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Hydrolytic polycondensation of trimethoxymethylsilane under ultrasonic irradiation

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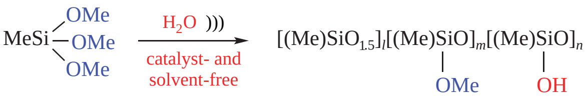
The hydrolytic polycondensation of trimethoxymethylsilane in the absence of catalyst and solvent under ultrasonic irradiation was performed, the effect of reagent ratio, power, temperature and irradiation duration on the process outcome was estimated. Thus obtained polyorganosilsesquioxanes were characterized by ^{1}H NMR and IR spectroscopy as well as gel permeation chromatography.



$$\mathrm{MeSi(OMe)_3} \xrightarrow[\text{catalyst- and solvent-free}]{\mathrm{H_2O}\ )))} [\mathrm{(Me)SiO_{1.5}}]_l[\underset{\mathrm{OMe}}{\mathrm{(Me)SiO}}]_m[\underset{\mathrm{OH}}{\mathrm{(Me)SiO}}]_n$$

Keywords: hydrolytic polycondensation, alkoxysilanes, trimethoxymethylsilane, polyorganosilsesquioxanes, ultrasonic irradiation.

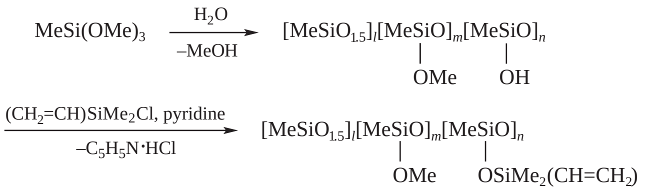
The hydrolytic polycondensation (HPC) of functional silanes is today the basic process for producing oligomeric and polymeric siloxane products. The current trends in the development of the chemistry of organosilicon compounds are based on the ’green chemistry’ principles and involve the use of alkoxysilanes instead of chlorosilanes as the starting reagents thus providing a more controllable and manageable flow of processes and the absence of hydrochloric acid wastes.[1–7] One of the problems in the HPC of alkoxysilanes is the need to use catalysts[8–11] and to obtain a product with specified characteristics, which complicates the production of polyorganosiloxanes and violates the green chemistry principles. In view of this, the search for new HPC processing in a non-catalytic version and its intensification remain urgent. Recent studies on the HPC of alkoxysilanes in a closed system[12–14] comprising vapor pressure upon heating showed that hydrolysis of alkoxysilanes could be performed in the absence of mixing, solvents, and catalysts. Ultrasonic irradiation is widely employed in catalysis for activation and acceleration of liquid-phase processes, for pre-reaction preparation of reagents, *etc.*[15,16] In organosilicon chemistry, ultrasonic irradiation is mainly used as an alternative to mixing, in particular, in the preparation of formulations with nanoparticles, in alkoxylation of chlorosilanes, and in polymerization of cycles.[17] In the case of sol-gel process with tetraethoxysilane in the presence of an acid catalyst, ultrasound acts as an effective initiator of fast mixing by creating cavitation and increasing the efficiency of contact between alkoxy group and water[18–20] thus giving materials with new properties such as gels with high density, fine and homogeneous structure.[18] However, despite the prospects of using ultrasonic treatment in the chemistry of silicones, the systematic data on its effect on the regularities of the HPC of alkoxysilanes are absent.

The purpose of this work was to study the solvent free HPC under ultrasonic radiation for trimetoxymethylsilane (TMMS) and to estimate the effect of reaction conditions on the composition of the resulting products. For this end, the monomer/water molar ratio, temperature and duration of the process, as well as the power of ultrasonic irradiation were varied (Table 1). The effect of ultrasound frequency on the hydrolytic polycondensation of TMMS has not been studied, since it is known that there is no significant effect on sonochemical processes in the frequency range of 20–35 kHz.[21]

The main problem in the HPC of trifunctional silanes is that gelation could occur in the course of the reaction. It is a direct consequence of the use of catalysts which increase conversion of formed hydroxysilyl groups, which makes difficult to monitor the progress of the reaction in the presence of catalysts. In this case, regardless of the process conditions, only soluble products were formed, and the process under ultrasonic irradiation occurred by the classical scheme of the HPC of TMMS to give soluble polymethylsilsesquioxane. To analyze the composition and stabilize the product, its hydroxy groups were blocked with chlorodimethylvinylsilane under conditions that did not violate the structure of the polymer chain (Scheme 1).[12]

The efficiency of blocking was estimated by IR spectroscopy, based on the absence of an absorption band in the region of 3600 cm^{-1} that is characteristic of stretching vibrations for OH groups (see Online Supplementary Materials, Figure S2).

The conversion of the starting monomer was determined by GC based on the content of TMMS in the reaction mixture.



$$\mathrm{MeSi(OMe)_3} \xrightarrow[-\mathrm{MeOH}]{\mathrm{H_2O}} [\mathrm{MeSiO_{1.5}}]_l[\underset{\mathrm{OMe}}{\mathrm{MeSiO}}]_m[\underset{\mathrm{OH}}{\mathrm{MeSiO}}]_n$$

$$\xrightarrow[-\mathrm{C_5H_5N{\cdot}HCl}]{\mathrm{(CH_2{=}CH)SiMe_2Cl,\ pyridine}} [\mathrm{MeSiO_{1.5}}]_l[\underset{\mathrm{OMe}}{\mathrm{MeSiO}}]_m[\underset{\mathrm{OSiMe_2(CH{=}CH_2)}}{\mathrm{MeSiO}}]_n$$

Scheme 1

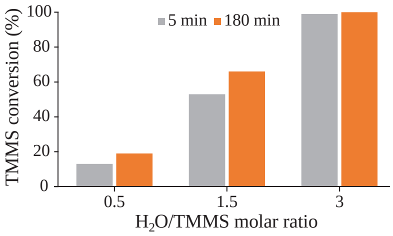


Figure 1 The dependence of monomer conversion on the water/TMMS ratio and the duration of ultrasonic irradiation at 15 °C and 300 W.

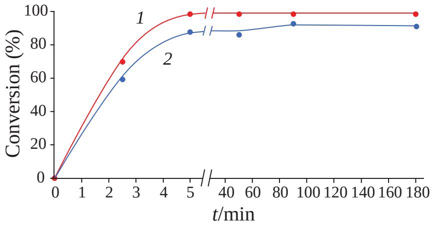


Figure 2 Conversion of (*1*) TMMS and (*2*) OMe groups for a monomer/water ratio of 1:3 at 15 °C and 300 W.

The quantitative content of residual methoxysilyl and dimethylvinylsilyl groups in the non-volatile blocked product was determined by ^{1}H NMR spectroscopy based on the ratio of integral intensities for protons in $MeSiO_{1.5}$, MeOSi and $(CH_2{=}CH)Me_2SiO$ fragments, respectively (see Online Supplementary Materials, Figure S1). Wherein the content of hydroxysilyl groups in the hydrolysis product corresponds to the content of dimethylvinylsilyl groups in its blocked derivative.

A study of the effect of the monomer/water ratio at 15 °C and 300 W on the regularities of HPC process under ultrasonic irradiation showed that complete homogenization of the reaction mixture was achieved in 5 min regardless of the reagent ratio, while the monomer conversion increases in proportion to the amount of water used for hydrolysis to reach 100% only if excess water is present (the monomer/water ratio is 1 : 3) (Figures 1, 2). A further increase in the duration of the sonication to 3 h does not raise the monomer conversion significantly, even in the case of a monomer/water ratio of 1:1.5 that is sufficient for complete hydrolysis of TMMS. Probably, HPC under ultrasonic irradiation mainly occurs at the interface, so when the interface disappears, the hydrolysis and condensation slow down considerably.

It should be noted that the duration of TMMS HPC until complete monomer conversion in the presence of excess water under sonication is comparable to that of similar processes in the presence of various catalysts.[22–26]

The composition and molecular weight characteristics of the products of TMMS HPC under ultrasonic irradiation at a power of 300 W for 3 h do not depend on the reagent ratio (see Table 1, entries 1–5).

Likewise, an increase in the ultrasonic treatment time from 2.5 to 90 min (entries 6–9) does not significantly affect the molecular mass distribution (MMD) of the resulting product that remains within the range from 200 to 10000. Only when the exposure time is prolonged to 180 min, a slight broadening of the MMD and an increase in the upper boundary of MM to 15000 are observed (entry 10). The resulting aqueous-alcoholic solutions of polymethylsilsesquioxanes are stable within 2 months. Raising the process temperature from 15 to 55 °C (entries 11–15) favors a regular broadening of the product MMD (see Online Supplementary Materials, Figure S4) and a decrease in the content of residual hydroxysilyl groups, which indicates that the contribution of intermolecular condensation to the

Table 1 Conditions of TMMS HPC under sonication and composition of the resulting products.

Entry	TMMS/H_2O ratio	*T*/°C	Power/W	*t*/min	TMMS conversion (%)	OMe-groups conversion (%)	Nonvolatile product yield (%)	M_p	[MeSiO1.5] / [OMe] / [OH] ratio (NMR data)	Mass content of groups (%)	
										OMe	OH
Reagent ratio TMMS/H_2O											
1	1 : 0.5	15	300	180	19	11	30	800	1 : 0.23 : 0.62	8	12
2	1 : 1	15	300	180	51	46	67	630	1 : 0.14 : 0.93	5	18
3	1 : 1.5	15	300	180	66	54	77	560	1 : 0.35 : 0.73	12	14
4	1 : 3	15	300	180	100	90	88	800	1 : 0.30 : 1.10	10	20
5	1 : 6	15	300	180	100	99	77	900	1 : 0.04 : 1.83	2	17
Time factor											
6	1 : 3	35	150	2.5	70	62	84	600	1 : 0.25 : 1.57	8	26
7	1 : 3	35	150	5	99	92	88	800	1 : 0.22 : 1.21	7	22
8	1 : 3	35	150	50	100	91	79	800	1 : 0.28 : 1.48	9	25
9	1 : 3	35	150	90	100	91	80	800	1 : 0.14 : 0.80	8	25
10	1 : 3	35	150	180	100	94	81	1000	1 : 0.18 : 0.86	6	17
Temperature factor											
11	1 : 3	15	150	90	100	95	41	800	1 : 0.14 : 0.92	5	18
12	1 : 3	25	150	90	100	95	65	800	1 : 0.16 : 0.88	6	17
13	1 : 3	35	150	90	100	95	78	900	1 : 0.14 : 0.80	5	16
14	1 : 3	45	150	90	100	94	91	1400	1 : 0.17 : 0.88	6	17
15	1 : 3	55	150	90	100	96	89	1000	1 : 0.13 : 0.55	5	12
Power factor											
16	1 : 3	15	150	180	100	91	79	800	1 : 0.27 : 1.34	9	23
17	1 : 3	15	300	180	100	90	88	800	1 : 0.30 : 1.10	10	20
18	1 : 3	15	600	180	100	96	82	800	1 : 0.12 : 0.64	5	13
19	1 : 3	15	900	180	100	95	73	800	1 : 0.15 : 0.86	5	17
20	1 : 3	15	1200	180	100	95	72	900	1 : 0.17 : 0.86	6	17

formation of HPC products increases with the process temperature.

With a growth of the ultrasound power (see Table 1, entries 16–18) from 150 to 600 W, a significant (twofold) decrease in the content of residual methoxy and hydroxysilyl groups is observed.

The molecular weight distribution of the products is nearly identical (see Online Supplementary Materials, Figures S4 and S5), which may indicate that the contribution of intramolecular condensation to the formation of polymethylsilsesquioxanes increases with a growth of the ultrasound power.

Further raising the ultrasound power to 1200 W results in a decrease in the yield of polymethylsilsesquioxanes, broadening of their MMD and an insignificant increase in the content of residual hydroxy groups. This may be due to the depolymerization processes occurring above a certain threshold of irradiation power.

Thus, using TMMS as an example, we have demonstrated that the application of ultrasound is a promising method for the organic solvent free hydrolytic polycondensation of alkoxysilanes in the absence of a catalyst. It ensures the formation of a soluble branched polymethylsilsesquioxane, while varying the irradiation power and the HPC temperature allows one to control the content of residual hydroxy and methoxy groups in the resulting product in a wide range.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.025.

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