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Low Dispersity Telechelic Polydimethylsiloxanes Synthesized in Ammonia Medium

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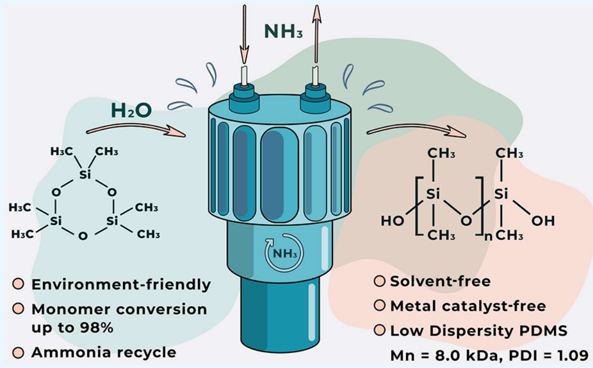
ABSTRACT: The polymerization of hexamethylcyclotrisiloxane (D_3^{Me2}) in liquid ammonia using water as an initiator has been studied. These polymers are of practical importance for a wide range of applications in the silicone industry. The effect of factors such as temperature, reaction time, and concentration of reactants on the polymerization process was evaluated. As a result, an environmentally friendly procedure for the preparation of narrowly dispersed telechelic polydimethylsiloxanes (Mn = 8.0 kDa, PDI = 1.11) with a monomer conversion of up to 98% was developed. The possibility of scaling up the process and recycling of ammonia was shown.



KEYWORDS: *ring-opening polymerization, telechelic polydimethylsiloxanes, ammonia medium, eco-friendly, ammonia recycling*

1. INTRODUCTION

Polyorganosiloxanes are a diverse and best studied class of polymers with inorganic backbone macromolecules. They have found widespread applications for a variety of uses, from electronics to mechanical engineering and construction industry to personal care products. Among these polymers, polydimethylsiloxanes (PDMS) hold a special place due to their unique physicochemical properties including plasticity, heat and frost resistance, oxidative and UV-stability, hydrophobic properties, and biological inertness.[1]

One of the fundamental approaches for the industrial production of PDMS involves the ionic polymerization of octamethylcyclotetrasiloxane (D_4^{Me2}). The polymerization proceeds according to the cationic (catalyst: a strong protic or aprotic acid) or anionic (catalyst: a strong base) mechanism.[2−5] Both of these processes have an equilibrium character so that side reactions actively proceed, leading to the formation of cyclic products and the dispersity broadening. Therefore, to isolate the target polymers, additional separation of low molar mass cyclic organosiloxanes is necessary.

The development of modern technologies requires more careful control over the properties of the resulting products.[6−12] One way of realizing this is the use of narrowly dispersed oligomers and polymers. Such compounds allow for tuning the properties of the products by varying the molar mass in a controlled manner. The application of narrowly dispersed reactive oligomers is especially relevant in the production of cross-linked elastomers whose properties are governed by the degree of network regularity. The low dispersity of such oligomers along with the corresponding arrangement of terminal functional groups encourages a shift toward more advanced processes for the production of state-of-the-art silicon elastomers.[13−16]

The basic method currently used to obtain low dispersity PDMS involves an anionic ring opening polymerization (ROP) initiated by organometallic compounds, *e.g.*, alkyllithium salts.[17,18] Hexamethylcyclotrisiloxane (D_3^{Me2}) is used as a monomer. This method requires careful control of the purity of the monomer and solvents in use, the complete absence of moisture, and an inert reaction atmosphere to prevent the occurrence of side reactions such as chain termination or transfer and depolymerization. As a rule, this process is terminated before it is completed. This is due to the fact that, at high degrees of D_3^{Me2} conversion, the abovementioned side processes actively take place leading to the dispersity broadening and formation of cyclic products.[5,19] As a result of these challenges, the application of this technique in industry is extremely limited.

Thus, the development of improved methodologies to produce low dispersity PDMS of various molar masses remains relevant in the chemistry of silicones. The attention of researchers was focused on the search for alternative

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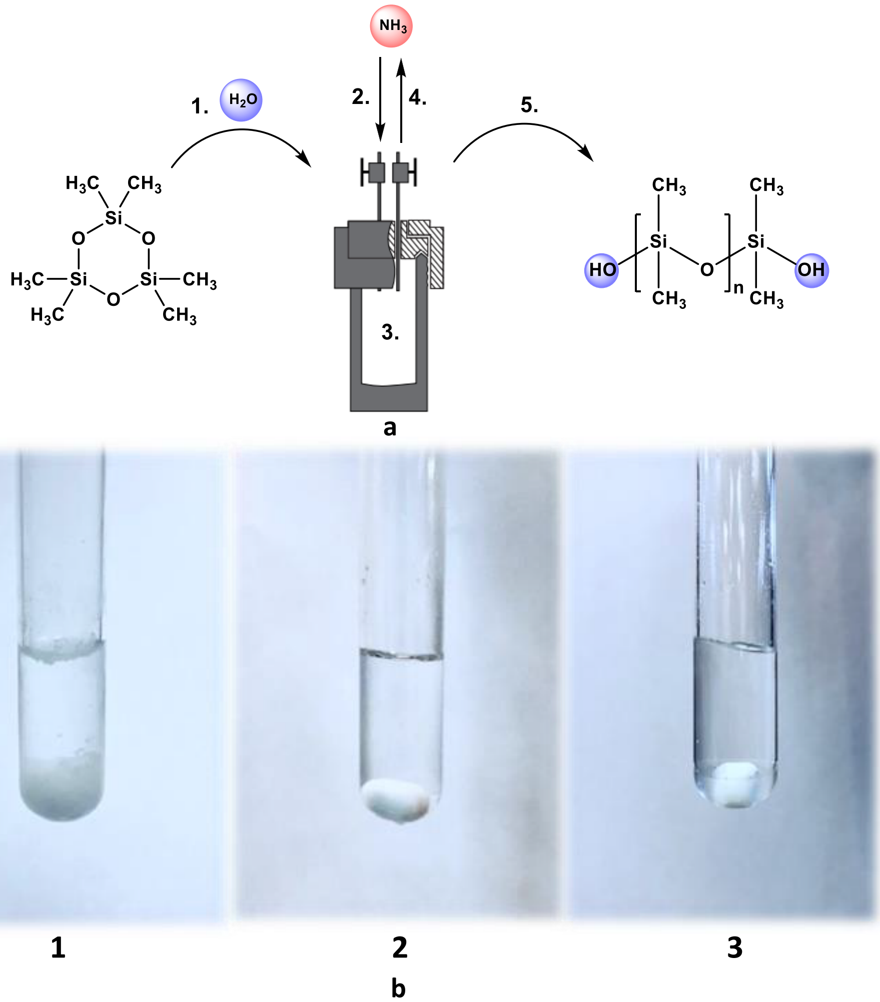

Figure 1. (a) Scheme of D_3^{Me2} polymerization in ammonia; (b) visualization of D_3^{Me2} polymerization in ammonia. Left panel: immediately after loading the reactants (**1**); central panel: after 10 min of the reaction (**2**); right panel: after completion of the reaction (**3**).

"catalyst−initiator" systems capable of initiating the polymerization of organocyclosiloxanes to provide low dispersity PDMS under mild conditions. For example, some studies employed organic acids and bases as catalysts for organocyclosiloxane ROP. Acidic catalysts such as trifluoromethanesulfonic acid CF_3SO_2OH,[20,21] bis(trifluoromethane)sulfonimide (TFSI-H),[22] and $B(C_6F_5)_3$ derivatives[23−25] are noteworthy. However, even on these catalysts, side depolymerization reactions occur rather readily and the resulting polymers have a fairly broad dispersity (PDI ≥ 1.7). As for base catalysts, only those with sufficiently high Brønsted basicity, such as phosphazene derivatives[26−28] and *N*-heterocyclic carbenes (NHCs),[29] were employed. However, even in these cases, the dispersity of the obtained PDMS was not low enough (PDI ≥ 1.5).

The synthesis of low dispersity polycarbosiloxane (PDI < 1.2) *via* organocatalytic ROP of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane using 1,5,7-triazabicyclo[4.4.0]dec5-ene (TBD) as a catalyst has been reported.[30] Unfortunately, the authors provided no size exclusion chromatography (SEC) data to confirm their results.

Fuchise et al.[31] have recently prepared low dispersity siloxane polymers using strong organic bases as catalysts. As a result of studies of organocatalytic living anionic polymerization of various organocyclotrisiloxanes initiated by water, the optimal conditions (temperature, solvents, time, and nature of the organocatalyst) for the synthesis of narrowly dispersed (PDI 1.03−1.16) polyorganosiloxanes with a specific symmetric structure in a broad range of molar masses (Mn = 2.64−102.3 kDa) were determined. The preparation of such polymers by conventional anionic polymerization using lithium derivatives as initiators is a challenge. However, the cited method needs further improvement because of the use of organic solvents. The PDMS obtained should be separated and the solvents purified from the remaining catalyst. Therefore, the development of modern convenient and efficient methods for the preparation of polyorganosiloxanes is still relevant.

An unexpected approach to addressing this issue turned out to be polymerization in liquid ammonia, in which ammonia acts both as a reaction medium and as a catalyst. Ammonia is one of the major products in the chemical industry; its annual global production exceeds 180 million tons. It is primarily used to produce nitrogen fertilizers (ammonium nitrate and sulfate, carbamide), explosives, polymers, nitric acid, and sodium bicarbonate (by the ammonia method) and also in medicine and as a cooling agent (R717) in freezing facilities. Although ammonia is a toxic compound, it is one of the main components of the nitrogen cycle in nature. Nitrogen, in turn, is an inexhaustible source for the production of ammonia, so the use of ammonia in organic and inorganic syntheses is advantageous both from economic and environmental reasons.[32−34]

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Table 1. MMC of End-Capped Polymerization Products 1a−j[a]

experiment	reaction time (h)	conversion D_3^{Me2} (%)	mole conversion D_3^{Me2} (mmol)	Mp (kDa)	Mw (kDa)	Mn (kDa)	Mn_{NMR}	PDI
1a	4	30	1.35	5.2	5.3	4.8	3.4	1.11
1b	4.5	37	1.66	6.1	6.0	5.5	3.6	1.10
1c	5	37	1.66	6.5	6.7	6.0	4.2	1.11
1d	5.5	40	1.80	7.2	7.2	6.3	4.5	1.12
1e	7	45	2.02	7.3	7.3	6.5	4.3	1.11
1f	8	54	2.43	7.5	7.4	6.6	4.2	1.11
1g	16	57	2.56	9.6	9.7	8.8	6.6	1.09
1h	20	68	3.06	10.3	10.4	9.4	6.9	1.10
1i	24	79	3.55	10.7	10.7	9.7	6.9	1.09
1j	48	96	4.32	10.9	11.1	9.9	7.5	1.11

[a]Reaction conditions: 30 °C, 1 g (4.5 mmol) of D_3^{Me2}, 2 μL (0.11 mmol) of H_2O, 5 g of NH_3.

Liquid ammonia is a useful solvent for many organic and inorganic compounds and therefore is a promising medium for chemical reactions.

Previously, we demonstrated the effectiveness of a similar approach to the condensation of phenylsilanols.[35−37] Here, we report our research on water-initiated anionic polymerization of hexamethylcyclotrisiloxane (D_3^{Me2}).

2. RESULTS AND DISCUSSION

Polymerization of D_3^{Me2} was carried out in a stirred high-pressure reactor with a 20 mL working volume (Figure 1a). The reaction temperature was varied from 30 to 100 °C. The reactor was charged with the required amounts of D_3^{Me2} and water in the first stage, (1); then, the reactor was cooled to −50 °C, and ammonia was added using a mass flow controller (MFC) (2). Next, the reactor was thermostated at 30 °C in an oil bath (3). Thereafter, the temperature was raised depending on the reaction temperature of choice. Upon completion of the reaction, the reactor was decompressed at room temperature (4), and the target polymer was isolated (5).

The molar mass characteristics (MMC) of the resulting polymers and the degree of D_3^{Me2} conversion rate were determined using SEC after preliminary end-capping of the terminal silanol groups of the polymer with vinyldimethylchlorosilane, as illustrated in Scheme S1.

In addition to SEC, all end-capped polymers were analyzed by ^{1}H and ^{29}Si NMR spectroscopies (Tables S1 and S2 and Figures S1−S28). It is important to note that such low dispersity telechelic polymers could later be successfully modified by hydrothiolation and hydrosilylation reactions. This approach makes it possible to introduce virtually any organic or organoelement moieties therein, *e.g.*, carboranes or other bulky substituents.[38,39] Also, such modification provides tracing the influence of these groups on the properties (rheological and thermal) of the resulting polymer.[40]

To study the polymerization process, it was important to check the solubility of the initial monomer (D_3^{Me2}) in ammonia first. For this purpose, transparent test tubes that can hold a pressure of up to 10 atm were used. Also, this experiment was carried out with thermostating at a temperature of 30 °C (Figure 1b).

Figure 1b shows that the D_3^{Me2} crystals dissolve in ammonia to form a transparent homogeneous solution within 10 min. After the completion of the reaction, the resulting PDMS is clearly visible, segregating into a separate phase.

2.1. Study on the Effect of Various Factors (Temperature, Water and D_3^{Me2} Concentration, and Reaction Time) on D_3^{Me2} Polymerization in Ammonia.

2.1.1. Effect of the Reaction Time. The influence of D_3^{Me2} polymerization time in ammonia on its conversion was studied at 30 °C in steel autoclaves with all other conditions (amounts of water, ammonia, and D_3^{Me2}) being equal. Table 1 and Figure S27 show that almost complete D_3^{Me2} conversion was attained in 48 h.

Figure 2 shows that polymer Mw increases proportionally to the degree of D_3^{Me2} conversion up to a certain time.

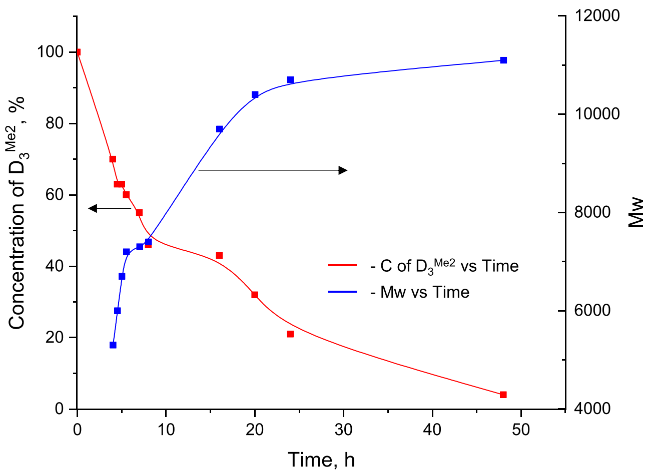

Figure 2. Degree of D_3^{Me2} conversion and Mw of **1a**−**1j** polymers as a function of reaction time.

Polymerization actively occurs during the first 10 h when approximately 50% of D_3^{Me2} is consumed. After 10−15 h of the reaction, the monomer consumption rate decreases and the growth of Mw also slows down. This is apparently due to the heterogeneous character of the process, which moves from the kinetic region to the diffusion one.

2.1.2. Effect of the Concentration of Reactants. 2.1.2.1. Amount of Water. The effect of the amount of added water on the MMC of polymerization products was studied at 30 °C, a reaction time of 48 h, and equal loadings of D_3^{Me2} and ammonia (1 g (4.5 mmol) of D_3^{Me2}, 5 g of NH_3). The amount of water (2 μL (0.11 mmol) of H_2O) used in the experiments on varying the reaction time was taken as the reference point. We assume that water is the initiator of D_3^{Me2} polymerization in this process. Consequently, the effect of its amount on the MMC should be similar to the action of the initiator in the classic anionic ROP initiated with *n*-butyllithium.[41−44] The results are presented in Table 2 and in Figure S29.

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Table 2. MMC of Polymerization Products 2a−4d[a]

experiment	amount of water: H_2O (μL)	amount of water: H_2O (mmol)	polymer:cycle ratio	Mn (kDa)	Mn_{NMR}	Mn_{LWF} (kDa)	PDI
1j	2	0.11	96:4	9.9	7.5		1.11
2a	5	0.28	92:8	5.7	3.8		1.13
2b	10	0.56	92:8	5.1	3.2		1.13
2c	20	1.1	77:23	4.1	2.5	1.0	1.13
2d	40	2.2	67:33	3.2	3.0	1.1	1.14
2e	60	3.3	63:37	3.1	2.3	1.1	1.13
2f	1000	56	51:49	1.4	0.9	0.6	1.11

experiment	amount of ammonia: NH_3 (g)	amount of ammonia: NH_3 (g/mL)	polymer:cycle ratio	Mn (kDa)	Mw (kDa)	PDI
1i	5	0.25	79:21	7.0	7.5	1.22
3a	3	0.15	78:22	9.5	10.7	1.12
3b	1.7	0.085	89:11	10.6	12.0	1.13
3c	1	0.05	88:12	11.2	12.7	1.14
3d	0.75	0.0375	98:2	12.6	20.7	1.65

experiment	reaction time (h)	temperature (°C)	Mn (kDa)	PDI	polymer:cycle ratio (%)	cycle ratio (%): D_3	D_4	D_5	D_6	conversion D_3^{Me2} (%)
1a	4	30	4.8	1.11	30:70	100	0	0	0	30.0
4a	4	60	5.7	1.13	40:60	99.6	0.4	0	0	40.2
4b	4	100	8.1	1.16	60:40	96.5	2.9	0.5	0	61.4
1i	24	30	9.7	1.09	79:21	100	0	0	0	79.0
4c	24	60	7.9	1.17	73:27	69	25	4.0	1	81.1
4d	24	100	11.3	1.45	93:7	13	72	12.0	3	99.1

[a]Reaction conditions: 48 h, 30 °C, 1 g (4.5 mmol) of D_3^{Me2}, 5 g of NH_3; 24 h, 30 °C, 1 g (4.5 mmol) of D_3^{Me2}, 2 μL (0.11 mmol) of H_2O; 1 g (4.5 mmol) of D_3^{Me2}, 2 μL (0.11 mmol) of H_2O, 5 g of NH_3.

Table 2 shows that an increase in the amount of water actually reduces the molar mass of reaction products, which, in turn, also leads to a steady increase in the content of cyclic products.

As can be seen from Figure S29, both octamethylcyclotetrasiloxane (D_4^{Me2}) and larger cycles (D_5^{Me2} and D_6^{Me2}) are formed in the system, and the content of the latter products increases proportionally to the increase in the water amount (Figure S31).

We assume that the growing yield of cyclic products during polymerization caused by an increase in the amount of water in the system is due to the cyclization of low molar mass oligomers at the early growth stages rather than depolymerization, as might be expected. This is evidenced by a low dispersity of linear oligomers and the stability of non-strained siloxane bonds under reaction conditions as it will be shown below in a model experiment (see the Reaction Mechanism and Side Processes section).

To gain a better insight into the ongoing processes, we analyzed the low molar mass fraction formed in the reaction. For this purpose, terminal silanol groups in the polymerization product were end-capped (Table 2; experiment **2f**); then, low molar mass products were isolated at a temperature of 100 °C and a residual pressure of 1 mbar. Two fractions of volatile products were thus obtained. The volatile products and the distillation residue were studied by SEC (Figure S32) and ^{1}H and ^{29}Si NMR (Figures S20−S25). Figure S32 shows SEC curves of the original mixture **2f** (green), first volatile fraction **2f$_1$** (pink), second fraction **2f$_2$** (blue), and distillation residue **2f$_3$** (violet). It was found that the first fraction consists of cyclic compounds D_4^{Me2} and D_5^{Me2}, a small amount of D_3^{Me2} that was not involved in the reaction or was newly formed from the corresponding diol, and also 1,3-divyniltetramethyldisiloxane. The latter is formed in the end-capping reaction since vinyldimethylchlorosilane is added in excess. The major component of the second fraction is D_6^{Me2}, but it also contains low molar mass linear oligomers as indicated by NMR data (Figures S22 and S23). The distillation residue comprises linear telechelic PDMS. Thus, the analysis of the composition of the end-capped products confirmed validity of our assumptions about the non-depolymerization origin of cyclic fractions when using a large amount of water.

2.1.2.2. Amount of Ammonia. The effect of the ammonia amount in the reaction medium on the polymerization process was studied at 30 °C with a reaction time of 24 h. The amount of ammonia was varied, whereas all the other conditions were the same (Table 2).

As can be seen from Table 2, when the amount of ammonia is reduced from 5 to 1 g, the molar mass of the resulting polymer increases. This is apparently due to the growing concentration of reactive centers in the reaction medium and, hence, the reaction rate. If the amount of ammonia in the reaction medium decreases further, then the dispersity of the resulting polymer broadens and D_4^{Me2} and D_5^{Me2} appear in the reaction mixture, thus indicating the occurrence of side processes such as homocondensation of terminal silanol groups and depolymerization (Figure 3).

It should be noted that, when reducing the amount of ammonia in the reaction system, the process apparently switches to the homogeneous mode; therefore, the homocondensation reaction occurs more readily. To sum up, the concentration of ammonia is a key factor influencing the process and composition of the products. This effect is most pronounced in the low-concentration region.

2.1.3. Effect of Temperature. Data on the effect of temperature on the polymerization process using the same

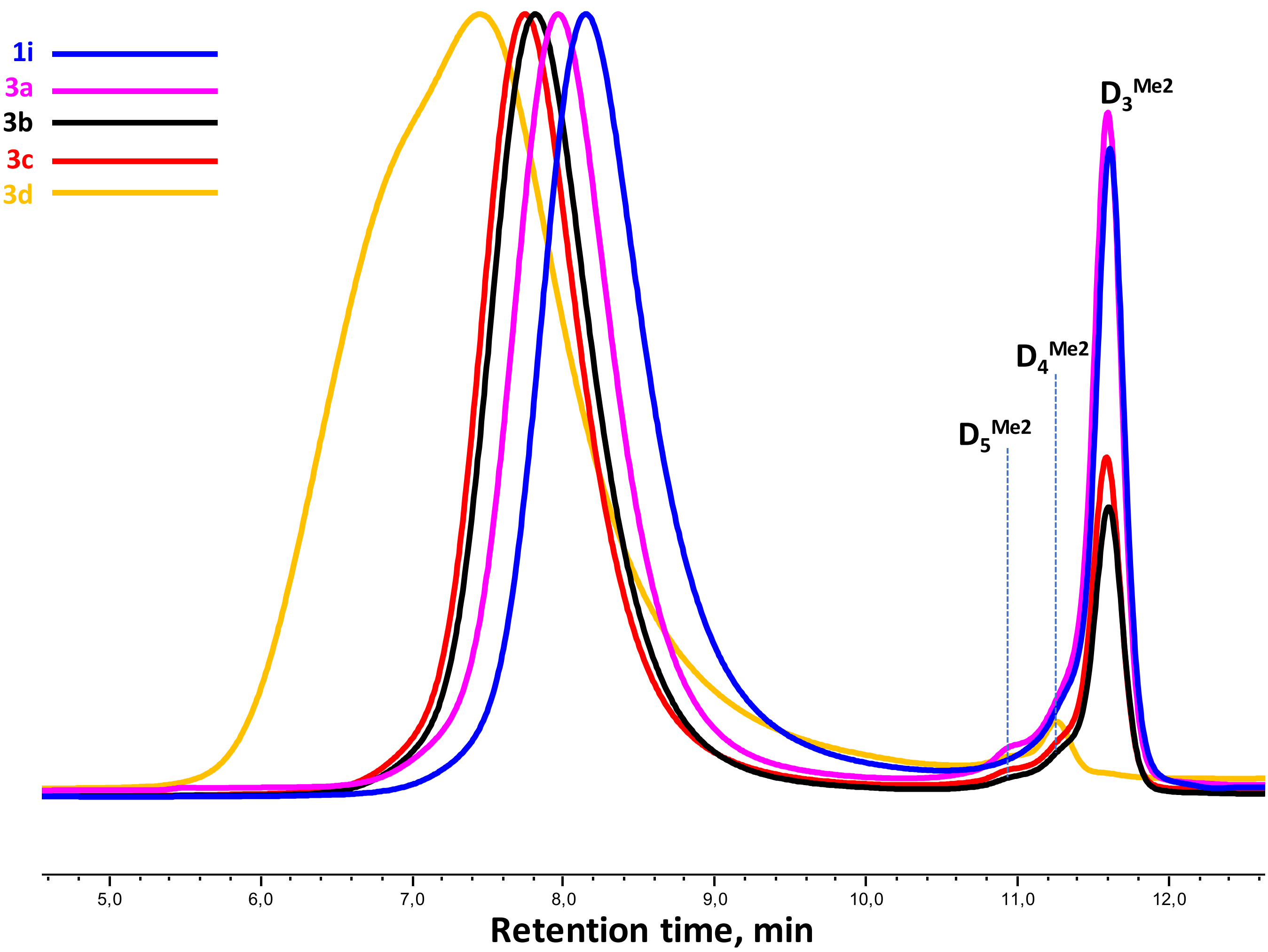

Figure 3. SEC curves of polymerization products **3a**−**3d** after decompression.

initial amounts of D_3^{Me2}, H_2O, and NH_3 and various reaction times (4 and 24 h) are presented in Table 2 and in Figure 4.

As is evident in Figure 4a and Table 2 (experiments **1a**, **4a**, and **4b**), the conversion of D_3^{Me2} for the reaction performed within 4 h in the temperature range of 30−100 °C increases proportionally to the temperature. However, D_4^{Me2} is formed already at 60 °C and D_5^{Me2} at 100 °C. In this case, the polymer dispersity increases insignificantly. With extending the reaction time up to 24 h, the content of cyclic compounds with more than three Si−O increases (Table 2, experiments **1i**, **4c**, and **4d**). This indicates that the side processes of chain transfer and depolymerization occur, *i.e.*, the process becomes equilibrium.

It is also worth noting that the dispersity of polymer obtained at 100 °C for 24 h is bimodal (Figure 4b, curve **4d**), indicating that **PDMS-(OH)$_2$** formed during polymerization undergoes condensation.

The obtained data suggest that D_3^{Me2} polymerization in ammonia at 30 °C is non-equilibrium, and the reaction reaches higher degrees of monomer conversion (96%) in contrast to the standard ROP initiated by butyllithium.[45] With an increase in the reaction temperature, the process becomes equilibrium, which follows from the occurrence of active condensation and depolymerization side processes.

3. REACTION MECHANISM AND SIDE PROCESSES

The body of the data obtained enables one to draw some conclusions about the putative reaction mechanism. It is similar to that reported elsewhere[31] and, more generally, to the mechanism of base-initiated ring-opening polymerization.[46]

Currently, there is no clear evidence of the nature of the active centers that initiate siloxane ring opening. We assume that ammonia reacts with water in the first stage to generate the dissociated $NH_4^+OH^-$ pair (Figure 5a). Its coordination with the oxygen of the D_3^{Me2} siloxane bond results in the cleavage of the siloxane ring to provide a linear trisiloxane active center bearing a silanol group at one end and a complex of NH_3 with the silanol group on the other. Ring cleavage can yield siloxane moieties with smaller dimensions like in the case of ROP initiation by *n*-BuLi.[47] This conclusion is indirectly confirmed by experiments with varied concentrations of ammonia and water. It should be reminded that, at a low concentration of ammonia or a large amount of water, 8- and 10-membered rings are formed. Given the mild reaction conditions (30 °C, 24 h), these rings most probably arise *via* homocondensation of silanol groups. Accordingly, D_4^{Me2} and D_5^{Me2} can only be formed from silanol moieties containing two, three, or four Si−O units. The initiation mechanism will be studied in more detail in the nearest future.

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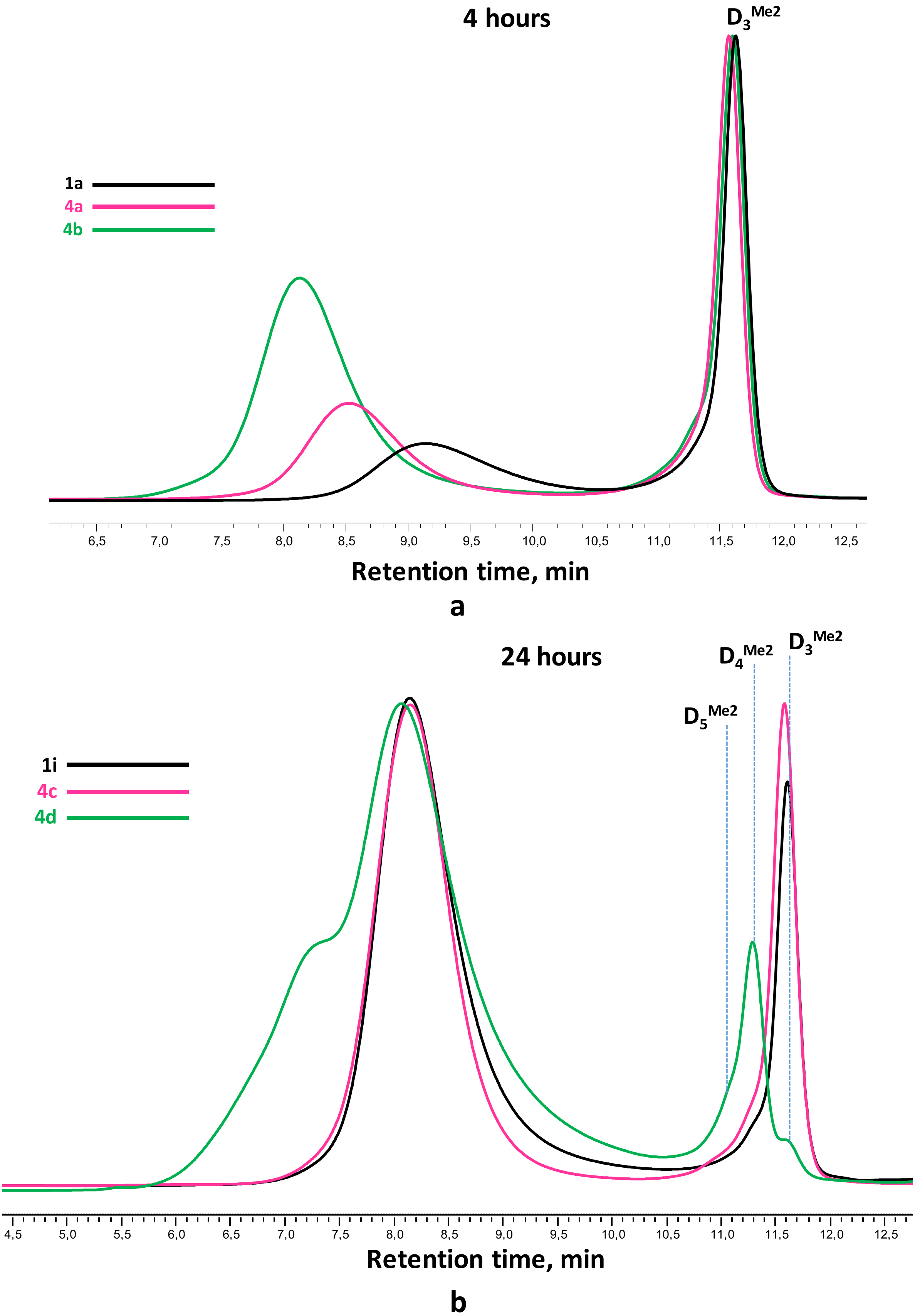

Figure 4. SEC curves of polymerization products **4a**−**4d** after decompression for reaction times of 4 (a) and 24 (b) h.

To find out whether ammonia can cleave the siloxane bond in the presence of water under the experimental conditions, we carried out an experiment with **PDMS-($OSiMe_2Vin$)$_2$**. In this system, an active center with terminal OH groups cannot be

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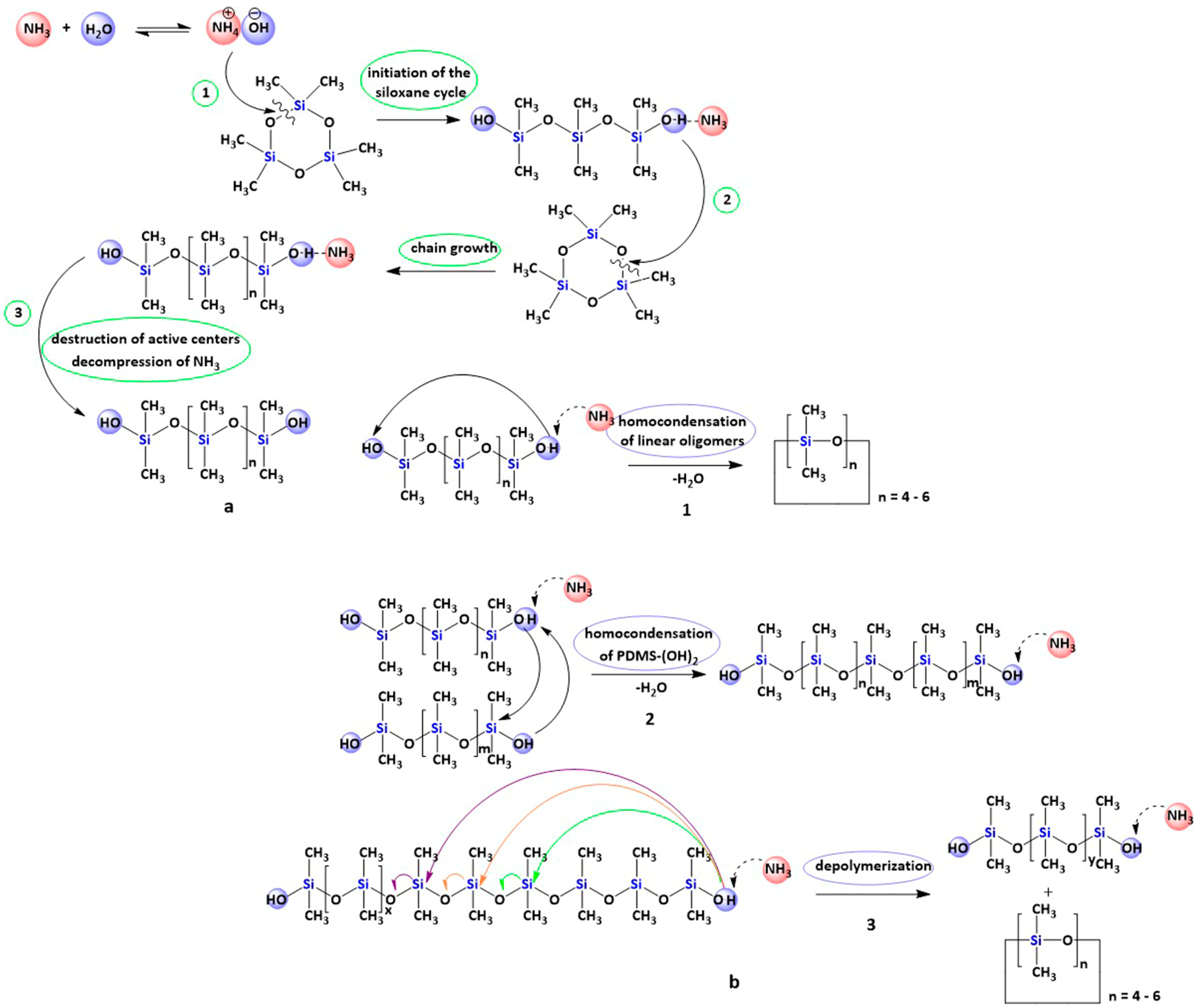

Figure 5. (a) Scheme of D_3^{Me2} polymerization in ammonia medium; (b) schemes of side reactions: homocondensation of linear oligomers (**1**), homocondensation of **PDMS-(OH)$_2$** (**2**), and depolymerization (**3**).

formed without cleavage of the siloxane bond. Since D_3^{Me2} is much more prone to the ring-opening cleavage than the non-strained Si−O−Si bond in **PDMS-(OSiMe$_2$Vin)$_2$**, $NH_4^+OH^-$ can cleave siloxane bonds in D_3^{Me2} but not in **PDMS-(OSiMe$_2$Vin)$_2$**. This experiment revealed that there is no reaction at 30 °C within 24 h, as is evident from the SEC curves (Figure S33). It is obvious that the MMC of the polymer before (blue curve) and after (pink curve) the experiment are identical. After that, we tested the stability of the siloxane bond in ammonia at elevated temperatures (Figure 6a).

The figure shows that an increase in temperature to 100 °C causes minor changes in the MMC of the original **PDMS-(OSiMe$_2$Vin)$_2$**. A slight dispersity broadening is observed; less than 2% of D_4^{Me2} and D_5^{Me2} cyclic compounds are formed (Figure S34). The situation changes dramatically when raising the temperature to 150 °C. The value of the molar mass of products decreases from 8.0 to 4.0 kDa; the dispersity significantly broadens (PDI of 1.54). The formation of cyclic compounds becomes considerable (40%). These data indicate that depolymerization proceeds actively at temperatures above 100 °C. An equilibrium between linear and cyclic products is established in the system.

The next experiment was carried out with **PDMS-(OH)$_2$** at 30 °C and adding the same amount of water as in experiment **2f** (Figure 6b). As mentioned above, the ratio of cyclic and linear products in the latter experiment was approximately 50/50.

Figure 6b shows that, by carrying out the reaction in a NH_3/H_2O mixture, a high molar mass (MM) shoulder is observed for the starting **PDMS-(OH)$_2$**. The MM of the shoulder is 2 times higher than that of the initial polymer, which could indicate the dimerization of **PDMS-(OH)$_2$** through homofunctional condensation. Also, as can be seen from Figure 6b, D_4^{Me2} appears in the system due to depolymerization. Obviously, the formation of cyclic products in this case is only possible with the involvement of an active center, which is a complex of NH_3 with the silanol group. However, the amount of D_4^{Me2} does not exceed 2%, which supports the idea of a non-depolymerization mechanism for the formation of cyclic compounds upon D_3^{Me2} polymerization in the presence of a large amount of water.

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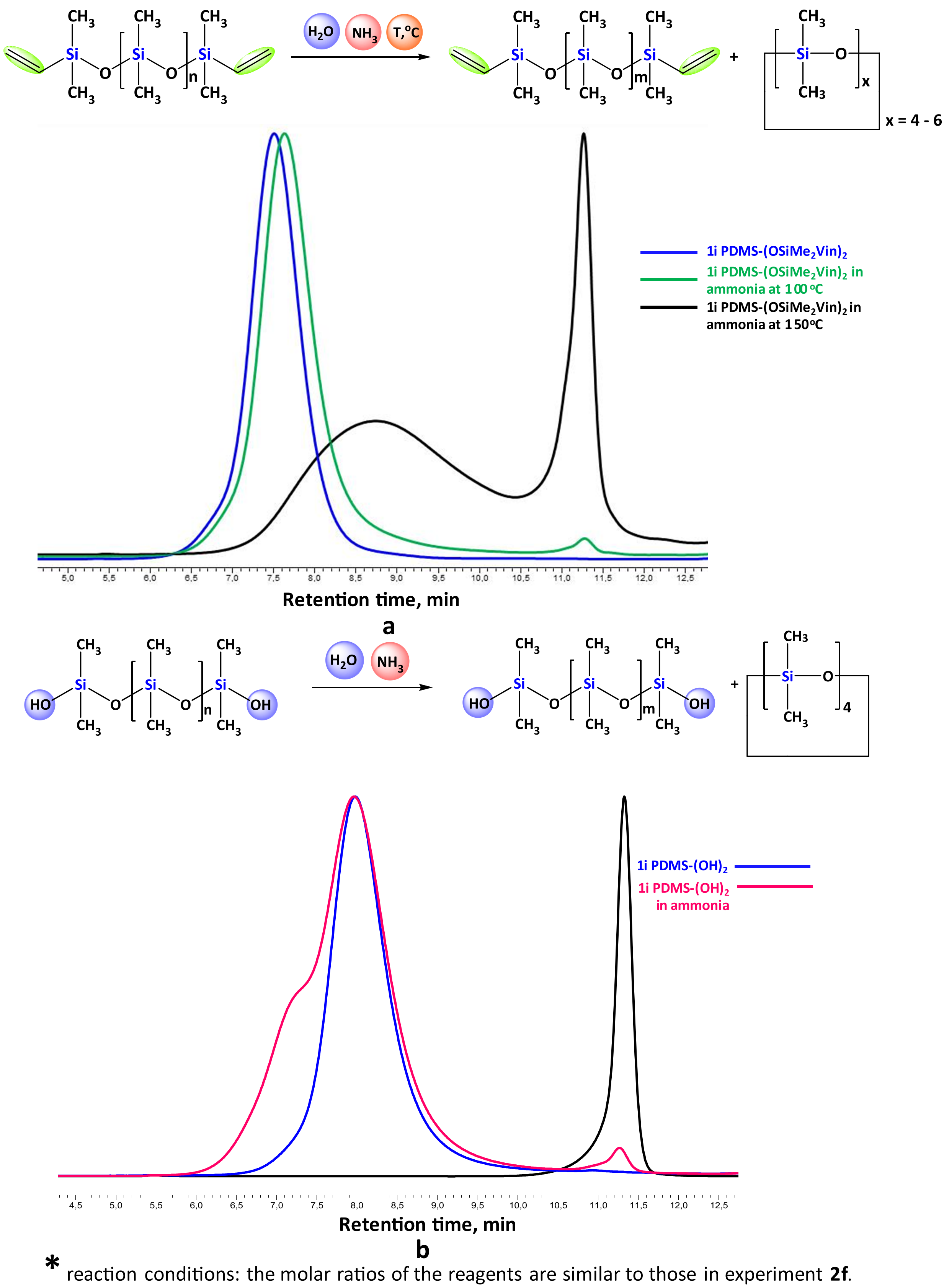

Figure 6. (a) SEC curves of the original **1i PDMS-(OSiMe$_2$Vin)$_2$** polymer (blue curve), at 100 °C (green curve), and 150 °C (black curve); (b) SEC curves of the **1i PDMS-(OH)$_2$** polymer before (blue curve) and after (pink curve) the experiment.

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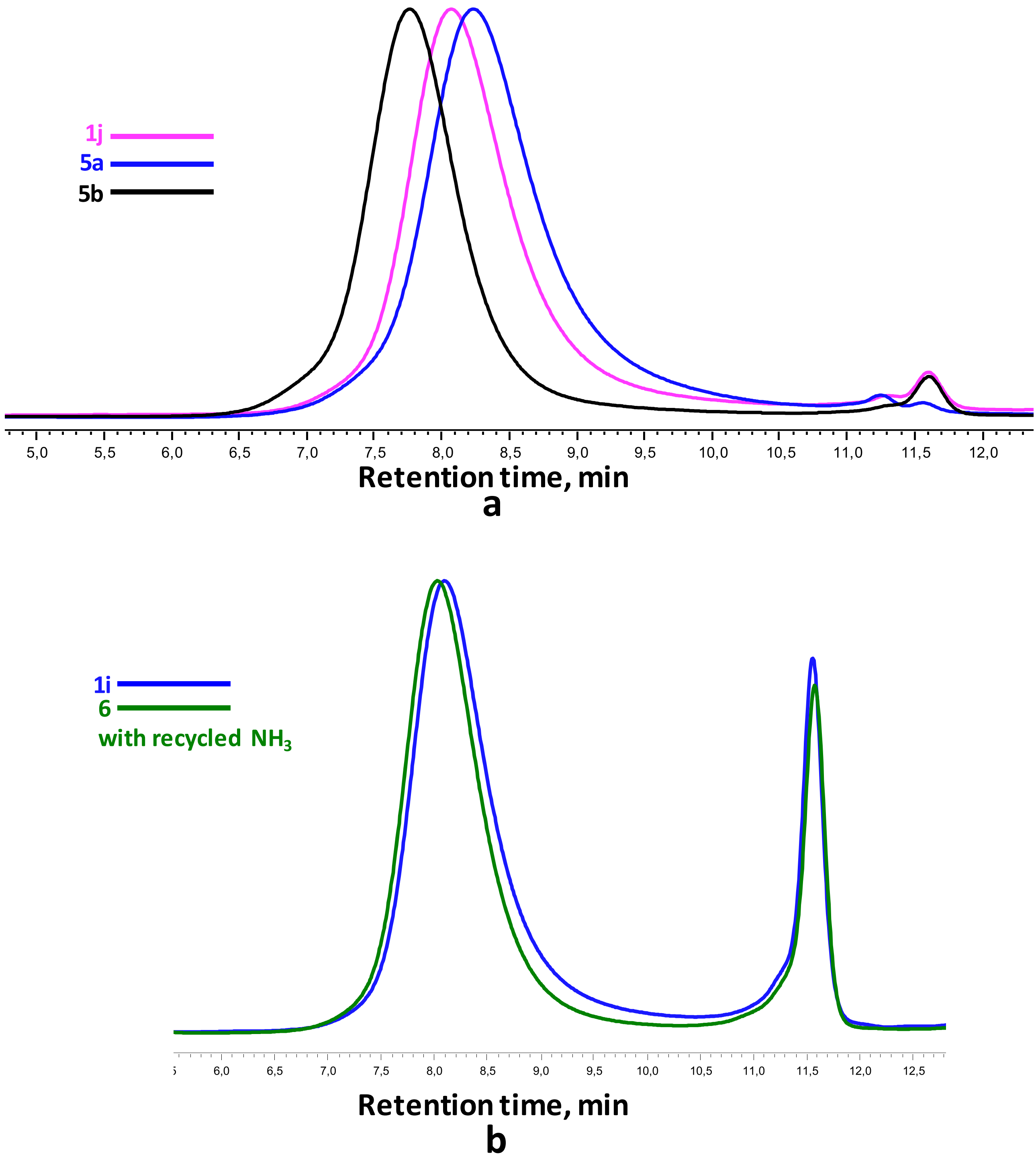

Figure 7. (a) SEC curves of **1j** and **5a**−**5b** polymers after decompression; (b) SEC curves of polymers **1i** and **6** after decompression obtained under standard conditions and with recycled ammonia, respectively.

Therefore, during the polymerization of D_3^{Me2} at 30 °C, side processes are only possible with participation of active centers, which are complexes of NH_3 with silanol groups.

According to the proposed reaction mechanism, the chain growth occurs *via* the reaction of active centers with the siloxane cycle. After the reaction is completed and ammonia is decompressed, the active centers decompose. The resulting polymeric product is a telechelic polydimethylsiloxane bearing terminal silanol groups (see Figure 5a).

Moreover, a number of side reactions can occur to a different extent, depending on the reaction conditions. These reactions include homocondensation of linear dimethylsiloxanes to give cyclic products (Figure 5b (1)), condensation of terminal silanol groups into **PDMS-(OH)$_2$** (Figure 5b (2)), and depolymerization furnishing siloxane rings of various sizes (Figure 5b (3)).

Nevertheless, the obtained experimental data indicates that, by choosing optimal conditions for D_3^{Me2} polymerization in

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ACS Appl. Polym. Mater. XXXX, XXX, XXX−XXX

Table 3. MMC of Polymerization Products 5a–6[a]

experiment	D_3^{Me2} (g)	D_3^{Me2} (mmol)	H_2O (μL)	H_2O (mmol)	NH_3 (g)	D_3^{Me2} conversion (%)	Mw (kDa)	Mn (kDa)	PDI
1j	1	4.5	2	0.11	5	96	8.8	7.0	1.25
5a	4.25	19	8.5	0.47	21.25	98	8.1	6.2	1.31
5b	10	45	20	1.1	21.25	97	12.9	11.3	1.15

experiment	D_3^{Me2} conversion (%)	Mw (kDa)	Mn (kDa)	Mn_{NMR}	PDI
1i	79	10.7	9.7	6.9	1.09
6	80	12.0	11.0	6.8	1.09

[a]Reaction conditions: 48 h, 30 °C; 24 h, 30 °C, 2 μL (0.11 mmol) of H_2O, 1 g (4.5 mmol) of D_3^{Me2}.

ammonia medium, side reactions can be prevented almost entirely to provide polymers with narrowly dispersity.

4. PROCESS SCALING AND AMMONIA RECYCLING

4.1. Scaling of the Polymerization Process. An important part of the ongoing research was to assess the potential for industrial application of the proposed method. For this purpose, we scaled up the D_3^{Me2} polymerization process in ammonia. The reaction was carried out in an autoclave with a working volume of 50 mL, equipped with a mechanical stirrer (Figure S35). The amounts of D_3^{Me2}, H_2O, and ammonia were proportionally increased by a factor of 4.25 compared with experiment **1j**. In the next experiment, the D_3^{Me2} amount was increased to 10 g, and the amount of water was increased accordingly. The MMC of the resulting polymers were determined immediately after ammonia decompression, without capping the terminal silanol groups. The results are illustrated in Figure 7a and in Table 3.

It is also worth noting that, in experiment **5b**, a consistent pattern was observed, which had previously been found when studying the effect of the ammonia concentration, namely, the growth of the NH_3/D_3^{Me2} ratio with an increase in the MM of the products.

4.2. Ammonia Recycling. It was essential to show that ammonia used in the polymerization reaction can be reused in subsequent syntheses. For this purpose, D_3^{Me2} was polymerized for 48 h until its complete conversion to prevent the unreacted D_3^{Me2}, soluble in ammonia, from entering the next reaction medium. Then, ammonia was pumped into an identical reactor containing D_3^{Me2} and water through a drying column (Scheme S2 and Figure S36).

Polymerization using the recycled ammonia was carried out under conditions similar to the standard synthesis **1i** (30 °C, 24 h, 2 μL (0.11 mmol) of H_2O, 1 g (4.5 mmol) of D_3^{Me2}. In this case, it was important to know whether the reaction rates with starting and recycled ammonia would correlate. Therefore, this experiment was carried out until incomplete conversion of the monomer. Figure 7b presents chromatograms of the polymers obtained using "primary" (blue curve, **1i**) and "secondary" (green curve, **6**) ammonia.

In Table 3, MMC of end-capped polymers obtained under standard conditions and with recycled ammonia are given.

The above data show that the MMC of the polymer produced in the recycled ammonia are consistent with those of the polymer obtained under standard conditions. This experiment is a powerful demonstration of the possibility of ammonia recycling, thus confirming that the proposed method is commercially promising in terms of "green" chemistry.

To summarize, the studies described above helped us to determine optimal conditions for polymerization of D_3^{Me2} in ammonia. A high conversion of D_3^{Me2} (1 g, 4.5 mmol) is reached at 30 °C in the presence of 2 μL (0.11 mmol) of H_2O and 5 g of NH_3 within 48 h. Under these conditions, PDMS bearing terminal silanol groups with a Mn of up to 8.0 kDa and PDI of 1.11 are produced, which require no additional purification. This approach to the synthesis of narrowly dispersed polydimethylsiloxane telechelic compounds can be considered as wasteless and meets the requirements of "green" chemistry since the ammonia used in it can be recycled.

5. CONCLUSIONS

An environmentally friendly procedure to obtain narrowly dispersed telechelic polydimethylsiloxanes has been developed. Polymers can be formed requiring no additional stages of purification and separation to provide a virtually complete conversion of the cyclic monomer due to the use of ammonia as a reaction medium. This cannot be achieved by the classical anionic ROP method. We have shown that the present process can be scaled up, and ammonia can be recycled, thus demonstrating the potential of our method for commercial application.

The results obtained indicate the promise of using liquefied gases as active media for implementation of commercial technologies of silicon production, which not only simplify the synthesis and the control over molar mass characteristics but also provide great opportunities for further development of the suggested approach. Here, we used D_3^{Me2} as a model starting cyclosiloxane; in the follow-up studies, we will consider other, more readily available reagents and their mixtures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.2c00669.

Descriptions of the experimental synthesis technique, NMR spectroscopy data, size exclusion chromatography data, and photos of experimental setups (PDF)

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Notes

The authors declare no competing financial interest.

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