



SYNTHESIS OF LINEAR OLIGOMETHYLPHENYLPENTASILOXANES

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Abstract

A method for the synthesis of linear oligomethylphenylpentasiloxanes with terminal trimethylsilyl and methylphenylsilyl groups in one step by the alkaline hydrolysis of diethoxy(methyl)phenylsilane and subsequent interaction of sodium trimethyltriphenyltrisiloxanediolate with chlorotrimethylsilane or chloro(methyl)diphenylsilane has been studied.

Key words: oligomethylphenylsiloxanes, hydrolytic polycondensation, sodium methylphenyltrisiloxanediolate.

Introduction

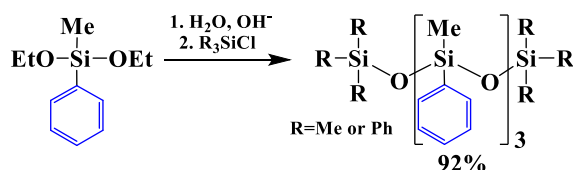
Oligomethylphenylsiloxanes are non-functional liquids of a linear or branched structure that are widely used as heat carriers and high-vacuum oils, dispersion media for heat-resistant oils and lubricants, and their properties depend on the ratio of methyl and phenyl groups [1, 2].

The main method for obtaining oligomethylphenylsiloxanes is the hydrolytic copolycondensation of the corresponding organochlorosilanes followed by the catalytic rearrangement of the hydrolysis products. In some cases, to produce narrow-dispersed oligomethylphenylsiloxanes of a linear structure, the hydrolysis products are preliminarily subjected to the thermocatalytic decomposition with the release of strained methylphenylcyclosiloxane [3, 4].

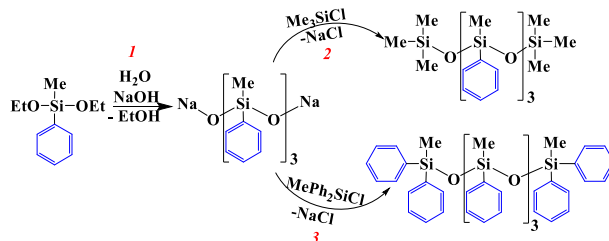
It is known that the use of metal silanates and siloxanates is one of the promising approaches to controlling the structure of oligoorganosiloxanes and the properties of materials based on them [5]. Recently, we have suggested a selective method for the formation of sodium hexamethyltrisiloxanediolates with 95% yields [6] and demonstrated that the structure of the initial reagent does not affect significantly the structure and composition of the resulting salts.

Results and discussion

It seemed interesting to evaluate the possibility of the directed synthesis of oligomethylphenylpentasiloxanes with terminal trimethyl- and methylphenylsilyl groups by the hydrolytic polycondensation of diethoxy(methyl)phenylsilane under alkaline conditions followed by blocking with the corresponding chlorotriorganosilane without a step of the catalytic rearrangement and without isolating the intermediate products.



At the first step, diethoxy(methyl)phenylsilane was hydrolyzed under the action of an aqueous solution of NaOH (MePhSi(OEt)₂/NaOH molar ratio was 3:2). After the addition of toluene, the azeotropes of the solvents and water were distilled off (Scheme 1, 1).



Scheme 1. General scheme for the synthesis of oligomethylphenylsiloxanes.

A toluene solution of the resulting siloxane was titrated with an acid to define the content of sodium ions, which was 16% relative to the siloxane product. This corresponds to the following formula: NaO[MePhSiO]₃Na.

Then the solution of the product of the alkaline hydrolytic polycondensation of diethoxy(methyl)phenylsilane was blocked with chlorotrimethylsilane (Scheme 1, 2) or chloro(methyl)diphenylsilane (Scheme 1, 3) to analyze the composition and structure of the resulting siloxanes, as well as to demonstrate the possibility of obtaining oligomethylphenylpentasiloxanes with terminal trimethylsilyl or methylphenylsilyl groups, respectively.

The efficiency of blocking the functional groups was determined using IR spectroscopy based on the absence of an absorption band at *ca.* 3200–3800 cm⁻¹, characteristic of the OH group stretches.

According to the results of gel permeation chromatographic (GPC) analysis, the products obtained are characterized by a

monomodal narrow molecular weight distribution with a molecular weight of the peak of 600 Da (Fig. 1).

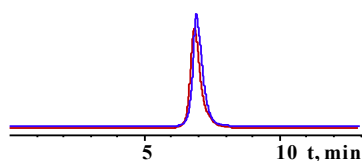


Figure 1. GPC curves of the hydrolysis product blocked with chlorotrimethylsilane (red) or chloro(methyl)diphenylsilane (blue).

According to the results of gas liquid chromatographic (GLC) studies (Fig. 2), the hydrolysis product blocked with chlorotrimethylsilane represented a mixture of mainly two components: α,ω -trimethyl(phenyl)siloxymethyltrisiloxane ($L_3 = 86\%$) and α,ω -trimethyl(phenyl)siloxymethyltetrasiloxane ($L_4 = 12\%$), which are the blocking products of sodium methylphenyltrisiloxanediolate and methylphenyltetrasiloxanediolate, respectively, as well as trace amounts of n-mers (2%).

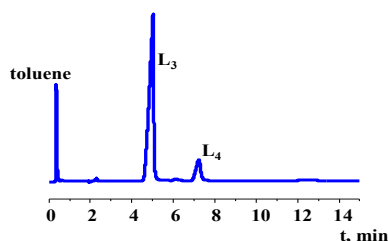


Figure 2. GLC curve of the product of blocking with chlorotrimethylsilane.

The ^1H NMR spectroscopic data of the product of blocking with chlorotrimethylsilane were in good agreement with the GLC data: on average, there were 3 MePhSiO units per 2 terminal Me_3SiO groups, as was evidenced by the ratios of the integral intensities of protons of the methyl and phenyl groups at the chain and terminal silicon atoms (Fig. 3, top).

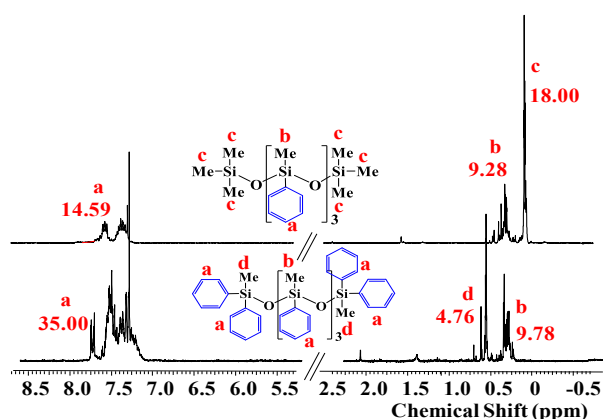


Figure 3. ^1H NMR spectra of the products of blocking with chlorotrimethylsilane (top) and chloro(methyl)diphenylsilane (bottom).

According to the data of ^1H and ^{29}Si NMR spectroscopy, the product of the alkaline hydrolysis of diethoxy(methyl)phenylsilane blocked with chloro(methyl)diphenylsilane also corresponded to the

theoretical structure $\text{Ph}_2\text{MeSiO}[\text{MePhSiO}]_3\text{SiMePh}_2$ (Fig. 3 (bottom), Fig. 4).

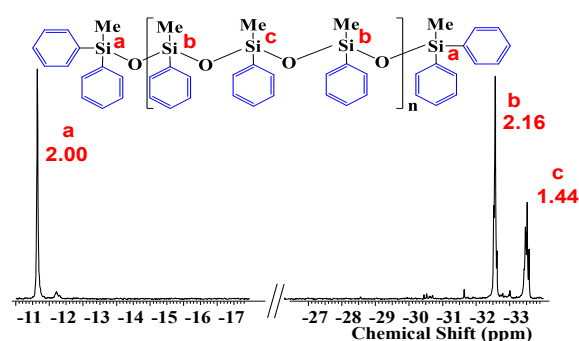


Figure 4. ^{29}Si NMR spectrum of the hydrolysis product blocked with chloro(methyl)diphenylsilane after removal of volatiles.

The yields of oligomethylphenylpentasiloxanes with terminal trimethyl- and methyl-diphenylsilyl groups were 94% and 92%, respectively.

Experimental section

Syntheses

General procedure for the synthesis of sodium trimethylphenylsiloxanediolate. Diethoxy(methyl)phenylsiloxane (DEMPS) (1240.5 g, 3.82 mol) was added to a mixture of NaOH (152.8 g, 3.82 mol), distilled water (156.0 g, 8.67 mol), and toluene (2.4 L) under vigorous stirring. The reaction mixture was refluxed for 1 h. Then the azeotrope of the solvents was distilled off until the vapor temperature of 110–111 °C. The content of sodium ions in the resulting solution calculated for the siloxane product was 16%, which corresponds to the following formula: $\text{NaO}[\text{MePhSiO}]_3\text{Na}$. The solution was divided into two parts for further blocking.

General method for blocking sodium trimethylphenylsiloxanediolate with chlorotrimethylsilane. The calculated amount of a solution of sodium trimethyltriphenyltrisiloxanediolate in toluene was added to a 30% solution of pyridine and chlorotrimethylsilane, taken in the amount of 1 mol equiv. per sodium ions in the solution of the alkaline hydrolysis product of DEMPS, at -15 °C and under vigorous stirring. After reaching room temperature, the resulting solution was washed with water to neutral pH, dried over anhydrous sodium sulfate, and evaporated to dryness. The target product was isolated as a transparent colorless liquid. ^1H NMR (CDCl_3): δ 7.27–7.57 (m, 14.59H, $\text{OSiCH}_3(\text{C}_6\text{H}_5)_2$), 0.25–0.43 (s, 9.28H, $\text{OSiCH}_3(\text{C}_6\text{H}_5)_2$), 0.00–0.06 (m, 18H, $\text{OSi}(\text{CH}_3)_3$) ppm. GLC: $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_2]_3\text{OSi}(\text{CH}_3)_3$ 86%, $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_2]_4\text{OSi}(\text{CH}_3)_3$ 12%.

General method for blocking sodium trimethylphenylsiloxanediolate with chloro(methyl)diphenylsilane. The calculated amount of a solution of sodium trimethyltriphenyltrisiloxanediolate in toluene was added to a 30% solution of pyridine and chloro(methyl)diphenylsilane, taken in the amount of 1.01 mol per 1 mol of sodium ions in a solution of the alkaline hydrolysis product of DEMPS, at -15 °C and under vigorous stirring. After reaching room temperature, the resulting mixture was filtered, the volatile products and

unreacted chloro(methyl)diphenylsilane were distilled off under vacuum of 1 mm Hg. ^1H NMR (CDCl_3): δ 7.20–7.68 (m, 35H, $\text{OSiCH}_3(\text{C}_6\text{H}_5)_2$), 0.50–0.70 (m, 4.76H, $\text{OSi}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$), 0.13–0.26 (m, 9.78H, $\text{OSi}(\text{CH}_3)(\text{C}_6\text{H}_5)$) ppm. ^{29}Si NMR (CDCl_3): δ 10.74 (2Si, $\text{O}_{0.5}\text{SiCH}_3(\text{C}_6\text{H}_5)_2$), 32.60–32.70 (2Si, $\text{OSi}(\text{CH}_3)(\text{C}_6\text{H}_5)$), 33.54–33.65 (1Si, $\text{OSi}(\text{CH}_3)(\text{C}_6\text{H}_5)$) ppm.

Conclusions

Therefore, the possibility of the directed synthesis of oligomethylphenylsiloxanes bearing different terminal groups by the alkaline hydrolysis of diethoxy(methyl)phenylsilane without isolating the intermediate products was demonstrated.

Acknowledgements

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