCF_3)_2 + EtOH \qquad (1)$$

$$CF_3COOH + EtOH \rightleftharpoons CF_3COOEt + H_2O \qquad (2)$$

$$Me_2Si(OCOCF_3)_2 + H_2O \longrightarrow Me_2Si(OCOCF_3)OH + CF_3COOH \qquad (3)$$

$$Me_2Si(OCOCF_3)_2 + HOMe_2Si(OCOCF_3) \longrightarrow (CF_3COO)Me_2SiOSiMe_2Si(OCOCF_3) + CF_3COOH \qquad (4)$$

Fig. 1. ^{1}H NMR spectra of the reaction mixture for the polycondensation of DMDES in TFA (1 : 3) in 0.5 (*1*) and 2 h (*2*).
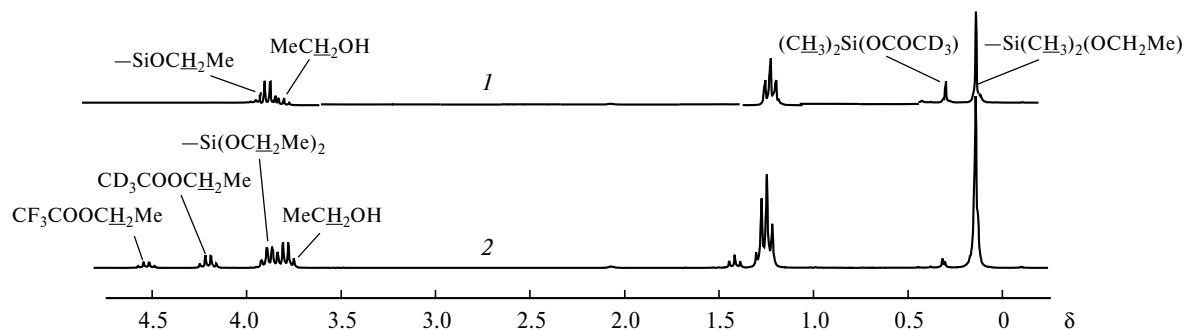
Fig. 2. ^{1}H NMR spectra of the reaction mixture for the polycondensation of DMDES in deuterated acetic acid in the presence of TFA (1 : 2.5 : 0.5) in 2 (*1*) and 30 h (*2*) after the start of the reaction.

The decrease in the concentration of TFA leads to a marked increase in the reaction time measured as a time until complete disappearance of alkoxy groups (Fig. 2).

Using a mixture of TFA with deuterated acetic acid (see Table 2, entry *3*) allows intensification of the DMDES polycondensation process compared with experiment in the presence of pure acetic acid; the reaction proceeds at

Table 3. Cationites properties

Cationite	Full exchange capacity/equiv. g^{-1}	Surface area /m^2 g^{-1}
KU-23 30/100	4.6	55—70
KU-2-8 H-форма	4.6	—
Lewatite Mono Plus S108H	4.5	—
Purolite CT175	4.9	20—40

room temperature, but the time to reach complete conversion of the alkoxy groups is sufficiently large, as the polycondensation process in these conditions proceeds according to the conventional mechanism *via* formation of silicon acetoxy derivative (see Scheme 2). In addition, after the exhaustion of TFA the water formation process is limited by the rate of esterification of acetic acid with ethanol.

The yield of cyclic products upon full conversion of the alkoxy groups was ~40%. Thus, the application of the TFA allows to carry out alkoxysilanes polycondensation at room temperature and at an acceptable duration of the process. However, the increase in the selectivity is not observed.

As it was already mentioned the process intensification occurs through acceleration of the etherification reaction. Therefore, in present work an influence of the addition of

Table 4. The influence of different sulfocationites on the polycondensation of dimethyldiethylsilane in active media and product compostion

Entry	Cationite	Reaction mass			τ/h	Product composition according to GPC^b	Product composition according to GC (%)				
		DMDES : AcOH (mol.)	T/°C	N^a (wt.%)			D$_3$	D$_4$	D$_5$	D$_6$	L$_n$
1	KU-23	1 : 10	20	10	30	91/9	—	53	29	10	8
2	KU-23	1 : 10	50	10	1	100	1	40	20	9	30
3	KU-23	1 : 3	50	10	1	93/7	—	41	20	9	30
4	KU-2-8.H-type	1 : 10	20	10	726	72/28	—	41	19	8	32
5	KU-2-8.H-type	1 : 10	50	10	2	85/15	2	46	6	18	27
6	Lewatite Mono Plus S 108H	1 : 10	20	1	173	79/21	—	61	17	—	21
7	Lewatite Mono Plus S 108H	1 : 10	20	10	30	63/37	1	39	14	4	41
8	Lewatite Mono Plus S 108H	1 : 10	50	10	4	86/13	—	35	17	8	39
9	Lewatite Mono Plus S 108H	1 : 3	50	10	4	57/42	—	40	14	4	42
10	Purolite CT175	1 : 10	20	1	150	91/9	3	33	12	3	49
11	Purolite CT175	1 : 10	20	10	2	100/0	2	62	22	6	8
12	Purolite CT175	1 : 3	20	10	4		—	67	2	6	2
13	Purolite CT175	1 : 3	50	10	1		1	70	23	5	1
14	Purolite CT175	1 : 3	50	1	5		—	71	22	5	2

^{a} Amount of cationites.
^{b} Content of low and high molecular weight peaks on the GC curve.

sulfocationites (SC) to system has been investigated. It is known that SC are used in the industry as a catalyst in the hydrolysis of alkoxysilanes of different functionality[36—39] and rearrangement of the hydrolysis products.[40] Macroporous (KU-23 30/100, Purolite ST175) and gel SC (KU-2-8, Lewatite Mono Plus S108H) differing by values of the exchange capacity and surface area (Table 3) were used. It is shown that the addition of any SC from this group to the reaction system allows to carry out the DMDES polycondensaton in anhydrous acetic acid at room temperature and to reduce the process time, that is, significantly improves workability of process in comparison with the process without condensation catalyst[20] (Table 4). Using of different types of SC varies considerably the process selectivity. For gel SC (see Table 4, entries *4—8*) an increase in the amount of injected SC reduces the yield of cyclic products, whereas for macroporous SC (see Table 4, entries *1, 2, 9—13*), on the contrary, increases the yield of the cyclic products. The rise of temperature to 50 °C increases to some extent the yield of low molecular weight products for both gel (see Table 4, entries *5, 7, 8*) and macroporous SC (see Table 4, entries *2, 3, 12, 13*). A decrease of the amount of acetic acid in the system containing KU-23 30/100 and Lewatite Mono Plus S108H (gel) at 50 °C (see Table 4, entries *3, 8, 11—13*) leads to insignificant decrease in the yield of low molecular part and does not influence the process duration time.

Different effects of the SC of different structure but of similar exchange capacity can be explained by the greater availability of catalytic sites (sulfo-groups) in the case of macroporous SC compared with SC of the gel structure. The catalytic activity of SC increases with an increase in the exchange capacity. The best yield of cyclic product at room temperature (92% for 2 h) is achieved using SC Purolite CT 175 having the highest value of the exchange
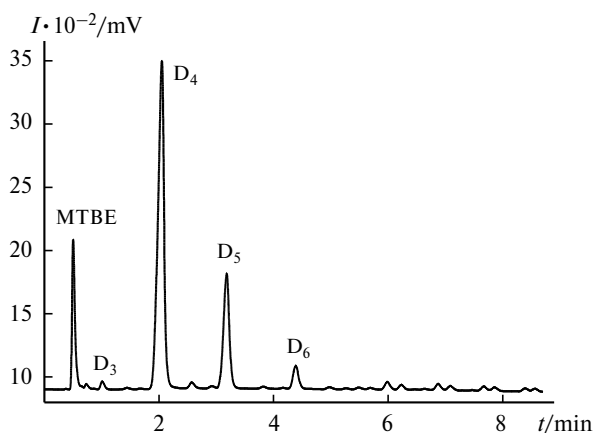
Table 5. The possibilities of different methods of DMDES formation from dimethyldiethylsilane

Reaction mixture	$T/°C$	Reaction time till full conversion of the alkoxy group/h	Y^* (%)
DMDES+AcOH	125	5	70
DMDES+AcOH+AcCl	20	1	55
DMDES+TFA	20	4	60
DMDES+AcOH+PuroliteCT175	20	2	100

* Yield of cyclosiloxane.

capacity of all investigated SC (4.9 equiv. g^{-1}). The GC curve of the product is shown in Fig. 3. In this case, changes in temperature, the ratio of the initial reagents and the amount of SC do not influence significantly the yield of cyclic products: in all cases, it was 98—99% at a minimum duration of the process.

Thus, the possibilities to intensify the process of the DMDES polycondensation in the active media by the addition of catalytic amounts of acetyl chloride and SC, and also by the change of AcOH for TFA have been considered in this study. The results obtained demonstrate the perspectives of the application of Purolite CT175 as a catalyst for the fabrication of dimethylcyclosiloxanes with 99% yield (Table 5).

Experimental

DMDES (Penta-91, Russia), anhydrous acetic acid (Techprom, Russia), TFA, acetyl chloride (both Acros), sulfocationites (KU-23, KU-2-8, Lewatite, Purolite) methyl-*tret*-butyl ether (MTBE, ECOS) were used. All reagents were preliminary prepared in accordance with conventional techniques. DMDES and acetic acid were distilled prior use. MTBE was distilled using a rotary evaporator.

^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer using an internal standard (Me_4Si), the solvents were $CDCl_3$ and CD_3COOD. The spectra were processed using ACDLABS program.

GC analysis was performed on a chromatograph Chromatec Analyst 5000 (Russia) with TCD detector and helium as a carrier gas, column 2 m×3 mm, stationary phase SE-30 (5%), applied to the Chromaton-H-AW. Registration and processing of the data were performed using the program Chromatec Analyst (Russia).

GPC analysis was performed on a chromatographic system consisting of a high-pressure pump STAYER Series 2 (Aquillon, Russia), refractometric detector Smartline RI 2300 (KNAUER, Germany) (eluent was THF) or refractometric detector RIDK 102 (Czech Republic) (eluent was toluene with addition of 2% THF), and column thermostat JETSTREAM 2 PLUS (KNAUER, Germany). Incubation temperature was 40 °C (±0.1 °C). The eluent flow rate was 1.0 mL min^{-1}. Columns (300×7.8 mm) were filled with sorbent Phenogel (Phenomenex, USA), particle size was 5 micrometers, pore size was 10^3 and 10^4 Å (separation range according to the specifications was up to 500 000 and

Fig. 3. GC curve of the product of the polycondenation of DMDES in the active media in the presence Purolite CT175 (see Table 4, entry *11*).

75 000 Da, respectively). Registration and processing of the data were performed using UniChrom 4.7 program (Belarus).

IR spectra were recorded on an Equinox 55/S spectrometer (Bruker). For the measurement liquid cell with KBr windows and solvent CCl_4C were used.

Condensation of DMDES in anhydrous acetic acid with addition of acetyl chloride (general procedure). A mixture of DMDES in anhydrous acetic acid and 0.5 wt.% of acetyl chloride was stirred at 25 °C until the disappearance of ethoxy group proton signals in the ^{1}H NMR spectra in the samples of the reaction mass. After completion of the reaction the mixture was added to MTBE and the organic phase was washed with water until neutral pH. The resulting solution was dried over sodium sulfate, filtered, and the solvent was removed on a rotary evaporator. The product was analyzed by GPC, NMR and IR spectroscopy. Then the fractionation was performed and the volatile fraction was analyzed by GC. The product analysis results are shown in Table 1. IR spectrum (CCl_4), ν/cm^{-1}: 3300 vw (SiOH); 2950 m; 2900 w; 2850 w; 1400 w; 1350 w; 1076 s (SiO); 1020 s (SiOSi); 850 s; 800 m; 700 w; 650 w (SiC). According to GC the product contains low molecular weight siloxane cycles. ^{1}H NMR (250 MHz, CDCl$_3$, δ): 0.16 (m, 6 H, SiMe).

Condensation of DMDES in TFA (general procedure). Mixture of DMDES and TFA was stirred in a vial for NMR at ~20 °C until complete disappearance of ethoxy proton signals in the ^{1}H NMR spectra in the reaction mass. The reaction time corresponding to 100% conversion was determined.

Condensation of DMDES in deuterated acetic acid with the addition of TFA. The mixture of DMDES, deuterated acetic acid and TFA was stirred in a vial for ^{1}H NMR at ~20 °C until the appearance of water signals in the spectra ^{1}H NMR of the reaction mass.

Methods of activating of sulfocationites. The required amount of sulfocationite was washed with distilled water until neutral pH of the wash water, dried in air to air-dry state and then incubated for 4 h at a residual pressure of 1 Torr and 80 °C.

Method of DMDES condensation in anhydrous acetic acid with addition of sulfocationites. To a mixture of DMDES and anhydrous acetic acid in a ratio of 1 : 10 or 1 : 3 1 10 wt.% of sulfocationite was added and stirred at 25 °C until complete disappearance of the signals of the ethoxy group in the ^{1}H NMR spectra in the reaction mixture. Then to the reaction mixture MTBE was added and the solution was washed with water until neutral pH. The resulting solution was dried over sodium sulfate, filtrated and the solvent was removed using a rotary evaporator. The product was analyzed by GPC, NMR and IR spectroscopy. Then the fractionation was performed and the volatile fraction was analyzed by GC. The product analysis results are shown in Table 4. IR spectrum (CCl_4), ν/cm^{-1}: 3300 vw (SiOH); 2950 m; 2900 w; 2850 w; 1400 w; 1350 w; 1076 s (SiO); 1020 s (SiOSi); 850 s; 800 m; 700 w; 650 w (SiC). According to GC the product contains low molecular weight siloxane cycles. ^{1}H NMR (250 MHz, CDC13, δ, ppm): 0.16 (m, 6 H, SiMe).

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