



SYNTHESIS OF ORGANOCYCLOSILOXANES CONTAINING A METHYLBENZYLSILOXANE MOIETY

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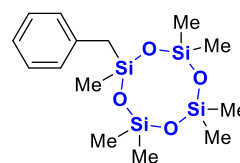
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Abstract

The synthesis of mixed polyorganosiloxanes is nowadays of paramount industrial importance for obtaining new copolymers by the simple ring-opening polymerization. In this work, the synthesis and characterization of a new mixed cycle with one methylbenzyl moiety are presented.

Key words: polyorganocyclosiloxanes, ring-opening polymerization, 1,5-disodiumoxyhexamethyltrisiloxane.



Introduction

Polyorganosiloxanes comprise a large and important group of diverse hybrid compounds and materials known as silicones. They play a key role among other polymers owing to their unique properties. One of the most important features of these materials is the minimal change of their mechanical and dielectric characteristics upon a moderate temperature rise. Many silicones maintain stability over a wide temperature range from –50 to 250 °C [1–4].

One of the main methods for obtaining polyorganosiloxanes of various structures is the ring-opening polymerization (ROP). It enables the production of high molecular weight polymers with relatively well-defined molecular weight compared to the polycondensation methods [5, 6].

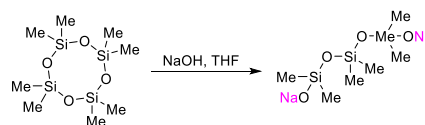
The main substrates used in these reactions are organocyclosiloxanes. The most important compounds of this class are octamethylcyclotetrasiloxane (D4) and hexamethylcyclotrisiloxane (D3). Cyclosiloxanes containing substituents other than methyl, such as ethyl, fluoroalkyl, phenyl, *etc.*, are used to obtain copolymers with the specific performance properties (oil resistance, heat resistance, improved cold resistance). Organocyclosiloxanes of mixed composition are of particular interest, since these monomers can ensure the required material properties at the molecular level [7, 8].

Organocyclosiloxanes are often obtained by the hydrolytic co-condensation or co-hydrolysis [9]. However, these methods do not allow for high-yield product formation, and if specific functional groups are required, they are not suitable for obtaining such materials.

An alternative approach to synthesizing mixed organocyclosiloxanes is the cyclization of 1,5-disodiumoxyhexamethyltrisiloxane with benzyldichloromethylsilane, which was considered in this work [10].

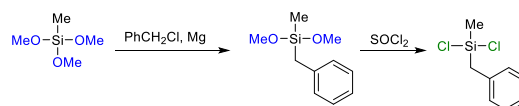
Results and discussion

1,5-Disodiumoxyhexamethyltrisiloxane was synthesized by the known methodology [11] according to the reaction depicted in Scheme 1.



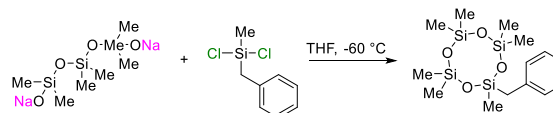
Scheme 1. Synthesis of 1,5-disodiumoxyhexamethyltrisiloxane.

Then benzyldiethoxymethylsilane was obtained using organomagnesium synthesis methods according to the procedure reported by Milenin *et al.* [12] (Scheme 2). Ethoxysilane was converted to benzyldichloromethylsilane upon treatment with thionyl chloride followed by the reaction of the product with the disodium siloxane salt.



Scheme 2. Scheme for the synthesis of benzyldichloromethylsilane.

The cyclization of 1,5-disodiumoxyhexamethyltrisiloxane was accomplished according to the methodology described in Ref. [11] (Scheme 3).



Scheme 3. Cyclization of 1,5-disodiumoxyhexamethyltrisiloxane with benzyldichloromethylsilane.

For this purpose, a 10% solution of the mentioned disodium salt in THF was prepared at 60 °C. Then, benzyldichloromethylsilane was rapidly added dropwise at –60 °C. The low temperature was used to prevent the Si–O bond cleavage. Subsequently, the excess of THF was evaporated on a rotary evaporator to isolate the reaction products, followed by addition of MTBE. The product solution was washed with water to neutral pH and passed through a layer of silica gel to remove residual pyridine, which was used earlier. Then MTBE was evaporated on a rotary evaporator, and the product was further purified by vacuum distillation at 1 mbar. The yield of the volatile fraction was 65%, with the product purity of 99%. The product was analyzed by gas-liquid chromatography, and its structure was confirmed using NMR and IR spectroscopy.

Conclusions

The alternative method for synthesizing mixed organocyclosiloxanes *via* cyclization of 1,5-disodiumoxyhexamethyltrisiloxane was successfully accomplished in this study. The synthesis afforded the target product in 65% yield with 99% purity, as was confirmed by the results of gas-liquid chromatography, NMR and IR spectroscopy analysis. This approach to mixed organocyclosiloxanes holds great promise for further research and development in the field of silicones and their applications.

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