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TBD-catalyzed anionic ring-opening polymerization of hexamethylcyclotrisiloxane: a new route for controlled synthesis of PDMS

Alice Corfa, Sylvain Caillol, Julien Pinaud*, Vincent Ladmiral*

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Abstract

Controlled anionic ring opening polymerization of hexamethylcyclotrisiloxane (D_3) was optimized for commercial and easy to use organic catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) using various types of initiators. Alcohols and silanols were compared for the synthesis of monofunctional and telechelic PDMS. Polymerizations were monitored by ^1H NMR spectroscopy, MALDI-TOF mass spectroscopy and SEC in order to compare the effects of the initiator structure and of the catalyst concentration. TBD was shown to control the AROP of D_3 when using silanols as initiator, thus affording well-defined PDMS structures. When alcohols were used as initiators, the polymerization proceeded with lower level of control due to slower initiation. These differences in initiation rates likely originate from the differences in pKa between silanols and alcohols.

Introduction

Polydimethylsiloxanes (PDMS) are high performance industrial polymers ubiquitous in our daily life, from cosmetics to construction materials.¹ They have unique properties (mechanical, resistance to ageing and hydrophobicity) that make them irreplaceable in many applications. They also exhibit specific properties such as flame retardancy, chemical inertness, exceptional flow properties and very low T_g due to their siloxane backbone.¹ Depending on the application, different topologies and molar masses are targeted. Industrially, PDMS is provided as oligomeric cyclic siloxanes for use as lubricants, as network for coating resins, or as cross-linked material for sealing elastomers or molds.^{1,2} The properties and behavior of the final material are directly related to the topology, molar mass, and chain-ends structure. Consequently, finding synthesis pathways leading to PDMS with controlled molar masses and structures is of high interest. The most common synthetic route to PDMS is the anionic ring opening polymerization (AROP) of hexamethylcyclotrisiloxane (D_3) or octamethylcyclotetrasiloxane (D_4). The polymerizations of D_3 and D_4 proceeds very differently due to the higher ring tension in D_3 than in D_4 .³ D_3 is less thermodynamically stable and rapidly opens to produce linear polysiloxanes via kinetically controlled AROP. However, the ROP of cyclosiloxanes is an equilibrated polymerization, and depolymerization (back-biting, Scheme 2) is driven by the formation of stable macrocycles. The polymerization of D_3 should thus be stopped at the highest D_3 conversion value. Under kinetic control, the polymerization is driven by the fast polymerization rate that allows the polymerization to reach high conversions before any thermodynamic equilibrium takes place. Unlike the aforementioned AROP, equilibrium polymerization of D_4 is carried out under thermodynamical condition due to the low ring tension of D_4 .⁴ In this case, propagation and back-biting are in competition, and the polymerization reaches a thermodynamic equilibrium driven by the temperature, the monomer concentration and the nature of the catalyst/initiator used.^{5,6} Usually, the AROP of D_4 is performed in bulk at relatively high temperature whereas D_3 can easily be polymerized at room temperature in solution.⁶ The formation of cyclic compound occurs *via* the back-biting reaction, and cyclic compounds D_x ($x=4, 5, \text{ or } 6$, mostly) are formed.⁷⁻⁹

AROP of cyclosiloxanes can be performed using different types of initiators or catalysts but the method mainly adopted by industry so far is the use of alkali hydroxide like KOH where HO^- initiates the polymerization and K^+ catalyzes the propagation. However, the AROP of cyclosiloxanes suffers from back-biting reaction that limits polymer chain length and results in the formation of undesired macrocycles that must be separated from the desired PDMS product. The counter cation has proven to have a strong effect on the back-biting and polymerization rates. The rate of polymerization increases strongly in the series $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{N}(\text{Et})_4^+$ with almost no macrocycles formed with the ammonium counter cation.⁶ This phenomenon hinted at the advantages of organic compounds for the synthesis of PDMS.

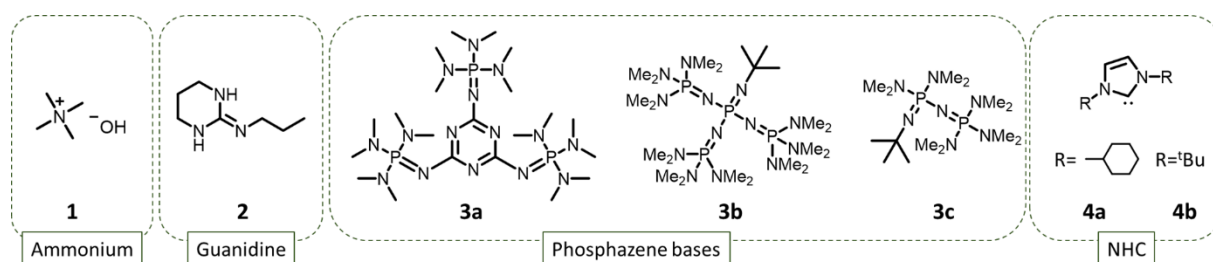
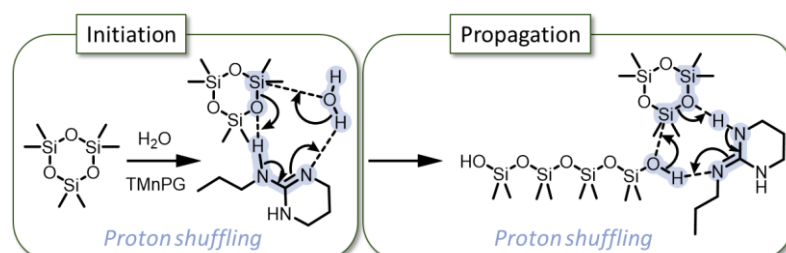


Figure 1. Organocatalysts used for the AROP of D_3 .

In the early 90's, phosphazene bases were found very effective for the organocatalytic ROP of cyclosiloxanes such as D_4 .¹⁰⁻¹² In 2022, Shi *et al.* focused on the use of the highly basic ($\text{pK}_b=33.3$) trisphosphazene catalysts 3a in Figure 1 for the polymerization of D_3 initiated by benzyl alcohol,¹³ and were able to produce PDMS ranging from 3 to 16 $\text{kg}\cdot\text{mol}^{-1}$. *N*-heterocyclic carbenes (NHC) also exhibit high catalytic activity for the synthesis of PDMS.¹⁴ In 2006, NHC (4a and 4b in Figure 1) were reported for the conversion of D_4 into high molar masses PDMS ($M_n = 100\text{-}200 \text{ kg}\cdot\text{mol}^{-1}$), albeit with relatively high dispersity (around 1.6).¹⁴ However, in 2023, NHC were shown to promote the ROP of D_4 without producing cyclic oligomers.⁴ Phosphazenes and NHCs are very efficient catalysts providing very high polymerization rate of D_3 and D_4 due to their high catalytic activity and high pK_b . However, this high catalytic activity also leads to stability issues of the catalyst that can easily react with air moisture or CO_2 .¹⁵

Guanidines were also proven very efficient catalysts for the synthesis of PDMS from D_3 .¹⁶⁻¹⁸ In 2018, Fuchise *et al.* published an important work on the scope of organocatalysts able to polymerize cyclosiloxane monomers, and showed that initiation by water could be used to produce telechelic PDMS via ROP even with non-distilled solvents.¹⁶ In the case of lactones, guanidine-based catalysts are known to have two activation modes: chain-end activation of the hydroxyl group or monomer activation of the $\text{C}=\text{O}$ of the ester.¹⁹ In the guanidine-catalyzed mechanism, initiation and propagation steps occur via chain end activation with a proton shuffle as shown in Scheme 1. In 2020, Fuchise *et al.* optimized the conditions of the AROP of D_3 catalyzed by 1,3-trimethylene-2-*n*-propylguanidine (TMnPG) or 1,3-trimethylene-2-ethylguanidine (TMEG), and initiated by water and silanols.¹⁷ Moreover, they demonstrated that organocatalysis with guanidines is a suitable method for the polymerization of many cyclosiloxanes, allowing the preparation of telechelic or monofunctional polymers.

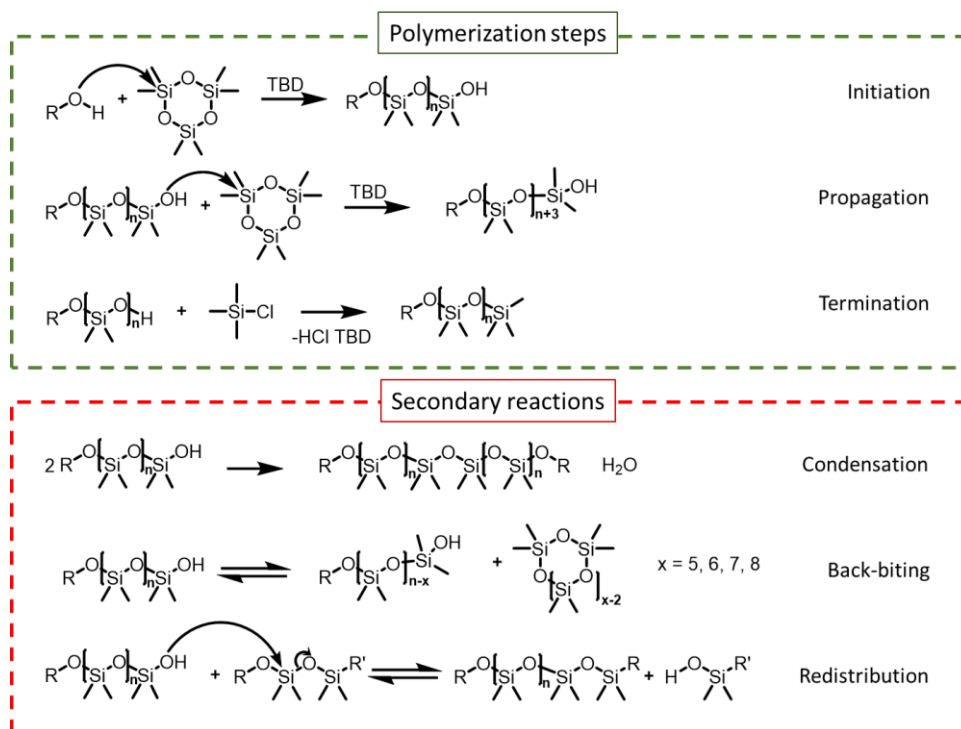


These previous reports open the way to the preparation of various types of polysiloxanes, which is a key issue for the production of polymers endowed with superior properties. In addition, organocatalysis appears as a valuable alternative to usual AROP as it can proceed at ambient temperature, with relatively short reaction times and easy handling of reactants. However, it should be noted that this last feature is not achieved when using NHC or phosphazene bases because of their strong basicity and reactivity. The guanidine-based organic catalysts recently studied for the ROP of D₃ or D₄ are not commercially available and require rigorous purification steps. It would thus be more convenient to turn towards less reactive and commercially available organic catalysts.

The present work thus aims at studying and optimizing the AROP of D₃ catalyzed by a stable and readily commercially available catalyst: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). TBD has proven to be a very efficient catalyst for many types of reactions, among which the ring opening polymerizations of lactones or cyclic carbonates.²⁰ As a guanidine-based catalyst, TBD can undergo monomer activation and chain end activation mechanisms for lactones. However, in the case of cyclosiloxanes, TBD is expected not to be nucleophilic enough to perform a nucleophilic attack upon the silicon atom. As a commercial and stable catalyst, it appears as a potentially viable alternative for the AROP of cyclosiloxanes. The present work reports kinetic studies of the ROP of D₃ using TBD as catalyst with different types of initiators as shown in Scheme 3. It highlights the influence of the pK_a and structure of the initiator on the kinetics of the AROP of D₃. Finally, it demonstrates the potential of TBD as catalyst for the synthesis of PDMS with molar masses up to 35,000 g·mol⁻¹ and low dispersities.

Results and discussion

The organocatalyzed AROP of D₃ proceeds *via* three steps: initiation, propagation and termination. In parallel, side reactions such as condensation, redistribution or back-biting shown in Scheme 2 can take place depending on the reaction temperature and catalyst structure and concentration. Initiation is usually achieved by hydroxyl group-containing molecules such as water, alcohol, or silanol when activated by basic catalysts. Controlled AROP is characterized by low dispersities, first order kinetics behavior, and linear evolution of molar mass with monomer conversion. These are the consequence of a fast initiation compared to propagation and the absence of any chain termination, implying that all the chains start and grow at the same pace.²¹

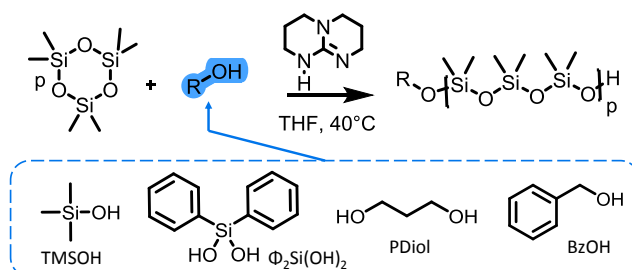


Scheme 2. Polymerization steps and side reactions occurring during ring opening polymerization (ROP) of hexamethylcyclorosiloxane using different types of initiators and TBD as catalyst.^{6,16}

In our study, silanols and alcohols initiators were thus compared to investigate the impact of their structure on the initiation step. We also examined the efficiency of TBD as an organocatalyst for the AROP of cyclorosiloxanes. Both difunctional (diphenylsilanediol and propanediol) and monofunctional (trimethylsilanol and benzyl alcohol) initiators (Scheme 1) were employed to determine the best TBD-catalyzed AROP conditions combining easy setup and high control ($\mathcal{D} < 1.15$) of the polymerization.

As mentioned previously, PDMS can be synthesized with various topologies depending on the target application. For many industrial uses, PDMS with high molar masses are needed to achieve desired mechanical properties. In consequence we attempted to optimize the experimental conditions, to produce PDMS with molar masses up to $50,000 \text{ g}\cdot\text{mol}^{-1}$.

Characteristics of polymerization



Scheme 3. Ring opening polymerization (ROP) of hexamethylcyclorosiloxane using different types of initiators and TBD as catalyst.

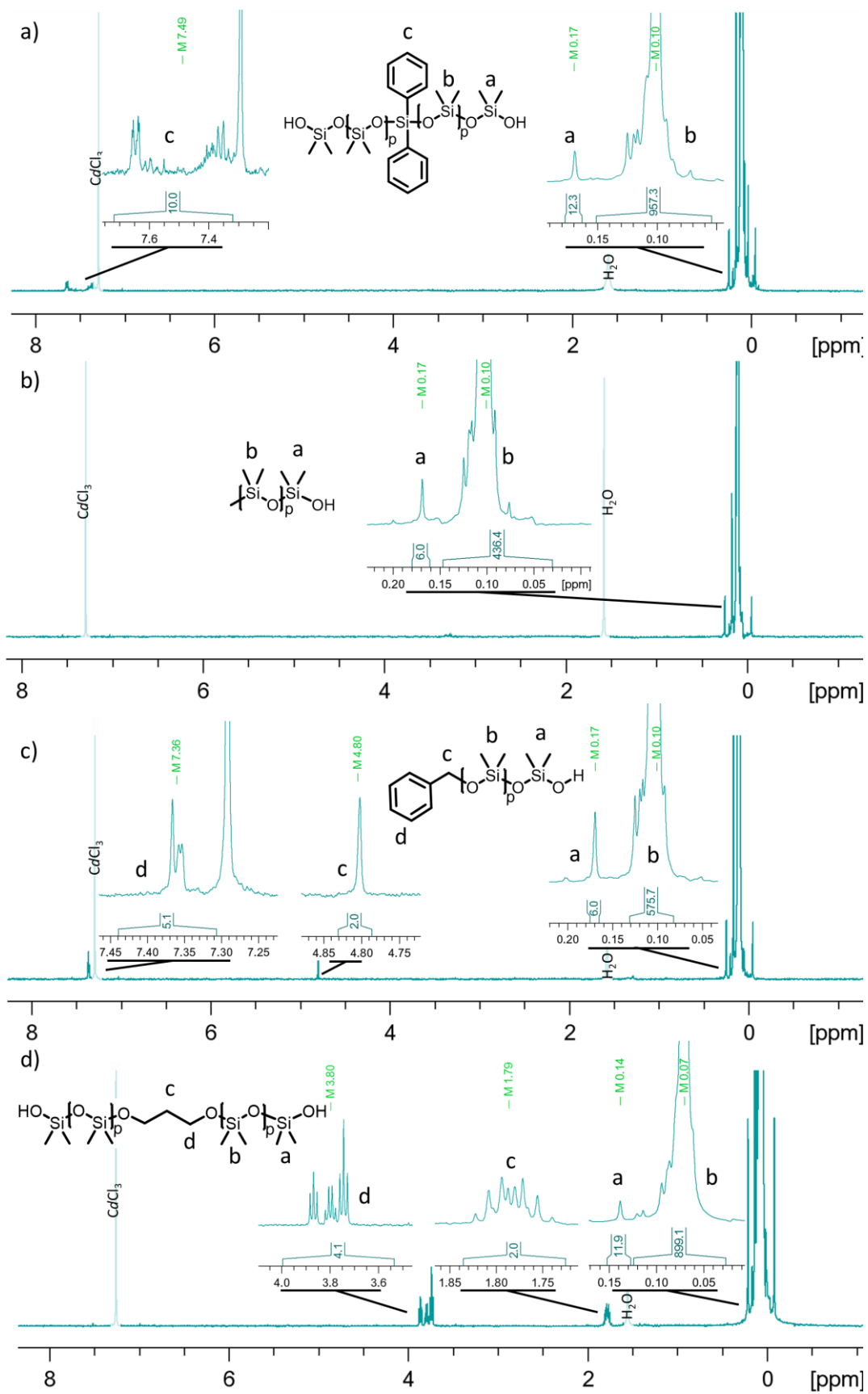


Figure 2. ^1H NMR spectra in CDCl_3 of precipitated PDMS initiated by: a) diphenylsilanediol, b) trimethylsilanol, c) benzyl alcohol, d) propane diol

Table 1. Results of TBD-catalyzed ROP of D_3 initiated by different alcohols and silanols.

Entry	Initiator (I)	$[D_3]_0/[I]_0/[TBD]_0$	$[D_3]_0/[OH]_0/[TBD]_0^a$	Conv (%) ^b	Time (min)	M_n (kg.mol ⁻¹)			\bar{D} ^e	k_{app} (min ⁻¹)
						CALC ^c	NMR ^d	SEC ^e		
1	TMSOH	50/2/0.2	25/1/0.1	97	130	5.5	5.6	5.7	1.16	0.024
2	TMSOH	50/2/1	25/1/0.5	94	25	5.3	5.5	6.6	1.20	0.108
3	BnOH	50/2/0.2	25/1/0.1	95	130	5.4	6.4	5.6	1.34	-
4	BnOH	50/2/1	25/1/0.5	96	33	5.4	7.3	6.9	1.30	-
5	$\Phi_2Si(OH)_2$	50/1/0.2	25/1/0.1	96	90	10.9	10.5	9.7	1.11	0.033
6	$\Phi_2Si(OH)_2$	50/1/1	25/1/0.5	95	18	10.5	12.2	11.0	1.18	0.159
7	PDiol	50/1/0.2	25/1/0.1	99	90	11.0	11.1	9.9	1.27	0.044
8	PDiol	50/1/1	25/1/0.5	95	22	10.5	11.3	12.0	1.30	0.124

^a $[D_3]_0 = 1.8 \text{ mol.L}^{-1}$. ^bCalculated from ¹H NMR normalizing D_3 and PDMS signals to 100. ^c $M_n^{calc} = conv./100 \times \frac{[D_3]_0}{[I]_0} \times M.W(D_3) + M.W.(I)$. ^dCalculated from the ¹H NMR signals of PDMS and of the initiator according to the following equations: for polymers initiated by $\Phi_2Si(OH)_2$, BnOH and PDiol: $M_n^{NMR} = \frac{(I_a + I_b) \times N^I}{I_c \times 6} \times M_{DMS} + M_I$ ($N^{\Phi_2Si(OH)_2} = 10$ and $N^{BnOH} = N^{PDiol} = 2$); and for polymers initiated by TMSOH: $M_n^{NMR} = \frac{I_b}{I_a} \times M_{DMS} + M_I$, ($M_{DMS} = 74.02 \text{ g.mol}^{-1}$, $M_{\Phi_2Si(OH)_2} = 216 \text{ g.mol}^{-1}$, $M_{BnOH} = 108 \text{ g.mol}^{-1}$, $M_{TMSOH} = 90 \text{ g.mol}^{-1}$, $M_{PDiol} = 76 \text{ g.mol}^{-1}$). ^edetermined by SEC in THF (1 ml.min⁻¹) using PMMA calibration.

In a first set of experiments (Entries 1-8, Table 1) TBD was used as organocatalyst for the AROP of D_3 in THF at 40 °C using the conditions depicted in Table 1. Four initiators were tested: benzyl alcohol (BnOH), trimethylsilanol (TMSOH), diphenylsilane diol ($\Phi_2Si(OH)_2$) and propane diol (PDiol). The crude products were precipitated in methanol and dried under high vacuum to give transparent oils. PDMS were obtained with molar masses and conversions ranging between 5,000 and 12,000 g.mol⁻¹ ($1.1 < \bar{D} < 1.3$) and between 95 and 99% respectively, as shown in Table 1. Telechelic PDMS were obtained in similar polymerization times as those reported by Fuchise *et al.* (*i.e.* 117min for $[D_3]_0/[H_2O]_0/[TBD]_0 = 50/1/0.50$). The resulting PDMS were characterized by MALDI-ToF mass spectrometry (Figure 5) and ¹H NMR spectroscopy (Figure 2).

In all ¹H NMR spectra of PDMS samples, dimethylsiloxane units in the PDMS chain exhibit a signal at 0.10 ppm and terminal dimethylsiloxane units are observed at 1.69 ppm. Additionally, for PDMS initiated by BnOH, benzylic chain-end is observed with an aromatic resonance at 7.32 ppm and a methylene signal at 4.70 ppm (Figure 2c), while for PDMS initiated by TMSOH, the TMS chain-end is observed at 0.07 ppm (Figure 2b), for those initiated by $\Phi_2Si(OH)_2$ the diphenyl group exhibits a signal at 7.50 ppm (Figure 2a) and for those initiated by PDiol, the propylene group shows two signals at 3.80 ppm and 1.78 ppm (Figure 2d).

Moreover, for each experiment, aliquots were withdrawn from the reaction media at specific time in the course of the polymerization, quenched with acetic acid and analyzed by ¹H NMR spectroscopy to determine monomer conversion and by steric exclusion chromatography (SEC) in THF to determine the average molar mass (M_n) and dispersity (\bar{D}) of the produced PDMS.

Conversion was calculated from ¹H NMR spectra (Figure S3) using the integration of the signals of D_3 at 0.20 ppm and of PDMS at 0.10 ppm. The signal of D_4 (around 0.15 ppm) resulting from backbiting side reaction (Scheme 1), was not observed for any polymerization at any conversion.

For each polymerization performed with monofunctional and telechelic initiator, pseudo first-order kinetic plots were constructed (Figure 3 and Figure 6). For both silanol and silane diol initiators (entry 1, 2 and 5, 6, Table 1), the pseudo first-order kinetics plots are linear, indicating a good control of the polymerization and allowing to determine k_{app} , the apparent rate of polymerization. k_{app} decreased with increasing $[I]_0/[TBD]_0$ ratio (Table 1, entries 1,2 and 5,6). For PDIol, k_{app} could be determined (0.0444 and 0.1245 min^{-1}) and are comparable to the value determined for silane diol-initiated AROP (0.0332 and 0.1595 min^{-1}). However, BnOH-initiated AROP did not lead to linear 1st order kinetic plot.

The evolution of the average number molar masses and dispersity with conversion were plotted in and Figure 4 and Figure 7 to better understand the kinetics differences between each initiator. PDMS produced by silanol-initiated AROP (entry 1,2 and 5,6, Table 1) display low dispersities ($\mathcal{D} < 1.2$), thus confirming the control of the polymerization. In contrast, PDMS produced by alcohols-initiated AROP (PDIol and BnOH) (entry 3, 4 and 7, 8, Table 1) exhibit higher dispersity ($\mathcal{D} > 1.27$).

In order to better understand the difference between the initiators, a parametric study was undertaken. Firstly, the effect of the difference of pK_a between alcohols and silanols was examined. TMSOH and BnOH were compared to highlight the difference between alcohol and silanol initiated AROP. Secondly, the effect of monofunctional and difunctional initiator was studied.

Influence of the pK_a

Interestingly, the kinetics of the AROP conducted using alcohols as initiators did not follow perfect first-order kinetics. Indeed, when benzyl alcohol was used as initiator (Entries 3-4, Table 1), k_{app} increased during the polymerization, indicating that the concentration of propagating species increased over the course of the polymerization. Nevertheless, at conversion higher than 70%, the k_{app} values of the BnOH-initiated polymerization were close to those of the TMSOH-initiated AROP (Table 1), suggesting that similar concentration of active species was reached in both cases. This may be explained by the slower initiation of BnOH compared to silanol groups caused by the higher pK_a of BnOH ($pK_{a, \text{BnOH}} = 15$, $pK_{a, \text{SiOH}} = 12$). This is confirmed by the evolution of the ^1H NMR spectra of the reaction mixtures for the AROP of D_3 initiated by BnOH (Figure S3a) and TMSOH (Figure S3b) at various reaction times, which show the slow decrease of the signal at 4.64 ppm assigned to $\text{CH}_2\text{-OH}$ in Figure Figure S3a, as opposed to the very fast disappearance of the silanol signal at 0.11 ppm (completely absent after only 2 min) in Figure S3b.

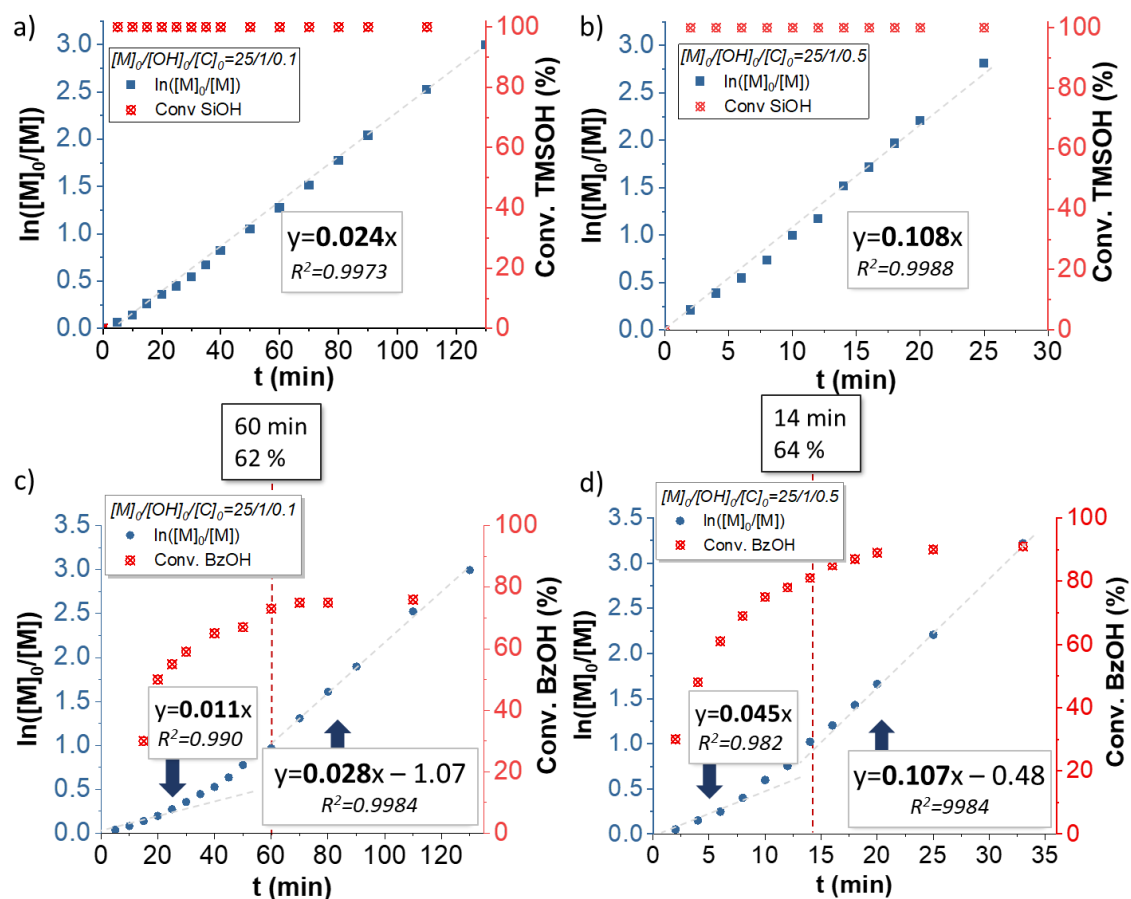
Additionally, the conversion of BnOH reached plateaus of 75% and 90% for $[\text{BnOH}]_0/[\text{TBD}]_0 = 1/0.1 = 10$ and $1/0.5 = 2$ respectively. In both cases the plateau was reached at about 60% conversion of D_3 . These observations indicate that initiation by BnOH occurs throughout the polymerization whereas it is almost instantaneous in the case of TMSOH. Consequently, in the case of initiation using BnOH, active centers are generated all along the polymerization, leading to the increase of k_{app} with time. It is nonetheless important to note that as in the case of AROP initiated with TMSOH, increasing TBD concentration leads to faster initiation with BnOH.

As expected, this slower initiation rates directly translates into PDMS with higher dispersities, although this effect is particularly pronounced in the early stages of polymerization ($\mathcal{D} = 1.8$ after 10 min vs $\mathcal{D} = 1.2$ after 40 min of reaction (Figure 4a). Moreover, for a similar conversion, the M_n values of the BnOH-initiated PDMS are higher than those of the silanol-initiated PDMS (Figure 4).

Decreasing the $[\text{BnOH}]_0/[\text{TBD}]_0$ ratio from 10 to 2 resulted in a faster initiation and thus in the production of PDMS with lower dispersity in the early stages of polymerization (Figure 4a). However, decreasing this ratio also promotes condensation reactions at lower monomer conversion (around

80%). This cannot be observed unambiguously on the AROP initiated by monofunctional initiators but is clear on the experiments carried out with difunctional ones (vide infra).

To sum-up, because of the similar nature and pK_a to the propagating chain ends, silanols are more efficient initiators than primary aliphatic alcohol for the AROP of D_3 using TBD as catalyst. Nevertheless, the variety of alcohol initiators offers the opportunity to design PDMS with specific functionalities. As such, when employing slower initiator such as aliphatic alcohols, higher catalyst/initiator ratios should be employed although high monomer conversion should not be reached to minimize the extent of side reactions such as condensation and potentially chain



scrambling.

Figure 3. Kinetic plot of the AROP of D_3 for: a) Entry 5 ; b) Entry 6 ; c) Entry 7 ; d) Entry 8.

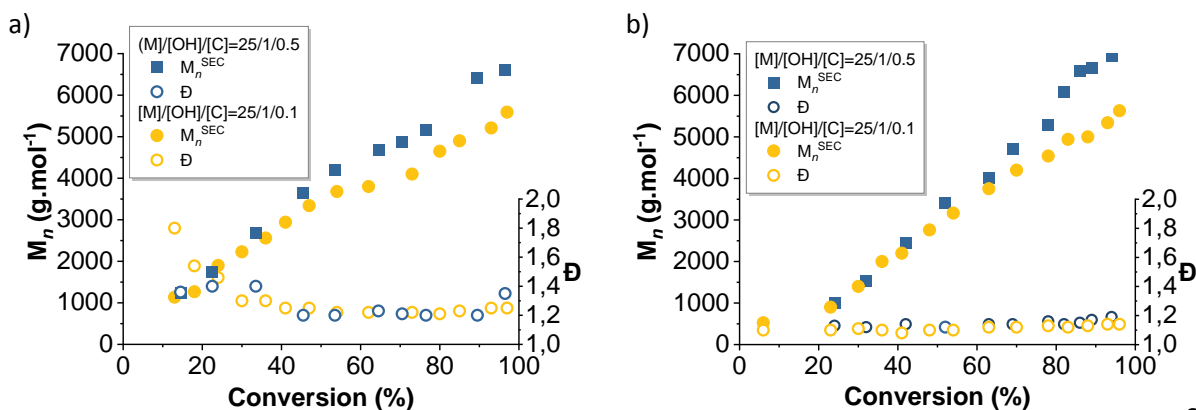


Figure 4. Evolution of number average molecular weight and dispersity with conversion of D_3 initiated with a) BnOH b) TMSOH.

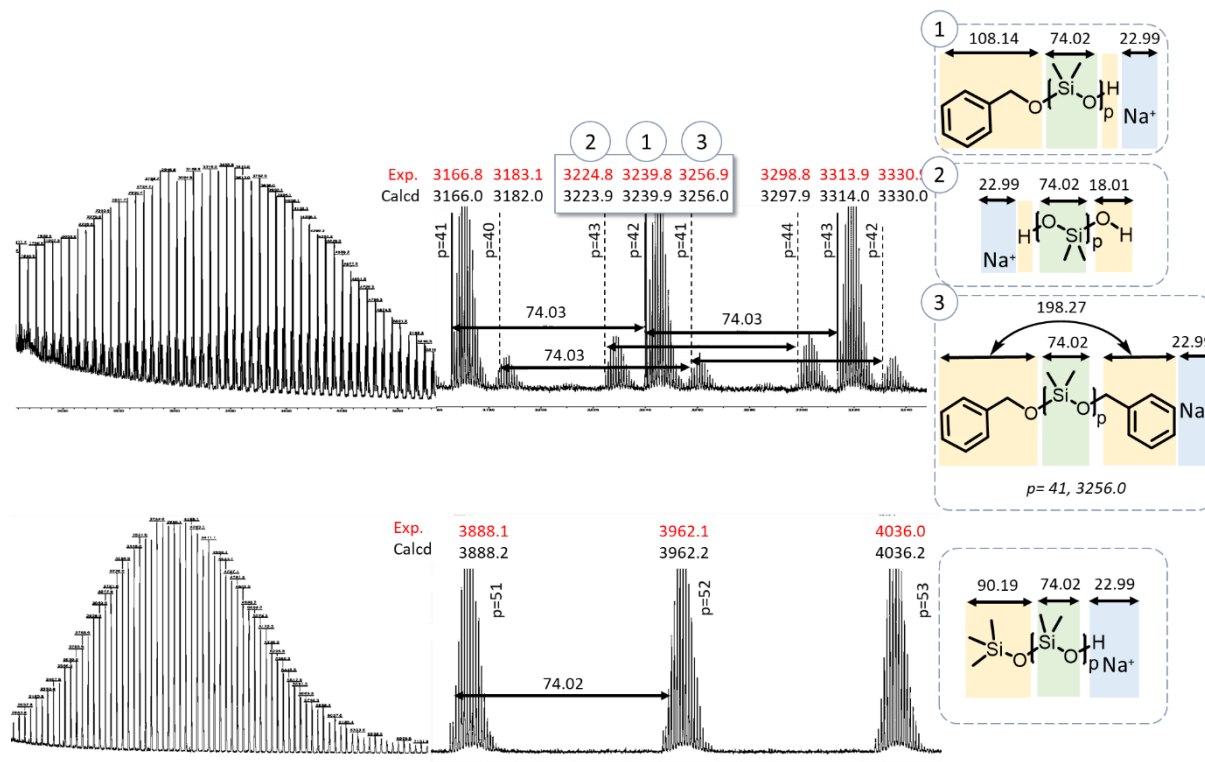
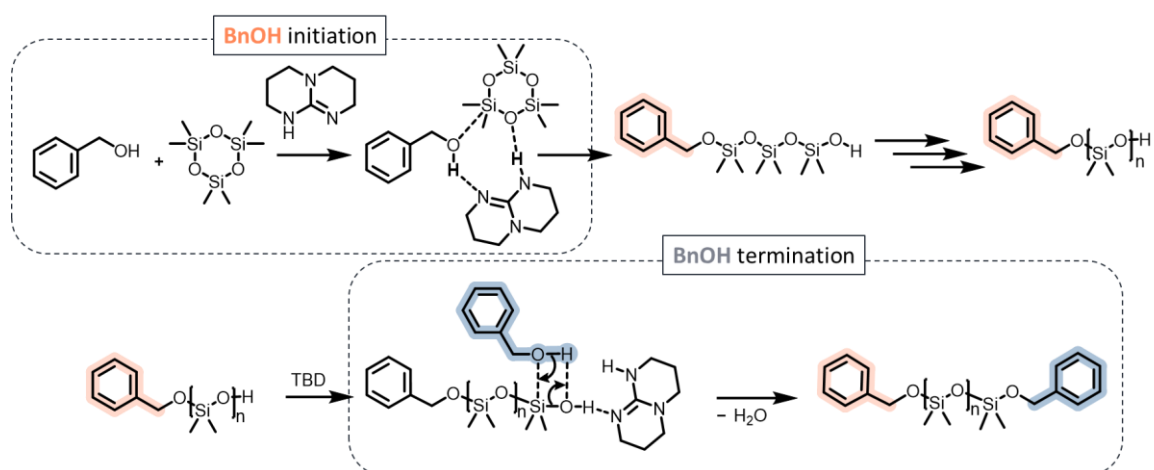


Figure 5. MALDI-TOF mass spectra of precipitated PDMS initiated by benzyl alcohol (top) and trimethyl silanol (bottom).

The MALDI-ToF spectra of PDMS initiated by TMSOH or BnOH allow to determine more precisely the structure of the polymers (Figure 5). The spectrum of the TMSOH-initiated PDMS (Figure 5, bottom) exhibits a main peak at $m/z = 3,966 \text{ g.mol}^{-1}$, which corresponds to about 52 DMS units, and translates into an average degree of polymerization of 17. The BnOH-initiated PDMS spectrum (Figure 5, top) shows a main population at $m/z = 3,239 \text{ g.mol}^{-1}$ (ca. 42 DMS units, average degree of polymerization of 14). The spectrum exhibits two secondary distributions corresponding to telechelic PDMS with silanol end-groups (distribution 2, in Figure 5), and to α,ω -dibenzyl-PDMS (distribution 3). The small population 3 is ascribed to telechelic BnOH-capped PDMS likely formed by termination of the growing chain with excess BnOH as shown in Scheme 4, or by condensation reaction (Scheme 2).

MALDI-ToF spectrum shown in Figure 5 corresponds to a PDMS sample taken at the early stages of polymerization (low conversions), when condensation reactions are minimal (vide infra). The hypothesis of termination by excess BnOH thus seems more probable. Indeed, the slow initiation leads to significant residual quantity of BnOH (33% free BnOH after 50 min and 50% conversion of D_3) available for such chain termination reaction. In Figure S5 and S7 (MALDI-ToF of $\Phi_2\text{Si}(\text{OH})_2$ and PDIol-initiated PDMS respectively) water initiation can be detected as a second population ($N^{\circ}2$) corresponding to chains with $M/z = n x M_{D_3} + M_{H_2O} + M_{Na}$. The third population detected in the MALDI-ToF spectrum of the PDIol-initiated PDMS corresponds to the chains terminated by excess PDIol via the same mechanism proposed above for the BnOH-initiated PDMS.



Scheme 4. Mechanism of BnOH initiated AROP of D_3 catalyzed by TBD

Influence of functionality: telechelic vs. monofunctional

Telechelic initiators (1,3-propane diol, Pdiol and diphenyl silane diol, $\Phi_2\text{Si}(\text{OH})_2$) were tested in identical conditions ($[\text{D}_3]_0/[\text{OH}]_0/[\text{TBD}]_0=25/1/0.1$ or 0.5) to be compared with their monofunctional analogs (BnOH and TMSOH). It is worth mentioning that, during an AROP with a monofunctional initiator, the presence of adventitious water produces a second polymer population of twice the molar mass of the expected polymer population. Moreover, condensation is known to occur more prominently toward the end of AROP (when the monomer concentration is low) also generating a secondary population with twice the molar mass of the desired polymer. However, using telechelic initiator will effectively mask the effect of initiation by adventitious water. The two different telechelic PDMS populations will effectively be very difficult to distinguish one from another. In consequence difunctional initiator will allow to study only the effect of condensation reaction.

As seen above, the initiation using alcohols is slower than that using silanols. The use of silane diol as an initiator for the TBD-catalyzed AROP of D_3 leads to rigorously linear pseudo 1st order kinetics (Figure 6). However, unlike the AROP initiated with BnOH, initiation using PDiol does not lead to a frank double slope in the first-order kinetic plot (Figure 6). ^1H NMR titration of difunctional initiators was not possible due to overlapping signals with the reaction solvent (THF). However, Figure 7b shows that the evolution of dispersity with monomer conversion behaves as in the case of the BnOH-initiated AROP, with high dispersity at low conversion, decreasing as the polymerization progresses (Figure 7b). The effect of the quantity of catalyst was also very similar (faster initiation and lower dispersity at higher catalyst loading).

Adventitious water is an issue in AROP initiated with alcohols or silanols as it generates a secondary population of polymer chains. Water is very hard to completely remove from the components of the polymerization (particularly from TBD that favorably hydrogen bonds with H_2O). Shi *et al.* proved that in the case of monofunctional initiation, a secondary population is always observed due to initiation by water.²² In the case of monofunctional initiators a more drastic drying procedure for TBD than for telechelic initiator was implemented to obtain monomodal SEC chromatograms. Even with rigorous distillation and drying steps, adventitious water remained, and lead to the production of a secondary population of chains, albeit in small proportion, but that still induced a noticeable increase of dispersity in the case of monofunctional initiators (entries 1 and 2). Moreover, the kinetics of the

polymerization is influenced by the quantity of residual water because of its ability to initiate polymerization. It decreases the real $[M]/[OH]$ ratio, and increases the k_{app} of the polymerization (see values of k_{app} for entry 1, 2, 5 and 6 in Table 1).

As described previously, increasing the catalyst to initiator ratio induces faster initiation, lowers initial dispersity, but also promotes condensation reactions and also likely other secondary reactions such as redistribution or back-biting. Indeed, using telechelic initiators enabled to highlight the condensation occurring towards the end of the polymerization at higher catalyst loading as shown in Figure S4 and S6. Figure 8 clearly evidences this secondary population which appears at 92% conversion for the AROP carried out at $[I]_0/[TBD]_0 = 0.5$, while it is significantly lower at 95% conversion for the polymerization carried out at $[I]_0/[TBD]_0 = 0.1$. Chain scrambling (redistribution) and back biting are also likely promoted by an increase of the catalyst loading, but these effects were

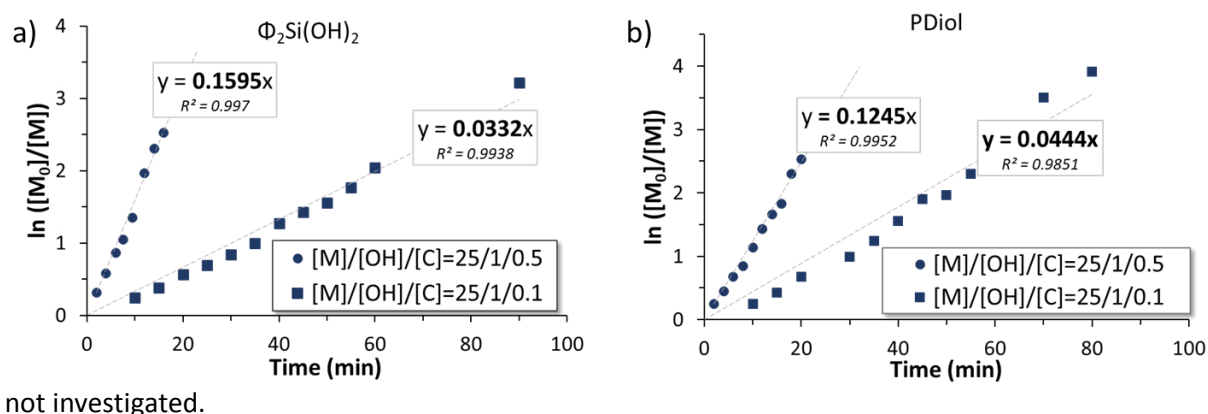


Figure 6. First order kinetics plot of ROP initiated by a) diphenylsilanediol, b) propanediol.

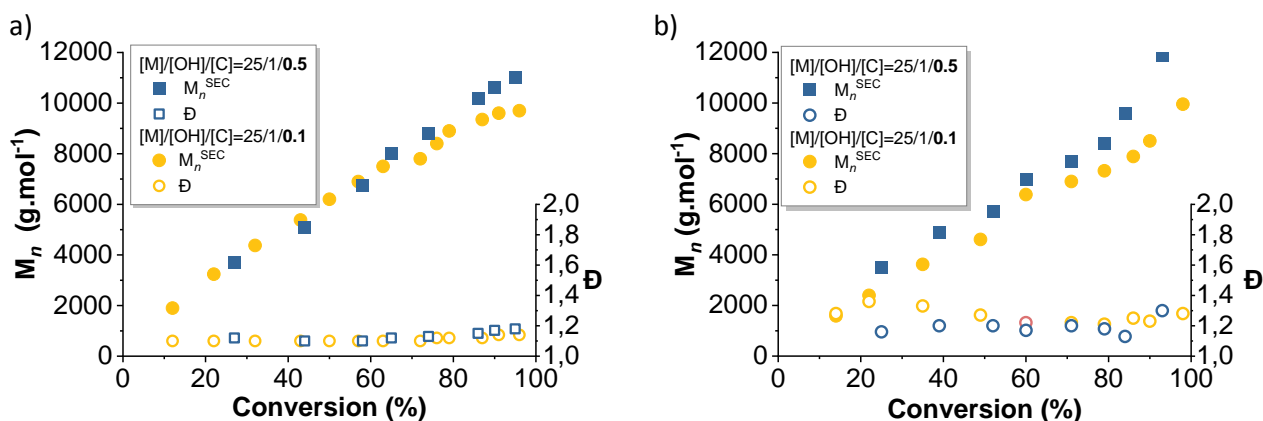


Figure 7. Evolution of number average molar mass and dispersity with D_3 conversion of PDMS prepared by TBD-catalyzed AROP of D_3 : a) initiated with $\Phi_2Si(OH)_2$, b) initiated with Pdiol.

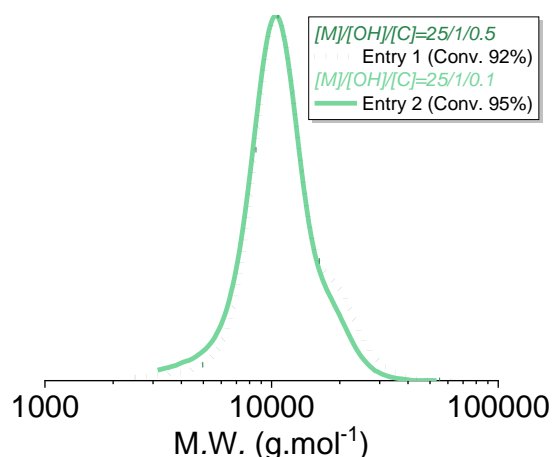


Figure 8. SEC traces of the PDMS corresponding to entry 1 (straight line) and 2 (dashed line) of

One of the aims of the present study was to evaluate the capacity of TBD to yield PDMS of high molar masses. Silane diol was thus chosen as initiator in order to use the best experimental conditions for controlled AROP of D_3 with TBD as catalyst.

$[D_3]_0/[I]_0$ ratios ranging from 100/1 to 500/1 were tested (Table 2). The polymerizations were carried out using identical monomer concentration (1.8 mol.L^{-1}). The catalyst concentration was also kept constant for every polymerization (0.008 mol.L^{-1}) and corresponded to the one used for entry 5 in Table 2. As a consequence, the $[TBD]_0/[I]_0$ ratio increased for polymerizations targeting PDMS with higher degree of polymerizations.

High molar mass PDMS ranging from 16 to 35 kg mol^{-1} were synthesized under these conditions. Nevertheless, the increasing $[TBD]_0/[I]_0$ ratio led to noticeable increase of dispersity for high molar mass PDMS. Indeed, condensation was observed on the GPC traces of these PDMS (Figure 9). However, decreasing the catalyst to initiator proportion in this case afforded PDMS with relatively high molar masses (35 kg.mol^{-1}) and low dispersity (1.17). Figure 9b displays the GPC traces of PDMS from entry 3 and 5 of Table 2 and shows that less condensation occurred during polymerization of entry 5, Table 2 with $[I]_0/[TBD]_0 = 1/0.7$, despite reaching a higher conversion. Indeed, \mathcal{D} decreased with the catalyst concentration, which is in good agreement with the conclusion of the kinetic study.

Table 2. Results from the AROP of D_3 initiated by diphenylsilanediol and catalyzed by TBD.

Entry	$[D_3]_0/[I]_0/[TBD]_0^a$	Conv. (%) ^b	Time (min)	M_n^{Calc} (kg.mol^{-1}) ^c	M_n^{SEC} (kg.mol^{-1}) ^d	\mathcal{D}
1	100/1/0.4	94	60	21.0	16	1.07
2	200/1/0.8	95	80	42.4	22	1.19
3	350/1/1.4	93	100	72.5	27	1.26
4	500/1/2	95	120	105.7	33	1.26
5	350/1/0.7	96	120	74.8	35	1.17

^a $[D_3]_0 = 1.8M$ ^b Calculated from ^1H NMR normalizing D_3 and PDMS signals to 100 ^c $M_n^{\text{calc}} = \text{conv.}/100 \times [D_3]_0/[I]_0 \times M(D_3)$ ^d Determined by SEC in THF (1 ml.min^{-1}) using a calibration PMMA standard

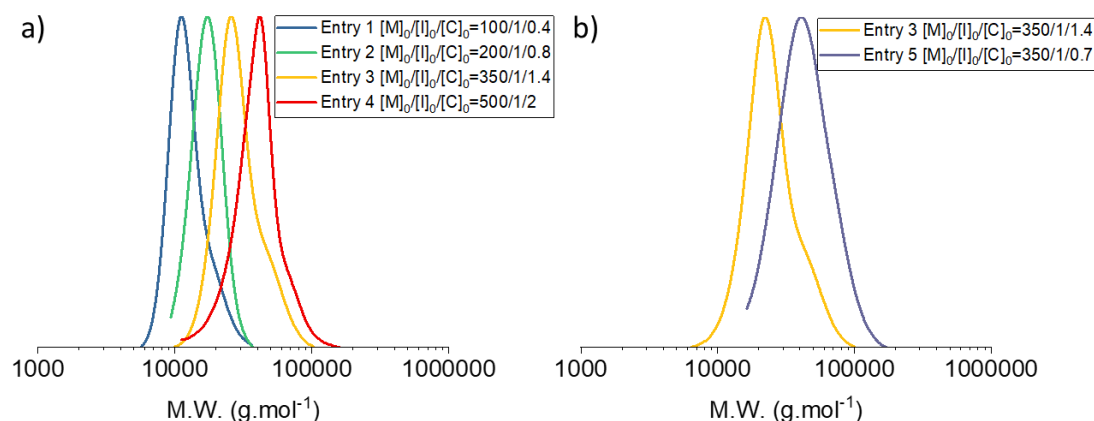


Figure 9. Size exclusion chromatograms of the PDMS prepared by AROP of D_3 and shown in Table 2.

Polymerization of D_4

As abovementioned in the introduction, D_4 can be another monomer of interest for the obtention of PDMS *via* thermodynamical control of the polymerization.

Table 3. Results from the AROP of D_4 initiated by diphenylsilanediol and catalyzed by TBD.

Entry	$[D_4]_0/[I]_0/[TBD]_0^a$	T (°C)	Conv. (%) ^b	Time (h)	D_5 (mol%) ^c	M_n^{Calc} (kg.mol ⁻¹) ^d	M_n^{SEC} (kg.mol ⁻¹) ^e	\mathcal{D}
1	50/1/1	40	75	18	10	11.3	10.1	1.41
2	50/1/10	40	86	4	18	13.0	16.0	1.60
3	50/1/5	40	84	6	15	12.6	15.6	1.56
4	50/1/5	60	88	4	16	13.2	13.1	1.58

^a $[D_4]_0 = 1.8M$ ^b Calculated from ¹H NMR normalizing D_4 and PDMS signals to 100 ^c Calculated from ¹H NMR ^d $M_n^{calc} = conv./100 \times [D_4]_0/[I]_0 \times M(D_4)$ ^e Determined by SEC in THF (1 ml.min⁻¹) using a calibration PMMA standard

A series of D_4 polymerizations were performed to verify if polysiloxanes could be prepared under TBD-catalyzed AROP conditions. As D_4 is a larger and more stable cyclosiloxane than D_3 , the AROP of this monomer under the conditions used for the polymerization of D_3 may be possible albeit in longer time, at higher temperature or at higher catalyst concentration. The polymerizations of D_4 were attempted in THF at 40°C (except for entry 4 for which T= 60°C) using $\Phi_2Si(OH)_2$ as an initiator and increasing $[TBD]_0/[I]_0$ from 1 to 10 while keeping $[D_4]_0 = 1.8 \text{ mol.L}^{-1}$ (Table 3). The monomer conversion was followed by ¹H NMR by quenching samples with a solution of acetic acid in THF. The polymers were characterized by ¹H NMR and size exclusion chromatography.

These polymerizations of D_4 produced PDMS with molar masses ranging from 10,100 to 15,600 g.mol⁻¹. For $[TBD]_0/[I]_0 = 1$ (Entry 1, Table 3), the conversion reached 75% after 18h and the resulting polymer had a molar mass of 24,000 g.mol⁻¹ and a relatively high dispersity (1.41). However, in the course of this polymerization, a non-negligible quantity of D_5 was formed (10 mol% of the final mixture of polymer and macrocycles). When the catalyst concentration was increased to 5 and then 10 to accelerate the polymerization, the reaction time was decreased from 18 to 6 and 4 h respectively while the conversion increased from 75 % to about 85 %. However, both the dispersity and the production of D_5 increased reaching 1.6 and 18 mol% respectively (for $[TBD]_0/[I]_0 = 10$). This

production of D_5 may explain the important decrease of the PDMS molar masses when high catalyst contents were used.

Experimental part

Materials

Hexamethyltricyclosiloxane (D_3) (97%), diphenylsilanediol and trimethylsilanol (TMSOH) were purchased from ABCR. D_3 was dried over CaH_2 at 90°C for 48h, and sublimated under reduced pressure prior to use. 1,3-propane diol, benzyl alcohol and THF (non-stabilized) were purchased from Sigma. 1,3 propane diol and benzyl alcohol were dried over CaH_2 for 48h, distilled under reduced pressure and stored over 4A molecular sieves. THF was dried over Na/benzophenone and distilled prior to use under reduced pressure at ambient temperature. TMSOH was distilled under reduced pressure at 40°C and stored over 4A molecular sieves. TBD was purchased from TCI. TBD and diphenylsilanediol were dried under vacuum ($7.5 \cdot 10^{-2}$ mbar) at 60°C for 2h prior to the preparation of solution in dry THF.

Size exclusion chromatography

SEC was recorded using a triple-detection GPC from Agilent Technologies with its corresponding Agilent software, dedicated to multidetector GPC calculation. The system used two PL1113-6300 ResiPore 300×7.5 mm columns with THF as the eluent with a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. The detector was a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at 35 °C. Polymethylmethacrylate (PMMA) standards were used for calibration between 540 and $2,210,000 \text{ g} \cdot \text{mol}^{-1}$. Samples were prepared by diluting 0.1 mL (1.8M) aliquots from the polymerization in 1 mL THF.

NMR

NMR samples were prepared with $CDCl_3$ as a solvent and the analyses were performed using a Bruker Avance I 400 MHz spectrometer at 25 °C. The 1H NMR spectra were recorded at 8 kHz for spectral width, 3 kHz for transmitter frequency offset, 4 s for acquisition time and 4 scans were performed.

MALDI-ToF

For MALDI-ToF analysis a Bruker RapifleX Instrument with a RapifleX computer were used. Structures of the obtained PDMS were analyzed by positive ion MALDI-TOF mass spectroscopy using dithranol as a matrix and sodium iodide as a cationization agent.

Polymerizations

A typical PDMS synthesis was performed as follows: Every piece of glassware was thoroughly dried using a heat gun under reduced pressure. D_3 (1 g, 4.5 mmol, 50 equiv) was directly sublimated in a Schlenk flask equipped with a magnetic stirrer bar. 1.8 mL of a solution of diphenylsilanediol in THF (0.05M) was added. Experimental $[M]_0/[I]_0$ was determined before catalyst was added by 1H NMR. TBD was solubilized in THF at 60°C to obtain a perfectly clear solution. 0.1 mL of a solution of TBD in THF (0.14 M) was added to start the polymerization at 40°C. Aliquots were sampled out of the reaction medium at different reaction times and the polymerization was quenched using an acetic acid/THF solution.

Conclusion

This study demonstrates that TBD, an easy to handle and commercially available catalyst, is able to catalyze the AROP of D_3 in a controlled manner depending on the initiator employed. Two types of initiators (alcohols and silanols) were compared under similar polymerization conditions. The pK_a of the initiator was shown to strongly influence the course of the polymerization. Initiators with a higher pK_a than those of the propagating silanol-derived species led to slow and incomplete initiation. Consequently, alcohol-initiated polymerizations were not perfectly controlled. This effect can be partly mitigated by increasing the catalyst concentration. However, increasing the catalyst concentration also promoted undesired condensation reactions especially at high monomer conversion. Indeed, higher catalyst loading also likely promote chain redistribution and back-biting reactions but these effects were not investigated. In addition, both monofunctional and telechelic initiators were assessed. Since the pK_a seems to be the key for a fast initiation, here the catalyst concentration allows to increase the initiation rate. In the same manner, the pK_b of the catalyst should be another key to fast initiation. However, as it was mentioned in the introduction, higher pK_b of catalyst is often correlated with lower stability. The use of monofunctional initiators (BnOH and TMSOH) makes the need to eliminate any incidental water critical. Indeed, difunctional initiators produce telechelic PDMS that mask the water-initiated chains. The use of difunctional initiators also makes it easier to observe condensation reactions when they occur. Remarkably, TBD was also efficient to polymerize D_4 although these polymerizations led to PDMS with relatively broad molar mass distributions ($1.54 < \bar{M} < 1.6$). In conclusion, TBD was found to be an efficient, commercially available and affordable organocatalyst for the polymerization of D_3 . Its evaluation as catalyst for other cyclosiloxanes and for the synthesis of silicones copolymers is underway in our laboratories.

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Associated content

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