



POLYMERIZATION OF HEXAMETHYLCYCLOTRISILOXANE IN AMMONIA INITIATED BY ALCOHOLS OF DIFFERENT STRUCTURES

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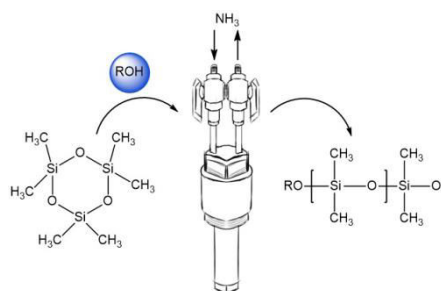
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Abstract

Functional polydimethylsiloxanes (PDMSs) containing an alkoxy group at one end of the polymer chain and a hydroxy group at the other end were obtained by the ring-opening polymerization of hexamethylcyclotrisiloxane (D₃) in liquid ammonia initiated by alcohols of different structures. This method implies the absence of organic solvents, which eliminates the stages of their purification and regeneration, and allows for obtaining telechelic PDMSs in full agreement with green chemistry principles.

Key words: polydimethylsiloxanes, polyorganosiloxanes, ring-opening polymerization, telechelic polydimethylsiloxanes.



Introduction

Polyorganosiloxanes are one of the most important classes of polymers. Among them, polydimethylsiloxanes (PDMSs) are of particular interest: their unique physicochemical properties (high elasticity, frost resistance, resistance to oxidation and UV radiation) in combination with biocompatibility and low toxicity ensure a wide range of applications, ranging from the paint and varnish and food industries to special-purpose areas [1–6].

A method for the synthesis of PDMSs by the polymerization of hexamethylcyclotrisiloxane D₃ in a liquid ammonia medium initiated by water was developed in the Laboratory of Organosilicon Compounds at INEOS RAS [7].

This work demonstrates the possibility of obtaining telechelic PDMSs by the polymerization in liquid ammonia using different alcohols as initiators.

Results and discussion

The polymerization of hexamethylcyclotrisiloxane D₃ was carried out in a reactor with a working volume of 20 mL (Fig. 1).

The process is accomplished in several stages: (1) the required amounts of D₃ and an initiator are loaded into the reactor, (2) ammonia is introduced upon cooling the reactor to –50 °C, (3) the reactor is thermostated at 30 °C, (4) the decompression is carried out at room temperature after the reaction completion, (5) the resulting polymer is recovered.

In the case of the polymerization of D₃ initiated by methanol (MeOH), the reaction time was varied (Table 1, Fig. 2). The conversion degree and molecular weight characteristics (MWC) of the resulting polymers (1–3) were determined by gel permeation chromatography (GPC). The results obtained show that the complete conversion of the monomer is achieved in

48 h, while the molecular weight (MW) of the resulting polymer remains virtually unchanged over time.

In the experiments with ethanol used as the D₃ polymerization initiator, the polymers with $M_n = 3.6\text{--}4.0$ kDa and PDI = 1.27–1.31 were also obtained (Table 2). In this case, almost complete conversion of D₃ was reached in 48 h (Fig. 3). However, the GPC curve of polymer 6 contains a high-molecular shoulder, which may be due to the occurrence of the side condensation process. Therefore, in this case the optimal reaction time is 24 h.

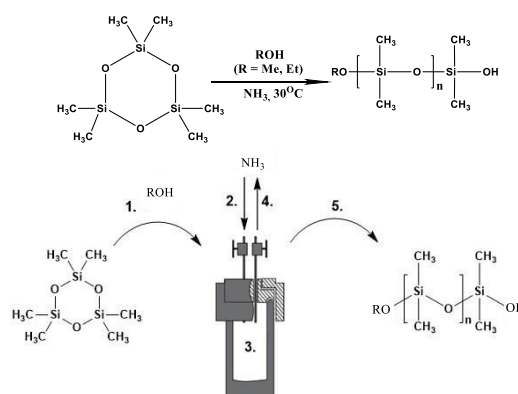


Figure 1. Polymerization of D₃.

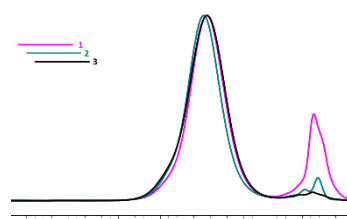
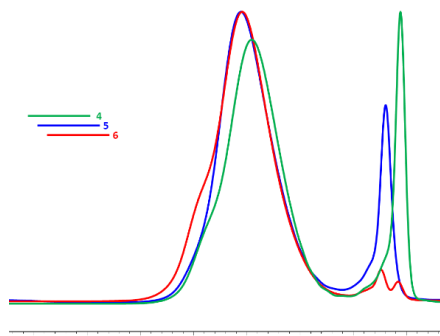


Figure 2. GPC curves of polymers 1–3.

Table 1. Molecular weight characteristics of polymers 1–3

Sample	Time, h	M_n , kDa	M_w , kDa	M_w/M_n	Conversion, %
1	20	3,7	4,4	1,19	79
2	24	3,9	4,6	1,19	95
3	48	3,7	4,6	1,23	100

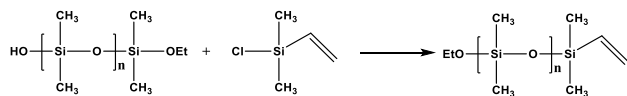
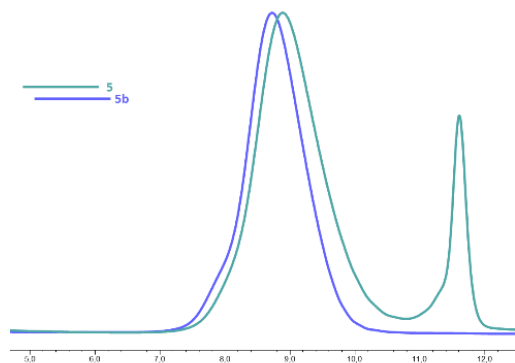
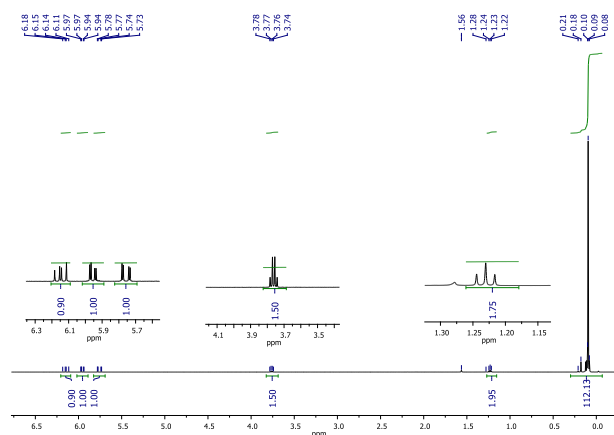
Reaction conditions: $n(D_3) = 4.5$ mol (1 g), $n(\text{MeOH}) = 0.45$ mmol (18 μL), $m(\text{NH}_3) = 5$ g, $T = 30$ °C.

**Figure 3.** GPC curves of polymers 4–6.**Table 2.** Molecular weight characteristics of polymers 4–6

Sample	Time, h	M_n , kDa	M_w , kDa	M_w/M_n	Conversion, %
4	20	3.6	4.6	1.27	79
5	24	3.9	4.9	1.27	84
6	48	4.1	5.3	1.31	100

Reaction conditions: $n(D_3) = 4.5$ mol (1 g), $n(\text{EtOH}) = 0.45$ mmol (24 μL), $m(\text{NH}_3) = 5$ g, $T = 30$ °C.

To confirm the structure of polymer 5, the reaction of terminal OH-blocking with chloro(dimethyl)vinylsilane was carried out according to the scheme presented in Fig. 4 (for the GPC curve and ^1H NMR spectrum of the resulting polymer, see Figs. 5, 6). This also shows the possibility of obtaining precursors for the synthesis of block copolymers or comb-shaped polymers.

**Figure 4.** Blocking reaction.**Figure 5.** GPC curves of polymers 5 and 5b before and after blocking.**Figure 6.** ^1H NMR spectrum of the blocked polymer (reaction time 24 h).

It should be noted that, the ^1H NMR spectrum of blocked polymer 5b (reaction time 24 h) shows a discrepancy between the integral intensities of the proton signals of the vinyl and ethoxy groups, which indicates that the reaction mixture also contains the polymerization products bearing two terminal silanol groups: HO-PDMS-OH. In future studies, the conditions for blocking will be optimized in order to obtain a polymer containing both ethoxy and silanol groups.

Experimental section

General remarks

Hexamethylcyclotrisiloxane was purchased from ABCR and purified by boiling with CaH_2 followed by distillation. Chloro(dimethyl)vinylsilane and pyridine were purchased from ABCR and Acros Organics, respectively, and were used without purification. Methanol, ethanol, and toluene were refluxed and distilled over CaH_2 followed by drying over molecular sieves. Anhydrous ammonia was purchased from Spectra Gases Inc.

The ^1H NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz, Germany). The chemical shifts are given relative to TMS and the residual signal of chloroform ($\delta = 7.25$ ppm). The GPC/SEC analysis was performed in toluene (1 mL/min) using a Shimadzu Prominent system equipped with a RID-20A refractive index detector. The GPC/SEC columns (Phenogel) were calibrated using polystyrene standards (PSS).

Syntheses

Polydimethylsiloxanes (1–6). A mixture of hexamethylcyclotrisiloxane (40 mmol) and the corresponding alcohol (4 mmol) in liquid ammonia (5 g) was stirred in a reactor at 30 °C. After the reaction completion, the decompression was performed to remove ammonia from the reaction medium. The resulting polymers were transparent oils.

Polydimethylsiloxane with the vinyl terminal group (5b). A mixture of chloro(dimethyl)vinylsilane (0.72 mmol), pyridine (0.72 mmol), and polymer 5 (0.17 mmol) in dry toluene (10 mL) was stirred at room temperature for 24 h. After the reaction completion, the resulting mixture was washed with water until neutral pH. Polymer 5b was dried over Na_2SO_4 , the solvent was removed under vacuum.

Conclusions

Using D₃ and alcohols (ethanol and methanol) in the presence of ammonia, which is produced industrially in large quantities, the polydimethylsiloxanes with $M_n = 3\text{--}4$ kDa containing various functional groups at the chain ends were synthesized. This method for producing PDMS offers the following important advantages: it not only involves the use of commercially available reagents, but also eliminates the use of solvents. The results obtained indicate the prospects for further investigations of this method, as well as its development and possible industrial scaling.

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