



CONDENSATION OF α,ω -OLIGODIMETHYLSILOXANOLS IN AMMONIA: A NEW METHOD FOR THE SYNTHESIS OF POLYDIMETHYLSILOXANES WITH THE LOW CONTENT OF CYCLOSILOXANES

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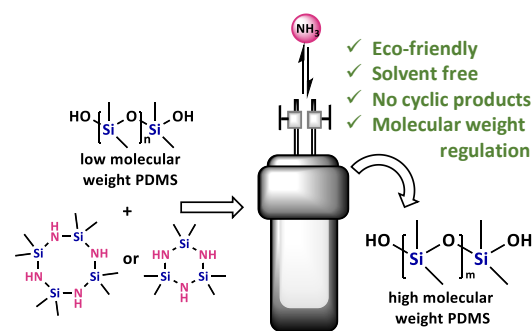
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Abstract

A new efficient approach to the production of high molecular weight polydimethylsiloxanes (PDMSs) is developed based on the condensation of α,ω -oligodimethylsiloxanols in ammonia. This method provides control over the molar mass of the target PDMSs in a wide range ($M_w = 11.0$ – 82.0 kg/mol). The use of cyclic silazanes as dehydrating agents allows for suppressing the side cyclization processes.



Key words: polydimethylsiloxanes, polycondensation, ammonia, green chemistry.

Introduction

Modern materials science imposes increasingly stringent requirements for the quality of both new and already known polymers. Nowadays, one of the most important parameters is the absence of low molecular impurities in a polymer, the presence of which can change the properties of the target material for the worse.

One of the most popular organoelement polymers is polydimethylsiloxane (PDMS) which is widely used both at the household level and in high-tech industries. This is caused by a complex of valuable physicochemical properties: hydrophobicity, bioinertness, high thermal and thermooxidative stability, etc. [1, 2]. There is a large variety of approaches to the synthesis of PDMS based on the polymerization and polycondensation processes [3, 4]. However, one of the main drawbacks of the known methods for its synthesis is the presence of low molecular weight compounds in the target products—dimethylcyclosiloxanes, which deteriorate the physicochemical characteristics of materials. In this respect, a promising method for the synthesis of PDMS is the ring-opening polymerization of hexamethylcyclotrisiloxane in the presence of basic organocatalysts in a mixture of organic solvents [5–12]. This approach enables the production of PDMSs in a wide range of molar masses without the formation of cyclic by-products at almost complete monomer conversion. However, the use of organic solvents and catalysts leads to certain limitations of the mentioned method from an industrial point of view. The condensation processes are used less frequently than the polymerization ones. This is due to the actively occurring side

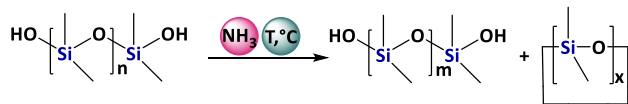
cyclization processes during the growth of a macromolecule [13]. The search for new highly efficient approaches to the synthesis of PDMS with a low content of cyclic products that would comply with the principles of green chemistry is an urgent task.

Earlier our research group developed the methods for obtaining silicones based on the polymerization and polycondensation reactions in ammonia. In the first case, the ring-opening polymerization of hexamethylcyclotrisiloxane in the presence of water afforded narrowly dispersed telechelic PDMSs with terminal hydroxy groups in the ranges of molar masses from 3 to 10 kg/mol [14]. In the case of the polycondensation of *cis*-tetraphenylcyclotetrasiloxanetetraol, we have shown that it is possible to obtain ladder poly(phenylsilsesquioxanes) (L-PPSQs) with controlled molar masses (from 15 to 1000 kg/mol) by varying the synthesis temperature. A peculiarity of high molecular weight L-PPSQs obtained by this method is their lower brittleness, which along with good mechanical and thermal characteristics makes them promising objects for use in materials science [15]. In both cases, ammonia acts simultaneously as a catalyst and a solvent. The advantage of both processes is the isolation procedure of the target polymers: the removal of ammonia from the reaction mixture by decompression affords the final polymer product. Furthermore, the developed methods enable ammonia recycling and its use in subsequent reactions, which makes them consistent with the principles of green chemistry.

The goal of this work was to show the possibility of producing PDMS with a low content of cyclosiloxanes by the condensation of α,ω -oligodimethylsiloxanols with controlled molar mass characteristics (MMCs) in ammonia.

Results and discussion

The condensation in ammonia was carried using commercially available α,ω -oligodimethylsiloxane (**PDMS-(OH)₂**) according to Scheme 1.



Scheme 1. Condensation in ammonia.

For this purpose, **PDMS-(OH)₂** was placed in a high-pressure steel reactor (Fig. 1). Then the required amount of ammonia was loaded into the reactor through a gas flow regulator at -40 °C. The reactor was heated to the required temperature. The reaction mixture was agitated with a magnetic stirrer for a specified time.

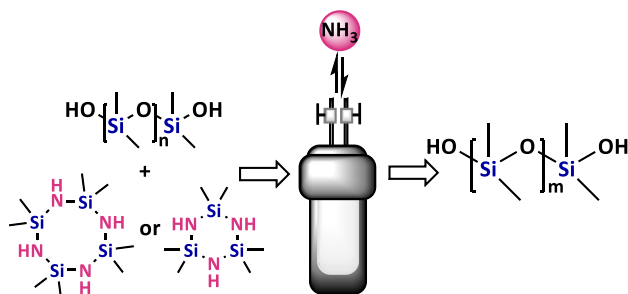


Figure 1. General scheme for the reactions in ammonia.

Table 1 lists the data for three experiments (samples 1–3). As can be seen, an increase in the reaction time leads to an increase in the content of cyclic dimethylsiloxanes in the reaction mixture (exp. 2). The same pattern is observed with an increase in the process temperature from 70 to 90 °C and an increase in the reaction time to 24 h (exp. 3).

Figure 2 shows the SEC curves for initial **PDMS-(OH)₂** and the experiments performed. From the presented diagrams, it is clear that the molar masses (MMs) of the resulting polymers slightly exceed that of initial **PDMS-(OH)₂**. At the same time, a significant amount of cyclic low molecular weight products is formed in all experiments. This implies that, in addition to the condensation processes that lead to an increase in the molar mass of initial **PDMS-(OH)₂**, it actively undergoes depolymerization. This can be caused by the formation of water as a result of the homocondensation of terminal **Si-OH** groups. The released water molecules interact with ammonia to form ammonium hydroxide which, under the reaction conditions, promotes the cleavage of the siloxane bond [14].

Therefore, it was decided to add a dehydrating agent in order

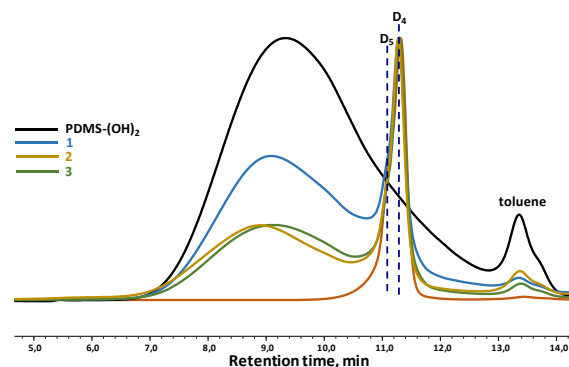
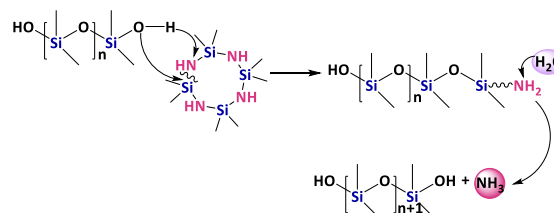


Figure 2. SEC curves of products 1–3 and initial **PDMS-(OH)₂**.

to avoid the side processes of depolymerization. Octamethylcyclotetrasilazane (**D_{4NH}**) was used as such an agent. The choice of this reagent was dictated by the fact that the interaction of **D_{4NH}** with the terminal silanol groups leads to the cleavage of a siloxane ring. The following hydrolysis results in the formation of siloxane and the release of ammonia, which ensures the absorption of released water in the system (Scheme 2). Furthermore, the choice of **D_{4NH}** rather than the silazane rings of other sizes was due to the fact that this compound is crystalline and is formed in good yield (40–50%) upon ammonolysis of dimethyldichlorosilane (DMDCS) [16]. The suggested process utilized low loadings of **D_{4NH}** (68 mg), so in the initial stage of the investigations, the addition of a solid compound seemed to be preferable for a more accurate adherence to the ratios of the cycle to the terminal **Si-OH** groups.



Scheme 2. Interaction of **D_{4NH}** with the silanol group.

The experiments were carried out according to the scheme depicted in Fig. 1, except for the fact that, in addition to **PDMS-(OH)₂**, the reactor was charged with the calculated amount of **D_{4NH}** before ammonia injection. The first experiment with **D_{4NH}** was carried out at the **PDMS-(OH)₂/silazane** molar ratio of 3:2 in the presence of 5 g of ammonia (Table 2, exp. 4). The reaction time was 8 h. Figure 3 shows the SEC curves of initial **PDMS-(OH)₂**, the reaction product, and octamethylcyclotetrasiloxane (**D₄Me₂**) used as an external standard.

Table 1. Reaction conditions and molar mass characteristics of products 1–3^a

Sample	<i>T</i> , °C	Time, h	<i>M_p</i> , kg/mol	<i>M_n</i> , kg/mol	<i>M_w</i> , kg/mol	PDI	HMWF/LMWF, % ^b
1	70	4	4.2	3.1	5.0	1.63	74:26
2	70	24	4.8	3.8	6.1	1.61	60:40
3	90	24	3.9	3.3	5.3	1.59	60:40

^a **PDMS-(OH)₂** loading: 1 g (0.31 mmol); NH₃ loading: 5 g;

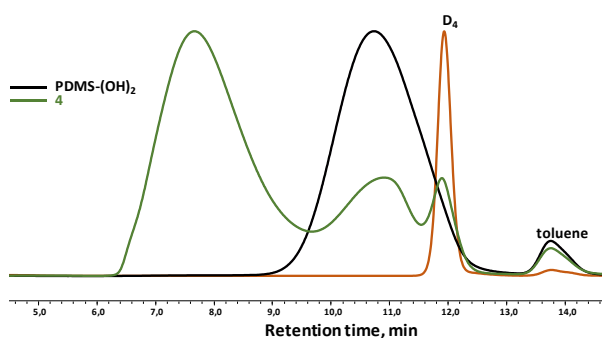
^b according to the SEC data.

Table 2. Reaction conditions and molar mass characteristics of products 4–7^a

Sample	NH ₃ , g	Time, h	M _p , kg/mol	M _n , kg/mol	M _w , kg/mol	PDI	Ratio of linear/cyclic products, % ^b		
							HMWF	LMWF	cycles
4	5	8	72.4	48.1	69.7	1.44	70	22	8
5	5	16	73.9	43.5	67.1	1.54	70	12	18
6	2.5	16	46.8	29.3	45.8	1.56	88	9	3
7	1	16	33.0	22.0	32.8	1.51	96.5	3	0.5

^a PDMS-(OH)₂ loading: 1 g (0.31 mmol); D_{4NH} loading: 0.068 g (0.23 mmol); temperature: 100 °C;

^b according to the SEC data.

**Figure 3.** SEC curves of product 4 and initial PDMS-(OH)₂.

As can be seen from Fig. 3 and Table 2 (sample 4), the use of D_{4NH} does result in a significant increase in the product MM ($M_p = 72.4$ kg/mol). However, the cyclization process cannot be completely suppressed. In addition, the resulting products contain a significant amount of the low molecular weight polymer (LMWF). This is likely to be due to the fact that all D_{4NH} is spent for the formation of the high molecular weight product. The remaining part of PDMS-(OH)₂ reacts according to the process of homofunctional condensation with the release of water. This leads to the formation of cyclic products, as we have seen in the above-mentioned examples.

At the next step, the conditions for the condensation of PDMS-(OH)₂ in ammonia were optimized. For this purpose, the effect of the parameters such as the reaction time, ammonia concentration, temperature, molar ratio of PDMS-(OH)₂ to the dehydrating agent, and the structure of the silazane itself (D_{4NH} and D_{3NH}) was explored. Recently we have established that a decrease in the amount of ammonia in the system intensifies the course of the condensation processes [14]. Based on this, we carried out the experiments with different ammonia contents at the constant PDMS-(OH)₂/D_{4NH} molar ratio of 3:2 (Table 2).

Figure 4 demonstrates the SEC curves of products 5–7.

From Table 2 and Fig. 4 it is obvious that an increase in the reaction time to 16 h in the presence of 5 g of ammonia does not lead to significant changes in the molar mass characteristics (MMCs) of the reaction product (exp. 4 and 5). However, the content of LMWF increases, which confirms our assumption that released water leads to an equilibrium in the system between the HMW and LMW fractions. The picture changes with a decrease in the amount of ammonia in the system from 5 to 2.5 g (Table 2, Fig. 4, exp. 6). The product MM decreases, although the content of the cyclic components in the system is only about 3%. The content of the LMWF fraction almost does

not change at that. It should be noted that the MMCs of the LMW fraction in exp. 6 is closer to those of initial PDMS-(OH)₂ than in case of exp. 4 and 5. This indicates that a decrease in the amount of ammonia in the system leads to a reduction in the depolymerization processes. This is likely to be due to a decrease in the system polarity.

A further reduction in the ammonia content to 1 g (Table 2, exp. 7) confirms this hypothesis. Thus, the cyclic products were almost completely absent in exp. 7. The content of LMWF also reduced to 3%.

Hence, it can be concluded that the optimal conditions for the production of PDMS with a minimum amount of the cyclic products at the PDMS-(OH)₂/D_{4NH} molar ratio of 3:2 are the reaction temperature of 100 °C and the addition of 1 g of ammonia.

The next stage was the use of another dehydrating agent, namely, hexamethylcyclotrisilazane (D_{3NH}). This reagent is more available than D_{4NH}, which is caused by its higher yield upon the ammonolysis of DMDCS (up to 80%) as well as easier purification by distillation [17].

The reactions were carried out according to the analogous scheme (Fig. 1). The results of the experiments are summarized in Table 3.

The intensification of the condensation processes with a decrease in the amount of ammonia in the system should lead to the release of a larger amount of water. Therefore, in a series of the experiments with D_{3NH}, we also varied the PDMS-(OH)₂/D_{3NH} molar ratio. As can be seen from the results of these experiments, the variation of the amount of ammonia and the polymer/cycle ratio ensures the production of PDMS with controlled MM with almost complete suppression of the depolymerization processes which lead to the formation of cyclic products (Fig. 5).

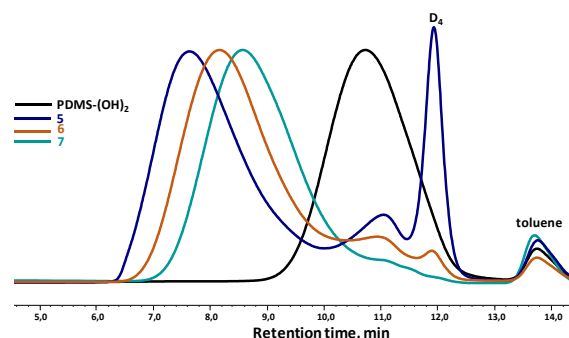
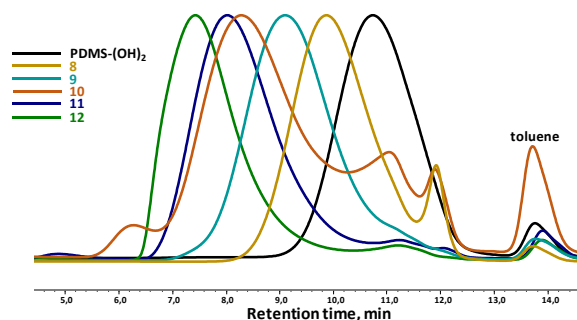
**Figure 4.** SEC curves of products 5–7 and initial PDMS-(OH)₂.

Table 3. Reaction conditions and molar mass characteristics of products 8–12^a

Sample	D _{3NH} , mg (mmol)	PDMS-(OH) ₂ /D _{3NH} ratio	NH ₃ , g	T, °C	M _p , kg/mol	M _n , kg/mol	M _w , kg/mol	PDI	Ratio of linear/cyclic products, % ^b		
									HMWF	LMWF	cycles
8	51 (0.23)	3:2	2.5	100	10.8	8.3	11.4	1.37	95	–	5
9	68 (0.31)	1:1	2.5	100	21.0	15.7	23.3	1.48	95	4	1
10	100 (0.46)	2:3	2.5	100	42.6	26.6	40.6	1.53	76	17	7
11	100 (0.46)	2:3	1	100	53.3	32.6	51.2	1.57	95	4	1
12	100 (0.46)	2 : 3	1	120	89.0	54.9	82.0	1.49	95.8	4	0.2

^a PDMS-(OH)₂ loading: 1 g (0.31 mmol); reaction time: 16 h;

^b according to the SEC data.

**Figure 5.** SEC curves of products 8–12 and initial PDMS-(OH)₂.

Experimental section

General remarks

Anhydrous ammonia was purchased from Spectra Gases Inc. Silanol terminated polydimethylsiloxane (PDMS-(OH)₂) was purchased from Gelest. The molar mass characteristics of PDMS-(OH)₂ were as follows: $M_p = 3.8$ kg/mol, $M_n = 1.7$ kg/mol, $M_w = 4.0$ kg/mol, PDI = 2.35, viscosity at 25 °C = 45–85 cSt. Octomethylcyclotetrasilazane (D_{4NH}) and hexamethylcyclotrisilazane (D_{3NH}) were synthesized according to the published procedures [16, 17].

SEC analysis was performed on a Shimadzu chromatograph using a RID-20A refractive index detector, a PSS SDV analytical 10³ Å column (300 × 8 mm), 10⁴ Å column (300 × 8 mm), and toluene as an eluent.

Syntheses

The required amount of PDMS-(OH)₂ and D_{4NH} or D_{3NH} were loaded into an autoclave equipped with a magnetic stirrer. Then the autoclave was filled with the required amount of NH₃ under chill-down using an IN-FLOW mass flow meter (Bronkhorst, Netherlands). The autoclave was thermostated at the required temperature. After the reaction completion, the decompression was performed at room temperature.

Conclusions

In this work, we have shown that the condensation of α,ω -oligodimethylsiloxanols in ammonia at temperatures of about 100 °C leads to dynamic equilibrium in the system between the processes of condensation and depolymerization. This occurs due to the release of water during the homocondensation of the terminal silanol groups. The depolymerization results in the formation of undesirable cyclic dimethylsiloxanes (up to 40%). The addition of a dehydrating agent, such as

hexamethylcyclotrisilazane or octamethylcyclotetrasilazane, dramatically changes the situation. Thus, the optimized reaction conditions (initial polymer/dehydrating agent ratio of 3:2, 100 °C, 1 g of ammonia) allowed us to almost completely avoid the cyclization processes. Moreover, the variation of the ratio of the reagents and the content of ammonia in the system provides control over the molar mass characteristics of the target PDMSs, which makes this approach promising for industrial implementation.

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