



SYNTHESIS OF LINEAR POLYMETHYLPHENYLSILOXANE IN AN AMMONIA MEDIUM

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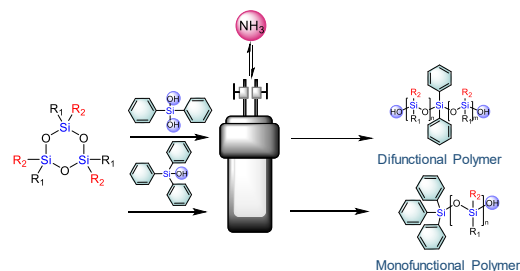
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Abstract

The experiments on ring-opening polymerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (D_3^{MePh}) in liquid ammonia in the presence of initiators such as diphenylsilanediol ($\text{Ph}_2\text{Si}(\text{OH})_2$) and triphenylsilanol ($\text{Ph}_3\text{Si}(\text{OH})$) were carried out. The effect of the reaction time on the molecular weight characteristics of the resulting polymers was studied.



Key words: ring-opening polymerization, organocyclotrisiloxanes, functional polyorganosiloxanes, ammonia.

Introduction

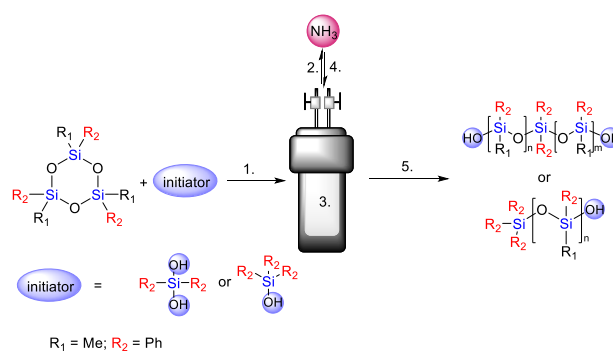
One of the current trends in the chemistry of organosilicon compounds is the synthesis of polyorganosiloxanes with a strictly specified architecture of macromolecules. From a practical point of view, the production of linear polysiloxanes with different organic substituents at the silicon atom is of particular interest. These compounds can be obtained by the ring-opening polymerization of the corresponding organocyclotrisiloxanes [1–5]. Interesting results were obtained by Fuchise *et al.* [6–12] using water or silanols as initiators, and strong organic bases such as amidines, guanidines, and phosphazene derivatives as catalysts. Thus, polyorganosiloxanes of various structures and functionality were synthesized. Nevertheless, this method requires further improvement due to the use of organic solvents. The resulting polymers must be isolated, and the solvents must be purified from the catalyst residues. Therefore, the development of modern convenient and effective methods for producing polyorganosiloxanes is still urgent.

Earlier our group has developed a method for synthesizing linear telechelic polydimethylsiloxanes in ammonia by the ring-opening polymerization of hexamethylcyclotrisiloxane in the presence of water [13]. In this case, ammonia acts as both a catalyst and a solvent. The advantage of this process is the isolation procedure of the target polymers: removing ammonia from the reaction mixture by the decompression affords a ready polymer product. This method also allows one to recycle ammonia and use it in subsequent reactions, which makes it consistent with the principles of green chemistry.

In this work, we suggest an approach that allows for the application of silanols of various structures as initiators for the synthesis of linear polyorganosiloxanes in ammonia using the ring-opening polymerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane as an example.

Results and discussion

The polymerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (D_3^{MePh}) was carried out in a high-pressure reactor with a working volume of 20 mL. At the first stage, the required amounts of the monomer and initiator were loaded into the reactor (1), then, upon cooling to $-50\text{ }^\circ\text{C}$, ammonia was introduced using a mass flow controller (MFC) (2). The reactor was thermostated at $30\text{ }^\circ\text{C}$ (3). After the reaction completion, the decompression was performed at room temperature (4), thus affording the target products (5) (Scheme 1).



Scheme 1. General scheme for the polymerization of D_3^{MePh} in ammonia.

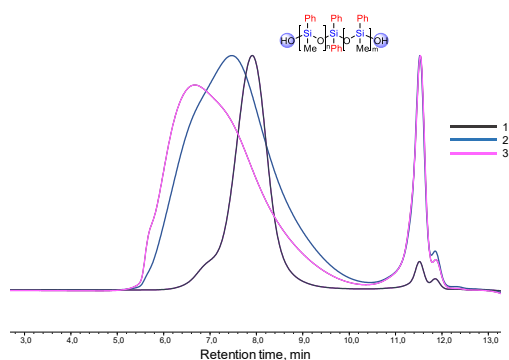
Table 1. Reaction conditions and molecular weight characteristics of products 1–6

Sample	Initiator	Reaction time, h	Conversion of D_3^{MePh} , %	M_n , kg/mol	M_w , kg/mol	PDI
1	$\text{Ph}_2\text{Si}(\text{OH})_2$	4	98	10.9	12.9	1.2
2		8	99	11	20.0	1.8
3		24	99	14	27.0	1.9
4	Ph_3SiOH	4	96	9.7	13.0	1.3
5		8	98	9.6	12.9	1.3
6		24	99	10.0	14.6	1.4

Reaction conditions: 30 °C, 1.84 g (4.5 mmol) of D_3^{MePh} , 0.02 g (0.11 mmol) of $\text{Ph}_2\text{Si}(\text{OH})_2/0.03$ g (0.11 mmol) of Ph_3SiOH , 5 g of NH_3 .

The effect of the polymerization time of D_3^{MePh} in ammonia on the molecular weight characteristics of the resulting linear polymethylphenylsiloxanes was studied (Table 1).

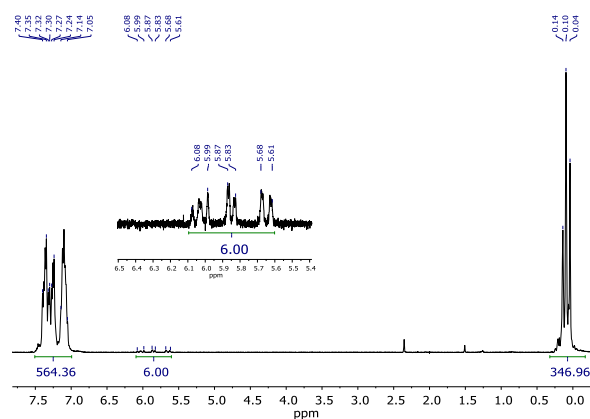
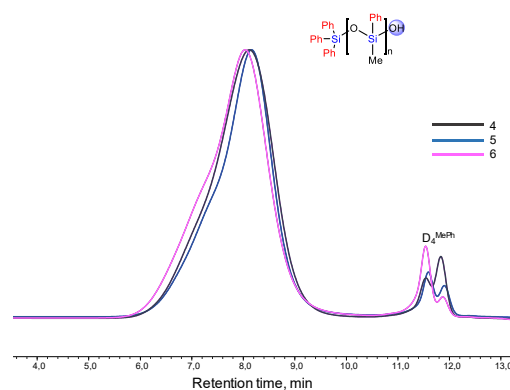
The presented data show that, when diphenylsilanediol is used as an initiator, the optimal reaction time is 4 h. During this period, almost complete conversion of the monomer is achieved, while no active side condensation and depolymerization processes are observed (Fig. 1). An increase in the reaction time leads to broadening of the molecular weight distribution of the resulting polymethylphenylsiloxane and intense formation of four-membered methylphenylcyclosiloxane D_4^{MePh} in the mixture of products.

**Figure 1.** GPC curves of polymethylphenylsiloxanes 1–3 after the decompression.

The polymethylphenylsiloxane obtained in experiment 3 had a fairly narrow molecular weight distribution. This suggests that it can be used as a rigid block for obtaining hybrid PDMS copolymers. For polymer 3, the reaction of blocking of the terminal hydroxy groups with chloro(dimethyl)vinylsilane in the presence of pyridine as an HCl acceptor was carried out. The average degree of polymerization (n) was determined by ^1H NMR spectroscopy and composed 100 (Fig. 2).

Figure 3 shows the GPC curves of the products of the D_3^{MePh} polymerization initiated by triphenylsilanol in ammonia over different reaction times (experiments 4–6, Table 1).

It is obvious that an increase in the reaction time almost does not affect the molecular weight characteristics of the resulting polymethylphenylsiloxanes but leads to an increase in the content of D_4^{MePh} in the mixture. This may be due to the fact that an increase in the polymer molecular weight by the polymerization mechanism is sterically hindered; therefore, under the reaction conditions, thermodynamically most favorable product D_4^{MePh} is formed over time as a result of the depolymerization processes. The presence of a high-molecular

**Figure 2.** ^1H NMR spectrum of polymer 3 after blocking the terminal OH groups with chloro(dimethyl)vinylsilane.**Figure 3.** GPC curves of polymethylphenylsiloxanes 4–6 after the decompression.

shoulder on the GPC curves of polymers 4–6 indicates the occurrence of the dimerization of polymethylphenylsiloxanes with terminal hydroxy groups under the reaction conditions.

Experimental section

General remarks

Anhydrous ammonia was purchased from Spectra Gases Inc. 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisiloxane, diphenylsilanediol, triphenylsilanol, chloro(dimethyl)vinylsilane were purchased from ABCR. Pyridine was purchased from Acros Organics.

The GPC analysis was performed on a Shimadzu chromatograph using a RID-20A refractometer as a detector, a PSS SDV analytical 10^3 Å column (300×8 mm), and toluene as an eluent.

The ^1H NMR spectrum was recorded on a Varian Inova 400 spectrometer at 400 MHz. The ^1H chemical shifts were measured relative to TMS using residual signal of the solvent (CDCl_3).

Syntheses

The required amounts of D_3^{MePh} and $\text{Ph}_2\text{Si}(\text{OH})_2$ or Ph_3SiOH were loaded into an autoclave equipped with a magnetic stirrer. Then the autoclave was filled with NH_3 (5 g) under chill-down using an IN-FLOW MFC (Bronkhorst, Netherlands). The autoclave was thermostated at 30 °C. The process was conducted at 30 °C and 10 atm for 4–24 h. After the reaction

completion, the decompression was performed at room temperature.

Conclusions

Using the synthesis of linear polymethylphenylsiloxanes as an example, we showed that the application of silanols of various structures as the ring-opening polymerization initiators enables the production of polyorganosiloxanes of various structures and functionality. The results obtained and the simple and convenient synthetic scheme allow for concluding that this approach is promising from the viewpoint of obtaining not only linear polyorganosiloxanes with tunable structures, functionality, and molecular weight characteristics, but also silicones of a more complex architecture.

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