



HYDROLYTIC POLYCONDENSATION OF MONOSODIUMOXY(METHYL)(DIETHOXY)SILANE UNDER CONDITIONS OF AN EXCESS OF WATER

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Cite this: *INEOS OPEN*, 2024, 7 (1–3), 59–60
DOI: 10.32931/io2425a

Received 10 May 2024,
Accepted 16 July 2024

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Abstract

The synthesis of polysodiumoxy(methyl)siloxanes by the hydrolytic polycondensation (HPC) of monosodiumoxy(methyl)(diethoxy)silane under mild conditions is proposed. Ethanol, propan-2-ol, and butan-1-ol are chosen as the solvents for the HPC. It is shown that the HPC with an excess of water from 25% to 100% (relative to the stoichiometric amount) leads to the product deviation from an ideal structure.

Key words: hydrolytic polycondensation, polyfunctional matrix, alkoxy sodium salts, monosodiumoxy(methyl)(diethoxy)silane, polysodiumoxy(methyl)siloxane.



Introduction

The practical importance of organosilicon polymers was first demonstrated in 1937 by the member of the Academy of Sciences of the Soviet Union K. A. Andrianov. Owing to the high energy of the Si–O bond, silicones feature high heat resistance, good frost resistance, and high dielectric characteristics. They are resistant to the action of most acids and alkalis [1] and therefore are of great interest in various industries [2].

One of the most popular methods for the synthesis of polyorganosiloxanes is the HPC of alkoxy silanes [3], which in the non-catalytic version proceeds slowly [4] and thus is carried out in the presence of acidic or basic catalysts [5]. Of particular interest are the reactions where the monomer that participates in the HPC contains a catalytically active group in its structure, such as 3-(aminopropyl)triethoxysilane [6]. Monosodiumoxy(organo)alkoxy silanes $R_n(R'O)_{3-n}SiONa$, where R and R' are organic substituents and $n = 0, 1, \text{ or } 2$, are organosilicon monomers which also contain a catalytically active group [7]. An example of the application of these monomers is the synthesis of polymethylsilsequioxane dendrimers [8].

Somewhat later, using the reverse sequence of selective conversion of the functional groups in the HPC, a highly functional polymeric polymethylsilsequioxane matrix was obtained that contains -ONa functional groups at each silicon atom of the main chain [9, 10]. The selectivity of the synthesis of a linear structure with a sodiumoxy group at each silicon atom was ensured by the independence of the functional groups of the initial monomer. It was demonstrated that such an approach opens up a fundamental possibility of producing linear polysodiumoxy(methyl)siloxane polymer matrices capable of further transformations [11]. In the cited reports, the syntheses were complex from the viewpoint of technical implementation

since the hydrolytic polycondensation was carried out in a high-boiling solvent with very slow introduction of water and simultaneous distillation of an alcohol. Furthermore, the molar masses of the polymer matrices were not high enough. In this work, a simplified version of the HPC of monosodiumoxy(methyl)(diethoxy)silane at room temperature in different organic solvents is considered. The effect of excess water on the chemical structure and molecular weight characteristics of the resulting polymers is evaluated.

Results and discussion

The synthesis of linear polysodiumoxy(methyl)siloxane was carried out in organic solvents, including ethanol, propan-2-ol, and butan-1-ol, varying the excess of introduced water from 25 to 100% (Fig. 1).

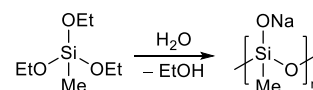


Figure 1. General scheme of the hydrolytic polycondensation of sodiumoxy(methyl)(diethoxy)silane.

The presented HPC scheme summarizes a combination of complex and multistep processes. The chemical structures and molecular weight characteristics of the resulting polysodiumoxy(methyl)siloxanes were estimated by analyzing their analogs blocked with chloro(dimethyl)viny silane using ¹H NMR spectroscopy and gel permeation chromatography (GPC), respectively (Fig. 2).

Any deviation from the stoichiometric ratio of the integral intensities of the proton signals corresponding to the vinyl substituent in the blocking group and the methyl unit at the silicon atom of the main chain indicated changes in the chemical structure or the occurrence of side processes (Table 1).

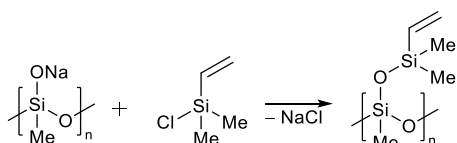


Figure 2. Blocking of polysodiumoxy(methyl)siloxane with chloro(dimethyl)vinyldisilane.

Table 1. Results of the GPC analysis

Solvent	Water excess, %	¹ H NMR H _{Me} /H _{(Me)₂} /H _{Vi} 3:6:3	GPC 200 KDa, toluene	
			M _N	M _W
Butan-1-ol, 30%	25	3:4.58:2.21	3000	6100
	50	3:4.28:2.05	3300	5800
	100	3:4.48:2.05	4700	45500
Propan-2-ol, 30%	25	3:5.11:2.54	4100	9900
	50	3:5.32:2.48	4300	12600
	100	3:5.53:2.60	2900	4500
Ethanol, 30%	25	3:5.39:2.61	3700	19800
	50	3:5.76:2.83	4200	23100
	100	3:5.83:2.86	5100	21100

The data presented in Table 1 suggest that in all cases there was a discrepancy between the integral intensities and the theoretically calculated values. The largest differences (20–30%) were observed in the case of the HPC in butan-1-ol. It seems logical that the maximum molar mass (45500) was achieved just at the maximum deviation from the ideal structure. The reduced intensity of the signals of vinyl group protons in the side substituent may indicate either the presence of branches in the polymer structure or the formation of cyclic products, which may lack terminal blocking groups. The smallest deviations from the ideal polymer structure were observed for the HPC in ethanol.

Conclusions

As a result of conducting the HPC reactions under different conditions, it was found that the introduction of an excess amount of water leads to changes in the structures of the resulting polymers, as was evidenced by the reduced integral intensities of the proton signals of the blocking groups. The observed deviations can be explained by branching in the polymer system when introducing a large excess of water. It also cannot be ruled out that the selected conditions for conducting the HPC are not optimal. This was indicated by the inverse dependence of the magnitude of deviations from the ideal with an increase of the water excess when the reactions were performed in ethanol in contrast to the observed direct dependence of the deviations for the HPC in butan-1-ol.

Acknowledgements

This work was supported by the Russian Science Foundation (project no. 22-43-04439).

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section. For ESI, see DOI: 10.32931/io2425a.

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