



SYNTHESIS OF LOW-MOLECULAR-WEIGHT OLIGODIMETHYLSILOXANES IN AN ACTIVE MEDIUM

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A. A. Trishina,^a E. V. Talalaeva,^a A. A. Kalinina,^{*a,b} and A. M. Muzafarov^{a,c}

^a Enkolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, ul. Profsoyuznaya 70, Moscow, 117393 Russia

^b MIREA—Russian Technological University, Lomonosov Institute of Fine Chemical Technologies, pr. Vernadskogo 78, Moscow, 119454 Russia

^c Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, str. 1, Moscow, 119334 Russia

Abstract

The hydrolytic polycondensation of diethoxydimethylsilane and hexamethyldisiloxane in an active medium in the presence of a catalytic amount of chlorotrimethylsilane has been studied. It is shown that this method allows for the selective synthesis of low-molecular-weight oligodimethylsiloxanes which do not contain residual reactive groups. The ratio of the reagents and the catalytic amount serve as effective tools for controlling the length of the resulting oligomers and the process duration.

Key words: polycondensation, oligodimethylsiloxanes, active medium.



Introduction

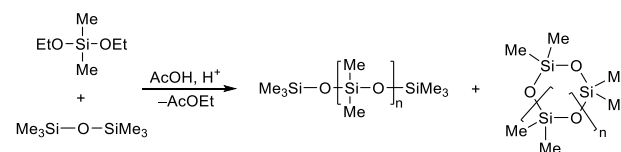
Oligodimethylsiloxanes are low-molecular oligomers consisting of linear dimethylsiloxane and terminal trimethylsilyl units. They are popular representatives of organosilicon products used as heat carriers, bases for oils and lubricants, as well as hydrophobic and anti-adhesive additives [1, 2]. The main method for the synthesis of oligodimethylsiloxanes is the hydrolytic polycondensation of the corresponding chlorosilanes followed by the catalytic rearrangement of the hydrolysis products, as well as the direct catalytic rearrangement of octamethylcyclotetrasiloxane and hexamethyldisiloxane [3, 4]. Earlier, as part of the transition to chlorine-free methods for the synthesis of polyorganosiloxanes, the process of hydrolytic polycondensation of diethoxydimethylsilane (DEDMS) in an active medium, namely, an excess of anhydrous acetic acid, was studied, and the factors leading to the selective formation of cyclosiloxanes or linear oligomers with terminal OH groups were identified. The introduction of trimethylalkoxysilanes into the DEDMS polycondensation process in excess anhydrous acetic acid as precursors of terminal trimethylsilyl groups representing the M-type units in order to obtain non-functional linear oligomers does not lead to a positive result: the linear oligomethylsiloxanes formed in this case contain residual hydroxy groups, which requires an additional step of trimethylsilylation. An alternative precursor of M-units is hexamethyldisiloxane (HMDS) [5]. Its application is associated with the need to add strong acids to the reaction mixture as a catalyst for the cleavage of the siloxane bond. In turn, the use of a catalyst in an active medium allows for a reduction in the amount of acetic acid and, as a consequence, a reduction in the volume of products requiring regeneration and recycling [6].

Hence, it seemed interesting to study the polycondensation of DEDMS and HMDS in the presence of catalysts in order to

obtain low-molecular-weight functional oligodimethylsiloxanes. The specific goal of this study was to evaluate the applicability of this method for the synthesis of short-chain oligodimethylsiloxanes with a chain length of 3 to 5 units.

Results and discussion

The polycondensation of DEDMS was carried out in an active medium in the presence of HMDS (Scheme 1), varying the molar ratio of DEDMS/HMDS from 1:1 to 3:1, using a catalytic amount of chlorotrimethylsilane (0.5 or 1 wt %) as a precursor of hydrogen chloride and acetic acid in the equimolar amount to alkoxy groups.



Scheme 1. General scheme for the polycondensation of DEDMS and HMDS in an active medium in the presence of an acid catalyst.

The reaction was conducted until the complete disappearance of the signals of ethoxy group protons in the ¹H NMR spectra of the evacuated samples of the reaction mixture (see Fig. S1 in the Electronic supplementary information (ESI)). Then, a three-fold mass excess of Na₂CO₃ was added to the reaction mixture to neutralize HCl.

The composition of the reaction products was determined by gas liquid chromatographic (GLC) analysis before and after the fractionation of the reaction mixture (Fig. S2 in the ESI). The reaction conditions and composition of the products are presented in Table 1. According to the results obtained, the

Table 1. Conditions for the condensation of DEDMS and HMDS in acetic acid in the presence of chlorotrimethylsilane and the composition of the products (L_n denotes linear oligomers $\text{Me}_3\text{SiO}[\text{Me}_2\text{SiO}]_{n-2}\text{SiMe}_3$, D denotes cyclosiloxanes $[\text{Me}_2\text{SiO}]_n$)

Entry	DEDMS/ HMDS/AA, mol	CTMS, wt %	n	t , h	Conversion of L_2 , %	L_n/D_n , %	Composition of the products								Yield of the oligomethyl- siloxanes, %	
							L_3	L_4	L_5	L_6	L_7	L_8	L_9	L_{10-15}		D_n
1	1/1/2	0.5	3	14	32	97/3	33	30	19	8	4	2	1	0	3	91
2	2/1/4	0.5	4	9.5	64	94/6	23	21	17	12	8	5	3	5	6	98
2a	2/1/18	0.5	4	2	53	87/13	25	20	15	13	7	4	3	0	13	83
3	3/1/6	0.5	5	9.5	81	92/8	16	15	15	12	9	6	4	15	8	99
4	1/1/2	1	3	4	22	99/1	40	28	18	8	3	1	1	0	1	77
5	2/1/4	1	4	4.5	34	94/6	14	18	18	15	11	7	5	7	6	71
6	3/1/6	1	5	4.5	47	87/13	13	14	16	14	10	7	5	8	13	90

polycondensation products, regardless of the reaction conditions, were a mixture of low-molecular-weight linear oligomers with a chain length of 3–15 units. The absence of OH groups in the resulting oligodimethylsiloxanes was confirmed by the IR spectroscopic data (Fig. S3 in the ESI).

A decrease in the amount of DEDMS relative to HMDS, a chain breaker, from 3:1 to 1:1 naturally prevented the cyclization (the content of cycles in oligodimethylsiloxanes decreased from 13 to 1–3%), with the main product being short-chain linear oligomers with a chain length of 3 to 5 units, the total content of which increased from 43 to 86%. An increase in the amount of acetic acid from 1 to 4.5 mol equiv. per 1 ethoxy group (Table 1, entries 2 and 2a, respectively), standard for non-catalytic processes in an active medium, was accompanied by a decrease in the time for complete conversion of alkoxy groups from 9.5 to 2 h, while the content of cyclic products increased from 6 to 13%, respectively, but the content of short-chain oligomers L_3 – L_5 remained unchanged (60%). A two-fold increase in the amount of the catalyst led to a reduction in the reaction time for the complete conversion of alkoxy groups by ~2 times, but did not affect the composition of the resulting products.

Conclusions

The performed investigations revealed that the polycondensation of DEDMS and HMDS in an active medium in the presence of a catalytic amount of chlorotrimethylsilane as a precursor of HCl is a promising method for the selective production of low-molecular-weight oligodimethylsiloxanes with a chain length of 3–5 units that do not contain residual reactive groups. The DEDMS/HMDS ratio serves as an effective tool for controlling the length of the resulting oligomers, while the catalyst loading allows for regulating the process duration.

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Corresponding author

* E-mail: kalinina@ispm.ru (A.A. Kalinina).

Electronic supplementary information

Electronic supplementary information (ESI) available online: the NMR spectra, GLC curves, and IR spectra. For ESI, see DOI: 10.32931/io2431a.

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