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Ring opening polymerization of cyclic oligosiloxanes without producing cyclic oligomers

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Abstract: A long-standing problem associated with silicone synthesis is contamination of the polymer products with 10 to 15% cyclic oligosiloxanes that result from backbiting reactions at the polymer chain ends. This process, in competition with chain propagation via ring-opening polymerization (ROP) of cyclic monomers, was thought to be unavoidable, and routinely leads to a thermodynamically controlled reaction mixture (polymer/cyclic oligosiloxanes = 85/15). Here we report that simple alcohol coordination to the anionic chain ends prevents the backbiting process and that a well-designed phosphonium cation acts as a self-quenching system in response to loss of coordinating alcohols to stop the reaction before the backbiting process begins. The combination of both effects allows a thermodynamically controlled ROP of the 8-membered siloxane ring D₄ without producing undesirable cyclic oligosiloxanes.

One-Sentence Summary: The complete conversion of cyclic oligosiloxanes in ring-opening polymerization was finally proven to be achievable.

Main Text: Since the discovery of polysiloxanes, commonly called silicones, in the first attempt to synthesize a stable silanone by F. Kipping in 1901 (1) and their first industrial production by Dow-Corning Corp. in 1943 (2), these organosilicon materials have found extremely wide-ranging applications in different forms (oil, rubber, gel, and resin) due to their particular chemical and physical properties (3). Despite important progress in their synthesis (4-6), a long-known but still unsolved drawback their systematic contamination with cyclic oligosiloxanes (about 10 to 15%), regardless of the methods used (3,4). Considering the potential toxicity of low molecular-weight cyclic siloxanes (7), capable of overcoming the human skin barrier (8), it is critical to address this contamination problem (9). Currently, nearly 50 % of new skin care products contain at least one type of silicone (10).

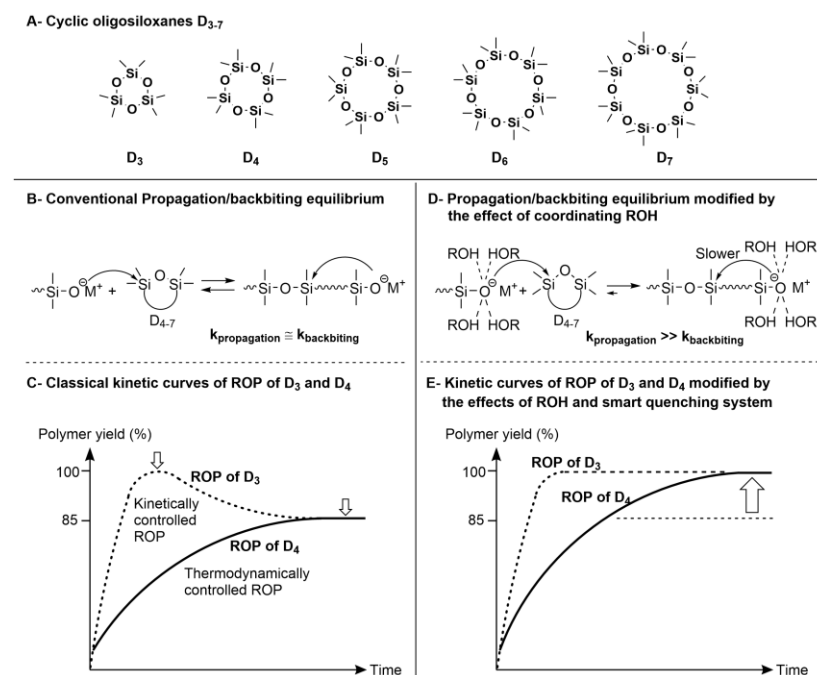


Fig. 1. Chain propagation / backbiting equilibrium. (A) Cyclic oligosiloxanes of different sizes (D₃₋₇). (B) Reversible processes: propagation via ROP of cyclic oligosiloxanes and backbiting of silanolate chain end. (C) Typical kinetic curves for the kinetically- and thermodynamically-controlled ROPs of cyclic oligosiloxanes (D₃: dashed line D₄: solid line, ref. 12). (D) Strongly favored propagation process due to the hampered backbiting by the alcohol coordination on the silanolate end. (E) Kinetic curves for the ROPs of cyclic oligosiloxanes (D₃ and D₄) improved by the effect of alcohols and of self-degradable phosphonium counter cation.

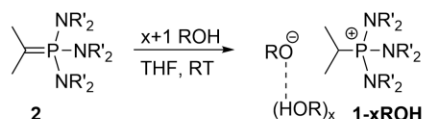
The problem arises from backbiting reactions at the polymer chain end to produce cyclic oligosiloxanes of different sizes (4 to 7 membered rings, D₄₋₇, Fig. 1A) (11,12). The rate of backbiting is competitive with the propagation *via* ring-opening of cyclic monomers, leading to a backbiting/propagation equilibrium, and therefore to a polymer/cyclic oligomers mixture in a thermodynamically controlled ratio (about 85 / 15, Fig. 1B). This means that, in the polymer chemistry of silicones, most of the reactions catalyzed by either acid or base, at the final stage,

end with a ROP process, leading to the same contamination (4). An exception is the ROP of hexamethylcyclotrisiloxane (D_3) (13, 14), which allows a significantly faster process [100 to 1000 times faster than that of octamethylcyclotetrasiloxane D_4] (12). In this case, with proper choice of initiator/catalyst and conditions, the ROP of D_3 is kinetically controlled and achieves complete monomer conversion (Fig. 1C, dashed line) (15-21), whereas the anionic ROP of other monomers (D_{4-7}) is under thermodynamic control affording the conventional polymer/cyclic oligomers mixture (Fig. 1C, solid line) (12). Thus, the achievement of the ROP of D_4 (most thermodynamically favored) without producing cyclic oligomers, by somehow preventing the backbiting process and altering the thermodynamic polymer/cyclic oligomers ratio (from 85 / 15 to 100 / 0) (Fig. 1E), would be a fundamental solution for this issue. Here we report that simple coordination of alcohols to the active silanolate chain ends prevents the backbiting process (Fig. 1D), and that well-designed phosphonium counter-cations act as a smart self-quenching system in response to the loss of coordinating alcohols to stop the reaction before the backbiting process starts. The combination of these two effects allows the thermodynamically controlled anionic ROP of D_4 without producing undesirable cyclic oligosiloxane contaminants (Fig. 1E).

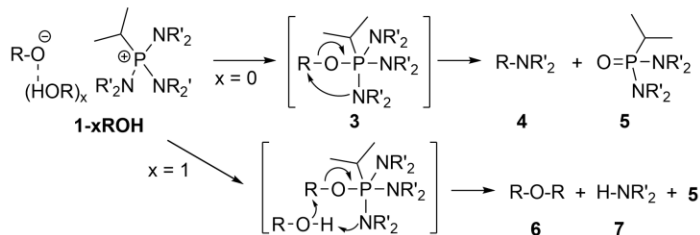
As already mentioned, the origin of the problem (incomplete ROP of cyclic oligosiloxanes) is the competitive rate of backbiting relative to propagation. Thus, we hypothesized that flexible coordination between weakly acidic alcohols and the anionic silanolate chain end should increase steric hindrance around the nucleophilic site and modulate the relative rates without excessively reducing the propagation rate (Figure 1D). Nucleophilic attack of the anionic chain end on silicon centers of the linear siloxane chains (backbiting process) could be significantly more hindered by this effect than attack on the sterically more accessible silicon atom of a rigid cyclic monomer for propagation process. Based on this hypothesis, we performed the ROP of D_4 in the presence of an excess of benzyl alcohol (5 equiv.) relative to tBuOK/Cryptand initiator (0.5 mol% vs. D_4) (21, 22) at 80 °C. Careful monitoring of the ROP demonstrated that the polymer ratio to cyclic oligomers (D_{4-7}) reaches 95 % after 6 hours and then gradually decreases to 89 % in 12 hours. This result suggests that there is a certain effect preventing the backbiting reactions which gradually disappears over time. This disappearance can be attributed to the loss of coordinating alcohols at the anionic chain ends either by chain transfer or by dissociation at the last stage of polymerization, leading to the conventional situation with the propagation/backbiting equilibrium. Probably for this reason, the effect of alcohol coordination has been ignored previously.

A possible solution is an automatic quench system responsive to the loss of coordinating alcohols. For this purpose, we considered the use of (*i*-propyl)tris(dialkylamino)-phosphonium alkoxides **1-xROH** that are stable only with the alkoxide anion stabilized by coordination of alcohols *via* weak hydrogen bonding interactions (Fig. 2A) (23). Without a sufficient number of stabilizing alcohols, the alkoxide readily attacks the P atom of the phosphonium cation, which, *via* a pentacoordinate intermediate **3**, affords either amine **4** and phosphine oxide **5** ($x = 0$) or ether **6**, amine **7** and phosphine oxide **5** ($x = 1$) (Fig. 2B) (24). The use of such phosphonium alkoxides **1-xROH** as initiator of ROP leads to the formation of silicones with alcohol-stabilized anionic silanolate chain ends which should behave in the same way. In other words, once coordinating alcohols are lost, the ionic pair (silanolate anion / phosphonium cation) at the chain end starts reacting to generate a neutral chain end (Si-NR₂ or Si-OR), and therefore, quenches the polymerization process.

A- Synthesis of ROH-free and ROH-stabilized phosphonium alkoxides



B- Decomposition mechanism of phosphonium alkoxides



C-Half-life time ($t_{1/2}$) of 1a,b,c-xBnOH (x = 0, 1, 4) at 80 °C

Steric hindrance around P atom			
	1a-4BnOH	1b-4BnOH	1c-4BnOH
	15 min.	40 min.	4 % decomposition in 24 hours
	1a-1BnOH	1b-1BnOH	1c-1BnOH
	< 5min.	< 5 min.	28 % decomposition in 24 hours
	1a-0BnOH	1b-0BnOH	1c-0BnOH
	< 5min.	< 5 min.	60 % decomposition in 24 hours

Fig. 2. Synthesis and stability assessment of initiators. (A) Synthesis of alcohol-stabilized (*i*-propyl)(tris-amino)phosphonium alkoxides **1-xROH**. (B) Proposed mechanism for the decomposition of phosphonium alkoxides **1-xROH** (x = 0, 1). (C) Effects of phosphonium cation (size) and of coordinating alcohols on the stability of phosphonium benzyloxides **1-xBnOH**. Half-life time of **1-xBnOH** (x = 0, 1 or 4) in C₆D₆ (M = 0.07 mol/l) at 80 °C. Half-life of **1-xROH** were determined by ³¹P-NMR.

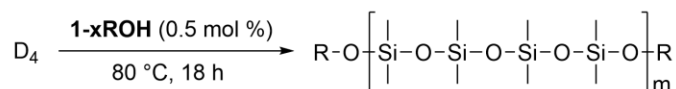
Thus, alcohol-free and -stabilized phosphonium alkoxides **1-xBnOH** were synthesized by the addition of benzyl alcohol (BnOH) to phosphonium ylides **2a-c** with different dialkylamino substituents (Figure 2A and C) (24). The number of coordinating alcohols (x) can be precisely controlled by the quantity of BnOH (x+1 equiv.) added to the ylide **2**. As expected, they are thermally labile and the least-hindered variant **1a-4BnOH** fully decomposes within 1 hour ($t_{1/2}$ = 15 min.) at 80 °C in C₆D₆ (M = 0.07 mol/l) to generate the corresponding dibenzylether **6**, dimethylamine **7** and phosphine oxide **5**. This result indicates that the decomposition proceeds with the intervention of an alcohol [Fig. 2B (x = 1)] and thus starts before complete loss of stabilizing alcohols. The decay gradually slows down as free benzyl alcohol in the media increases, each time **1a-4BnOH** decomposes. The effects of phosphonium cation structure and the quantity of coordinating alcohol on their stability (at 80 °C in C₆D₆) were then assessed in order to regulate the stability/decomposition balance (Fig. 2C).

As already mentioned, the decomposition of phosphonium alkoxides **1-xBnOH** starts with the nucleophilic attack of alkoxide on the central P atom of phosphonium cation (Fig. 2B). Therefore, the stability should be strongly related to the steric hindrance around the P atom. Indeed, an enhanced persistence of BnOH-stabilized phosphonium alkoxides **1a,b,c-4BnOH** with bulkier amino groups on the P atom (**1a** < **1b** < **1c**) was clearly shown by gradual slow-down of decomposition (Fig. 2C). More importantly, a strong acceleration of decomposition was observed for mono-coordinated phosphonium alkoxides **1a,b-1BnOH** ($t_{1/2(80^\circ\text{C})} < 5$ min.), which is critical in order to use them as smart self-quenching systems automatically triggered by the loss of coordinating alcohols. Alcohol-free phosphonium alkoxides **1a,b-0ROH** decompose at almost the same rate ($t_{1/2(80^\circ\text{C})} < 5$ min.) but with a poor selectivity due to the excessive reactivity of non-stabilized alkoxide ion. In this case, in addition to the phosphine oxide **5**, the formation of phosphines was also observed. The decomposition of phosphonium alkoxides *via* β -elimination triggered by deprotonation at the β -position of the substituent by the alkoxide to give a phosphine and an alcohol is known (23,24). High stability was observed for the most-hindered variant **1c-4BnOH**, with piperidino substituents, and it was not possible to estimate its half-life due to an exceedingly slow decomposition rate (4 % of decomposition at 80 °C in 24 hours). Phosphonium alkoxide **1c** remains persistent with a reduced number of coordinating alcohols (**1c-1BnOH**, 28 % of decomposition in 24 hours) and even in the absence of stabilizing alcohols (**1c-0BnOH**, 60 % of decomposition in 24 hours) and thus it was not suitable for our purpose.

The ROP of D₄ at 80 °C in the presence of the BnOH-stabilized phosphonium benzyloxide **1b-4BnOH** (0.5 mol% vs. D₄) as initiator led to complete conversion in 18 hours to produce a clean silicone polymer (99.6 %) with only a small amount of D₄ (0.4 %) (Fig. 3A), which was determined by ¹H- and ²⁹Si-nuclear magnetic resonance (NMR) analysis of resulting mixture. Despite the unusually high conversion, the polymerization is thermodynamically controlled as suggested by the large polydispersity index of resulting polymers ($I_p = 1.54$) (25, 26). The NMR-analysis demonstrates that the polymer chains are end capped with the neutral Si-OBn group, as expected to form *via* the decomposition of ionic chain ends ($x = 1$, Fig. 2B). After 18 hours, the system was totally deactivated, as evidenced by unchanged polymer size even after heating at 80 °C for a prolonged time (36 h) as well as by the absence of any further polymerizations upon adding another equivalent of D₄ to the mixture.

As expected, the stability of phosphonium alkoxides dramatically influences the ROP of D₄ (Fig. 3A). Indeed, the least-hindered cation **1a-4BnOH** is not persistent enough to complete the ROP (10 % silicone and 90 % unreacted D₄). More importantly, the ROP with the excessively stable initiator **1c-4BnOH** (persistent even in the absence of stabilizing alcohols), leads to a conventional polymer/cyclic oligomers mixture (polymer/D₄₋₇ = 83/17). These results clearly confirm the importance of an automatic quench system triggered, before backbiting begins, by the loss of alcohols, in order to benefit from the effect of alcohol-coordination to prevent the cyclic oligomer formation.

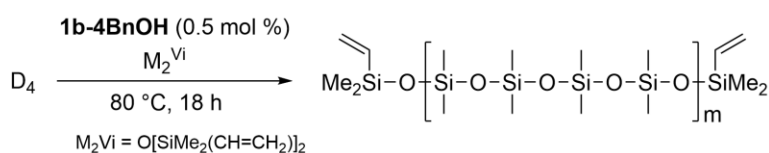
A- ROP of D₄ using different initiators (1a,b,c-xBnOH)



1a,b,c-xBnOH (Effect of phosphonium cation)

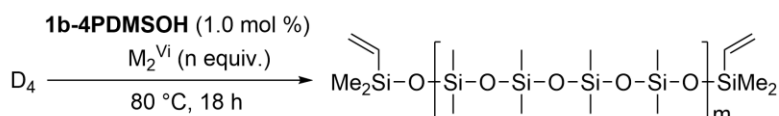
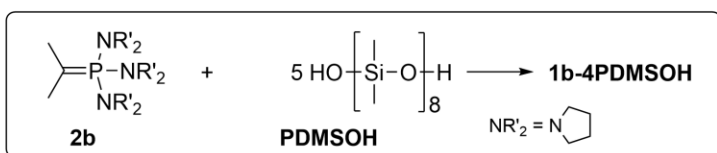
1	x	Silicones (%)	Mn [Mn _{Theo}] (g mol ⁻¹)	Mw (g mol ⁻¹)	Ip
1a	4	10	9182 [59324]	11541	1.26
1b	4	> 99	86170 [59324]	133090	1.54
1c	4	83	64530 [59324]	98890	1.53
1b	2	99	118870 [59324]	174860	1.47
1b	9	> 99	32310 [59324]	52700	1.63

B- ROP of D₄ (Initiator: 1b-4BnOH, end capping agent: M₂^{Vi})



M ₂ ^{Vi} /1b-4BnOH	Silicones (%)	Mn [Mn _{Theo}] (g mol ⁻¹)	Mw (g mol ⁻¹)	Ip
2.5	> 99	20830 [23730]	34710	1.67
5	> 99	10910 [11865]	18600	1.70
7.5	> 99	7470 [7910]	14590	1.82
10	> 99	5244 [5932]	9931	1.89

C- ROP of D₄ with a short PDMS-based initiator



n = 2.5: > 99 %, Mn = 10864 g mol⁻¹, Mw = 19855 g mol⁻¹, Ip = 1.83

n = 5.0: > 99 %, Mn = 5649 g mol⁻¹, Mw = 11234 g mol⁻¹, Ip = 1.99

Fig. 3. Fully converted anionic ring-opening polymerizations (ROP) of D₄. (A) Study of the effects of phosphonium cations on the ROP of D₄ with different initiators **1-xROH**. (B) Study of polymer size control by end capping agent (M₂^{Vi}) in the ROP of D₄ with the phosphonium benzyloxy initiator (**1b-4BnOH**). (C) Synthesis of PDMS-based initiator **1b-4PDMSOH** and its tests for the full ROPs of D₄ in the presence of M₂^{Vi}.

The size of the resulting polymer can be roughly regulated by the amount of alcohol added (about 1/5 of added ROH can effectively give rise to polymer chains) (Fig. 3A) (27). Therefore, the loss of coordinating alcohols should result mainly from dissociation rather than chain transfer

reactions. According to DFT calculations on the model reaction $[\text{Me}_3\text{Si}-(\text{OSiMe}_2)_4-\text{O}^-(\text{BnOH})_x \mathbf{1a}^+ \rightarrow \text{Me}_3\text{Si}-(\text{OSiMe}_2)_4-\text{O}^-(\text{BnOH})_{x-1} \mathbf{1a}^+ + \text{BnOH}$, $x = 1 - 4$], the Gibbs free energy for the dissociation of benzyl alcohol (BnOH) from the silanolate chain end is small for $x = 4$ (1.6 kcal/mol) and $x = 3$ (5.0 kcal/mol), whereas it is larger for $x = 2$ (11.8 kcal/mol) and $x = 1$ (15.2 kcal/mol). More precise polymer-size-control can be achieved using a disiloxane end-capping reagent 1,3-divinyl(tetramethyl)siloxane (M_2^{Vi}), without losing the full conversion character of ROP. Indeed, varying the amounts of M_2^{Vi} (2.5 – 10 equiv.) relative to $\mathbf{1b-4BnOH}$, the end-capped silicone polymers with a Mn close to the expected value (Mn_{Theo}) have been obtained with an excellent yield (> 99 %) (Fig. 3B).

PDMS-based initiators (28) (PDMS=polydimethylsiloxane) are common tools for increasing initiator solubility and minimizing impurities in silicone synthesis. Therefore, we considered preparing a PDMS-based initiator using short α,ω -dihydroxy-polydimethylsiloxanes (**PDMSOH** = $\text{HO}(\text{Me}_2\text{SiO})_8\text{H}$) instead of alcohols. The addition of **PDMSOH** (5 equiv.) to phosphonium ylide **2b** affords the PDMS-based initiator **1b-4PDMSOH**, stable at room temperature and decomposing at 80 °C in 2 hours ($t_{1/2} = 15$ min.) (Fig. 3C). The ROP of D_4 with this initiator (1.0 mol%), in the presence of M_2^{Vi} (2.5 or 5 equiv. vs. **1b-4PDMSOH**), afforded silicones with yields above 99 % and with the expected polymer sizes (Fig. 3C). After the reaction, no traces of short oligomer $\text{HO}(\text{Me}_2\text{SiO})_8\text{H}$ could be detected by NMR and GPC analysis, probably because of its consumption *via* poly-condensation processes. These results demonstrate that the silanol function (Si-OH) in PDMS can also act as stabilizer of anionic chain ends to prevent the cyclic oligomer formation. We conclude that the full ROP of D_4 is actually achievable.

References and Notes

1. F. Kipping, L. L. Lloyd, XLVII - Organic derivatives of silicon. Triphenylsilicol and alkyloxysilicon chlorides. *J. Chem. Soc., Trans.* **79**, 449-459 (1901).
2. N. R. Thomas, Frederic Stanley Kipping-Pioneer in silicon chemistry: His life & legacy. *Silicon* **2**, 187-193 (2010).
3. J. M. Zeigler and F. W. G. Fearon, Eds., *Silicon-based polymer science* (ACS Publication, Washington, DC, 1990).
4. M. A. Brook, *Silicon in organic, organometallic, and polymer chemistry* (Wiley-Interscience, New York, 1999).
5. I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, Selective and efficient platinum(0)-carbene complexes as hydrosilylation catalysts. *Science* **298**, 204-206 (2002).
6. A. M. Tondreau, C. C. Hojilla Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, Iron catalysts for selective anti-Markovnikov alkene hydrosilylation using tertiary silanes. *Science* **335**, 567-570 (2012).
7. L. Xu, Y. Shi, N. Liu, Y. Cai, Methyl siloxanes in environmental matrices and human plasma/fat from both general industries and residential areas in China. *Sci. Total Environ.* **505**, 454-463 (2015).
8. Mojsiewicz-Pienkowska, K. "Review of current pharmaceutical applications of polysiloxanes (Silicones)," in *Handbook of polymers for pharmaceutical technologies, processing and applications, Vol. 2*, V. K. Thakur, M. K. Thakur, Eds. (Beverly, MA: Wiley-Scrivener Publishing, 2015), pp.363-382.
9. K. Mojsiewicz-Pienkowska, M. Jamróiewicz, K. Szymkowska, D. Krenczkowska, Direct human contact with siloxanes (silicones) – Safety or risk Part 1. Characteristics of siloxanes (Silicones). *Front. Pharmacol.* **7**, 132 (2016).
10. <https://cosmethicallyactive.com/silicones-in-cosmetics-and-their-impact-on-the-environment/>
11. Equilibria between Linear and Cyclic Polymers in Methylpolysiloxanes: D. W. Scott, *J. Am. Chem. Soc.* **68**, 2294-2298 (1946).
12. J. Chojnowski, "Ring-opening polymerization of cyclosiloxanes" in *Silicon compounds: Silanes and silicones*, B. Arkles, G. Larson, Eds. (Gelest Inc Morrisville, PA, 2008) pp.389-405.
13. D₃ is more reactive than other larger cyclics (D₄₋₇) due to its more strained structure. The ring strain energy was calculated to be 11 kcal/mol higher than that of D₄.
14. J. D. Kress, P. C. Leung, G. J. Tawa, P. J. Hay, Calculation of a reaction path for KOH catalyzed ring-opening polymerization of hexamethylcyclotrisiloxane. *J. Am. Chem. Soc.* **119**, 1954-1960 (1997).
15. J. C. Saam, D. J. Gordon, S. Lindsey, Block copolymers of polydimethylsiloxane and polystyrene. *Macromolecules*, **3**, 1-4 (1970).
16. H. J. Hölle, B. R. Lehnen, Preparation and characterization of polydimethylsiloxanes with narrow molecular weight distribution. *Eur. Polym. J.* **11**, 663-667 (1975).

17. J. G. Zilliox, J. E. L. Roovers, S. Bywater, Preparation and properties of polydimethylsiloxane and its block copolymers with styrene. *Macromolecules* **8**, 573-578 (1975).
18. P. Boehm, M. Mondeshki, H. Frey, Polysiloxane-backbone block copolymers in a one-pot synthesis: A silicone platform for facile functionalization. *Macromol. Rapid Commun.* **33**, 1861-1867 (2012).
19. B. G. G. Lohmeijer, G. Dubois, F. Leibfarth, R. C. Pratt, F. Nederberg, A. Nelson, R. M. Waymouth, C. Wade, J. L. Hedrick, Organocatalytic living ring-opening polymerization of cyclic carbosiloxanes. *Org. Lett.* **8**, 4683-4686 (2006).
20. K. Fuchise, M. Igarashi, K. Sato S. Shimada, Organocatalytic controlled/living ring-opening polymerization of cyclotrisiloxanes initiated by water with strong organic base catalysts. *Chem. Sci.* **9**, 2879–2891 (2018).
21. M.-H. Yang, C.-K. Yang, C. C. Anionic Polymerization of Methyl(3,3,3-Trifluoropropyl)cyclotrisiloxane. *J. Chin. Chem. Soc.* **40**, 557-561 (1993).
22. The reaction conditions modified by the procedure proposed by S. Boileau has been employed.
23. S. Boileau, Ring opening polymerization of cyclic organosilicon compounds: Recent progress. *Makromol. Chem. Macromol. Symp.* **73**, 177-181 (1993).
24. P. A. Byrne, D. G. Gilheany, The mechanism of phosphonium ylide alcoholysis and hydrolysis: Concerted addition of the O-H bond across the P=C bond. *Chem. Eur. J.* **22**, 9140-9154 (2016).
25. A. Bessmertnykh, F. Ben, A. Baceiredo, G. Mignani, Anionic ring-opening polymerization of cyclic organosiloxanes using phosphorus ylides as strong non-ionic bases. *J. Organomet. Chem.* **686**, 281-285 (2003).
26. The polydispersity indexes (I_p) were calculated using the equation: $I_p = M_w/M_n$ where M_w is the mass-average molar mass and M_n is the number-average molar mass.
27. R. F. T. Stepto, Dispersity in polymer science. *Pure Appl. Chem.* **81**, 351-353 (2009).
28. The number of ROHs used to initiate the ROP, relative to the 5 ROHs available with the **1b-4BnOH** initiator. This was estimated by the ratio of the experimental M_n to the theoretical M_n ($M_{n,theo}$) expected by the ROP using 1 ROH of **1b-4BnOH**.
29. Mixtures obtained by the reaction of D_4 with KOH are commonly used as PDMS-based initiators for ROP of cyclic oligosiloxanes.
30. R. F. Weitkamp, B. Neumann, H.-G. Stammler, B. Hoge, The Influence of Weakly Coordinating Cations on the O-H...O-Hydrogen Bond of Silanol-Silanolate Anions. *Chem. Eur. J.* **27**, 915–920 (2021).
31. R. F. Weitkamp, B. Neumann, H.-G. Stammler, Synthesis and Reactivity of the First Isolated HydrogenBridged Silanol–Silanolate Anions. B. Hoge, *Angew. Chem. Int. Ed.* **59**, 5494–5499 (2020).
32. S. E. Wolf, U. Schlossmacher, A. Pietuch, B. Mathiasch, H.-C. Schroder, W. E. G. Muller, W. Tremel, Formation of silicones mediated by the sponge enzyme silicatein- α . *Dalton Trans.* **39**, 9245 (2010).

- 5 33. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- 10
- 15 34. Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215-241 (2008).
35. D. A. McQuarrie, *Statistical Mechanics*, (Harper Collins, New York, 1976).
36. R. L. Martin, P. J. Hay, L. R. Pratt, Hydrolysis of ferric Ion in water and conformational equilibrium. *J. Phys Chem. A* **102**, 3565-3573 (1998).
- 20 37. L. Falivene, V. Barone, G. Talarico, Unraveling the role of entropy in tuning unimolecular vs bimolecular reaction rates: The case of olefin polymerization catalyzed by transition metals. *Mol. Catal.* **452**, 138-144 (2018).
- 25 38. F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297-3305 (2005).
39. A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **113**, 6378–6396 (2009).

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Supplementary Materials

Materials and Methods

Figs. S1 to S172

Tables S1 to S4

References (30–39)