

Zwitterionic Polymerization to Generate High Molecular Weight Cyclic Poly(Carbosiloxane)s

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S Supporting Information

ABSTRACT: The zwitterionic ring-opening of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (TMOSC) with *N*-heterocyclic carbenes generates high molecular weight cyclic p(TMOSC). The NHC-mediated polymerization of TMOSC with 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes, **1**) generates the poly(carbosiloxane) p(TMOSC) with molecular weights from 27 000 < M_n < 80 000 Da ($1.4 < M_w/M_n < 2.2$) within 30 min at room temp. With the more nucleophilic carbene 1,3,4,5-tetramethyl-imidazol-2-ylidene (**4**), the ring-opening polymerization occurs within minutes at room temperature to generate cyclic p(TMOSC) with molecular weights up to $M_n = 940\,000$ Da ($M_w/M_n = 3.2$). The resulting p(TMOSC)s are predominantly cyclic as evidenced by dilute solution viscosity studies and MALDI-TOF MS. DFT calculations provide support for both zwitterionic and neutral, cyclic intermediates.

The synthesis of high molecular weight cyclic polymers is a formidable synthetic challenge. The entropic penalty of connecting the ends of a large linear molecule scales exponentially with molecular weight.¹ Cyclic polymers differ from linear chains by only one bond, but the topological constraint imposed by cyclization leads to unusual behavior.^{2–6} Although much is known of the differences of lower molecular weight cyclic and linear chains,^{7–12} the behavior of highly entangled cyclic macromolecules remains poorly understood,^{2–6} in part as a consequence of the challenges in preparing these materials.^{13–15}

Recent synthetic advances^{7,12–17} provide promising strategies for the synthesis of highly entangled, high molecular weight cyclic macromolecules.^{16,18} We have reported that zwitterionic¹⁹ ring-opening polymerizations can generate cyclic polyesters.^{13,18,20–27} Herein, we describe efforts to employ zwitterionic ring-opening polymerization^{13,18,19,28–30} to generate more hydrolytically robust high molecular weight cyclic macromolecules.

The ring-opening of the carbosiloxane 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (TMOSC)^{31–34} in the presence of *N*-heterocyclic carbenes 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes, **1**), 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**3**), or the guanidine 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) with alcohol initiators generates the linear p(TMOSC) (Figure 1a).^{34,35}

As *N*-heterocyclic carbenes and guanidines are both potent bases and nucleophiles,³⁶ two possible mechanisms can be

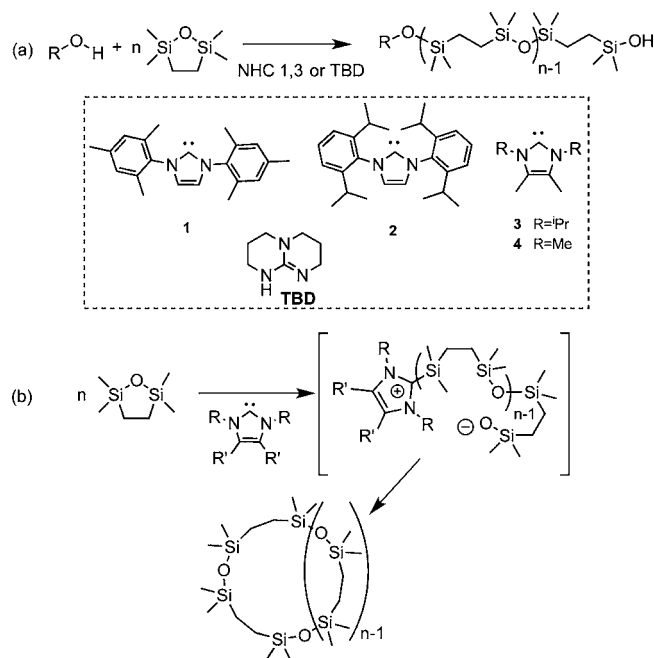


Figure 1. Organocatalytic (a) and zwitterionic (b) ROP of TMOSC.

considered for the ring-opening of carbosiloxanes: a hydrogen-bonding mechanism where the NHC binds to the alcohol to activate it for nucleophilic attack or a nucleophilic mechanism where the carbene attacks the silicon atom to mediate ring-opening.³⁷

We had proposed a H-bonding mechanism for the ROP of carbosiloxanes,³⁴ whereas Baceiredo had implicated a nucleophilic mechanism for the NHC catalyzed ROP of cyclic siloxanes.³⁵ The use of NHCs to activate tetravalent silicon has recently emerged as a useful strategy for mediating a variety of catalytic reactions.^{38–41} Although silicon adducts of NHCs are known,^{38,42,43} their formation and stability depends sensitively on the steric and electronic properties of the carbene and the silicon center.³⁸ Herein, we report a zwitterionic ring-opening polymerization of carbosiloxane monomer to generate high molecular weight cyclic p(TMOSC) (Figure 1b). These results provide a promising strategy for the synthesis of high molecular weight cyclic macromolecules and provide compelling, if indirect, support for the nucleophilic activation of carbosiloxanes by NHC nucleophiles.

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A variety of NHCs were screened for the polymerization of TMOSC in the absence of an alcohol initiator (Table 1, Figure

Table 1. Ring-Opening Polymerization of TMOSC with Carbenes 1–4

entry	NHC	[M]/[NHC] ^a	t (min)	conv. ^b	M _n (kg/mol) ^c	PDI ^d
1	1	100	5	10	27	1.41
			10	20	43	1.35
			30	64	66	1.66
2	1	50	5	27	55	1.39
			30	90	86	2.19
3	2	100	60	0		
4	3	100	0.08	>95	587	1.74
5	4	100	0.08	>95	942	3.18

^aMonomer to initiator ratio, [M]₀ = 1.0 M in THF. ^bConversion of monomer, determined by ¹H NMR. ^cNumber average molecular weight, determined by GPC (conventional PS calibration) for crude samples. ^dPDI = M_w/M_n, determined by GPC.

1b). The unsaturated carbene **1** containing mesityl substituents catalyzes the ring-opening polymerization of TMOSC in the presence³⁴ or absence of an alcohol initiator; in contrast, the more sterically hindered carbene **2** did not exhibit any activity for polymerization (entry 3).

For the ring-opening polymerization of TMOSC (1.0 M) in tetrahydrofuran (THF) with carbene **1** in the absence of alcohols, the molecular weights increase with conversion and the molecular weight distributions range from 1.4 < M_w/M_n < 1.7 up to approximately 50% conversion (See Supporting Information Figure S1–S3).⁴⁴ These results are consistent with a chain growth mechanism. At longer times, the polydispersities increase to M_w/M_n = 2.2, likely as a consequence of intra- and intermolecular transesterification reactions mediated by the carbenes or the terminal siloxides of the growing zwitterions.³⁴ The molecular weights of the p(TMOSC) do not correlate directly to the starting monomer to initiator ratio, implicating the contribution of several chain-transfer or chain-extension steps in addition to the addition of monomer to the zwitterions.^{23,45}

The ring-opening polymerization of TMOSC with the more nucleophilic carbenes **3** and **4** in THF is extremely rapid, reaching 95% conversion within 5 min at room temperature and yielding molecular weights above 500 kDa. The polymerization of TMOSC with carbene **3** in DMSO is also very fast but leads to lower molecular weights. In THF, carbene **4** exhibited the most rapid polymerization with molecular weights nearing 1000 kDa within 5 s of initiation. The ring-opening polymerization of TMOSC with carbene **3** was carried out on a 20 g scale, affording an 84% yield of p(TMOSC) with a M_w = 1 250 000 (M_w/M_n = 2.7). These molecular weights are nearly an order of magnitude greater than those observed in previously investigated nucleophilic ZROP systems¹⁸ and are comparable to those obtained by ring-expansion metathesis polymerization.¹⁶ Although the mechanism for forming high molecular weight chains is unclear, we propose that the addition of zwitterions to cyclized chains might provide a means of generating high molecular weight cyclic p(TMOSC).

Evidence for the cyclic structure of these polymers was obtained by gel-permeation chromatography (GPC) utilizing an in-line light-scattering detector and viscometer. The intrinsic viscosities of the polymers resulting from polymerization of TMOSC with carbene **1** or carbene **3** in the absence of an

alcohol initiator were compared to those synthesized with an alcohol initiator using the guanidine-based catalyst 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD). The ratio of these intrinsic viscosities was obtained from Mark–Houwink plots and found to range between 0.67–0.70 (Supporting Information Figure S3, S4). These data indicate that the p(TMOSC) generated under these conditions are predominantly cyclic^{16,46} but do not rule out the presence of small amounts of linear chains.^{5,47}

The polymerization of TMOSC with carbene **3** was also carried out for 24 h to generate low molecular weight p(TMOSC) (M_n = 3100 Da, M_w/M_n = 6.12). Analysis of the resulting sample by MALDI-TOF Mass Spectrometry revealed ions corresponding to cyclic p(TMOSC) (Figure 2). Although

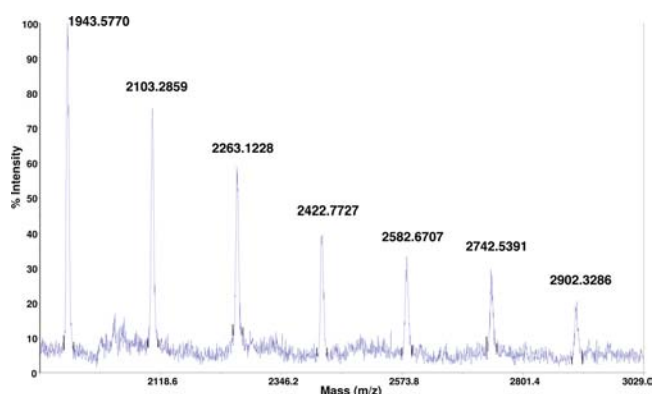


Figure 2. MALDI-TOF MS spectrum of cyclic p(TMOSC) oligomers. p(TMOSC)₁₄ = C₈₄H₂₂₄Si₂₈O₁₄Na⁺, m/z 2264.0.

the cyclic chains generated under these conditions might also arise from depolymerization reactions of higher molecular weight chains,^{46,48} the absence of linear chains with M_n < 3000 Da and the intrinsic viscosities of the higher molecular weight samples are consistent with the generation of cyclic polymers.

The p(TMOSC) materials generated from the zwitterionic ring-opening polymerization of TMOSC are amorphous, sticky materials. No glass transition temperature was observed down to –80 °C by DSC. To assess the hydrolytic stability of these materials, a sample of cyclic p(TMOSC) with M_n = 497 000, M_w/M_n = 1.81 (PS), was dissolved in a 10 v/v % aqueous THF solution for 16 h. A GPC chromatogram of the resulting polymer showed no decrease in molecular weight (M_n = 507 000 Da) or broadening of the polydispersity (M_w/M_n = 1.81), indicating that the cyclic p(TMOSC)s are hydrolytically stable under these conditions. Under basic conditions, a slight decrease in molecular weight was observed (M_n = 340 000 Da, M_w/M_n = 1.95), whereas in acidic solution, significant degradation of polymer was observed (M_n = 83 000 Da, M_w/M_n = 2.19).

The facile ring-opening polymerization of the carbosiloxane TMOSC and the generation of cyclic p(TMOSC) polymers implicates a nucleophilic zwitterionic ring-opening mechanism (Table 1).^{13,18,20–27} Nucleophilic attack of the N-heterocyclic carbene at the silicon atom of the carbosiloxane would generate zwitterionic intermediates that could add monomers to propagate. Cyclization could occur either at the silyl-imidazolium terminus or at internal silicon atoms of the growing zwitterion. The sensitivity of the ring-opening polymerization to the steric and electronic properties of the carbenes (Figure 1) is consistent with this hypothesis as the

sterically demanding carbene **2** exhibits no activity at room temperature in THF, whereas the smaller and more nucleophilic carbene **4** is extremely active.

Attempts to generate and isolate a zwitterionic intermediate have to date been unsuccessful. We carried out DFT calculations to assess the energies of likely intermediates (Figure 3). Optimized structures and relative enthalpies at

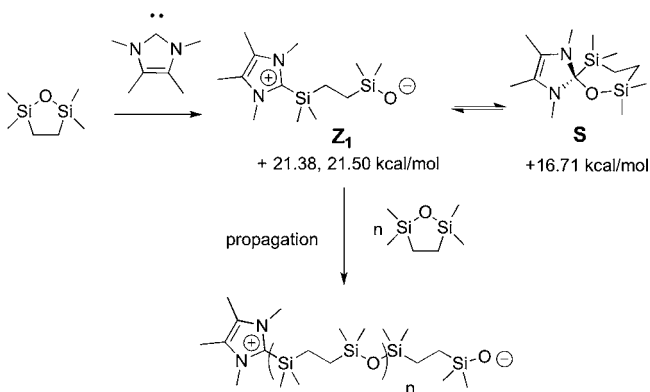


Figure 3. Proposed intermediates in the polymerization of TMOSC by carbene **4**.

298.15 K were calculated using Gaussian 09⁴⁹ at the M06⁵⁰/6-311G+(d,p) level of theory (see Supporting Information for computational details) in THF with the CPCM⁵¹ solvent model.

The enthalpies are referenced to TMOSC and carbene **4** at infinite separation in THF at 298.15 K. DFT calculations reveal two low-energy intermediates, the zwitterion **Z₁**, for which two local minima could be located at $\Delta H_{298.15} = 21.38$ and 21.50 kcal/mol, and a neutral spirocyclic intermediate **S** in which the TMOSC adopts a half chair conformation ($\Delta H_{298.15} = 16.71$ kcal/mol). We propose that the zwitterions are the active species mediating chain growth; the neutral spirocycles are likely dormant intermediates that reversibly open to the zwitterion.^{21,26}

In summary, the ring-opening polymerization of the carbosiloxane monomer TMOSC occurs readily with a series of *N*-heterocyclic carbenes in the absence of alcohol initiators to give high molecular weight cyclic p(TMOSC). These results illustrate the versatility of zwitterionic ring-opening polymerization^{11–13,18–30} for generating cyclic macromolecules. In addition, the generation of high molecular weight p(TMOSC) provides an intriguing class of entangled, high molecular weight cyclic macromolecules^{2–4} whose properties are currently under investigation.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600–1606.
- Halverson, J. D.; Lee, W. B.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. *J. Chem. Phys.* **2011**, *134*, 204905.
- Halverson, J. D.; Lee, W. B.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. *J. Chem. Phys.* **2011**, *134*, 204904.
- Kapnistos, M.; Lang, M.; Vlassopoulos, D.; Pyckhout-Hintzen, W.; Richter, D.; Cho, D.; Chang, T.; Rubinstein, M. *Nat. Mater.* **2008**, *7*, 997–1002.
- Roovers, J. In *Cyclic Polymers*, 2nd ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordrecht, 2000, p 347–384.
- McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834–1852.
- Topological Polymer Chemistry: Progress of cyclic polymers in synthesis, properties and functions*; Tezuka, Y., Ed.; World Scientific Publishing: Singapore, 2013.
- Cyclic Polymers*, 2nd ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordrecht, 2000.
- Endo, K. *Adv. Polym. Sci.* **2008**, *217*, 121–183.
- Deffieux, A.; Borsali, R. In *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH: Weinheim, 2007; Vol. 2, p 875–908.
- Yamamoto, T.; Tezuka, Y. *Polym. Chem.* **2011**, *2*, 1930–1941.
- Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 251–284.
- Brown, H. A.; Waymouth, R. M. *Acc. Chem. Res.* **2013**, *46*, 2585–2596.
- Jia, Z. F.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2085–2097.
- Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009**, *38*, 2202–2213.
- Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041–2044.
- Yamamoto, T.; Tezuka, Y. *Eur. Polym. J.* **2011**, *47*, 535–541.
- Shin, E. J.; Jeong, W.; Brown, H. A.; Koo, B. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2011**, *44*, 2773–2779.
- Suzuki, M. In *Encyclopedia of Polymer Science and Technology*, 4th ed.; John Wiley & Sons, Inc.: New York, 2013.
- Culkin, D. A.; Jeong, W.; Cshihony, S.; Gomez, E. D.; Balsara, N. P.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2627–2630.
- Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2007**, *129*, 8414–8415.
- Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813–5840.
- Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 4884–4891.
- Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093–2107.
- Shin, E. J.; Brown, H. A.; Gonzalez, S.; Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 6388–6391.
- Brown, H. A.; De Crisci, A. G.; Hedrick, J. L.; Waymouth, R. M. *ACS Macro Lett.* **2012**, *1*, 1113–1115.
- Shin, E. J.; Jones, A. E.; Waymouth, R. M. *Macromolecules* **2012**, *45*, 595–598.
- Guo, L.; Zhang, D. *J. Am. Chem. Soc.* **2009**, *131*, 18072–18074.
- Guo, L.; Lahasky, S. H.; Ghale, K.; Zhang, D. H. *J. Am. Chem. Soc.* **2012**, *134*, 9163–9171.
- Piedra-Aroni, E.; Ladavière, C.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2013**, *135*, 13306–13309.

- (31) Piccoli, W. A.; Haberland, G. G.; Merker, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 1883–1885.
- (32) Mazurek, M.; Chojnowski, J. *Macromolecules* **1978**, *11*, 347–356.
- (33) Suryanar, B.; Peace, B. W.; Mayhan, K. G. *J. Polym. Sci., Part A: Polym. Chem.* **1974**, *12*, 1109–1123.
- (34) Lohmeijer, B. G. G.; Dubois, G.; Leibfarth, F.; Pratt, R. C.; Nederberg, F.; Nelson, A.; Waymouth, R. M.; Wade, C.; Hedrick, J. L. *Org. Lett.* **2006**, *8*, 4683–4686.
- (35) Rodriguez, M.; Marrot, S.; Kato, T.; Stérin, S.; Fleury, E.; Baceiredo, A. *J. Organomet. Chem.* **2007**, *692*, 705–708.
- (36) Maji, B.; Breugst, M.; Mayr, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 6915–6919.
- (37) Chuma, A.; Horn, H. W.; Swope, W. C.; Pratt, R. C.; Zhang, L.; Lohmeijer, B. G. G.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L.; Rice, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 6749–6754.
- (38) Fuchter, M. J. *Chem.—Eur. J.* **2010**, *16*, 12286–12294.
- (39) Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2008**, *41*, 7399–7404.
- (40) Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 5390–5393.
- (41) Raynaud, J.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42*, 5996–6005.
- (42) Kuhn, N.; Kratz, T.; Blaser, D.; Boese, R. *Chem. Ber.* **1995**, *128*, 245–250.
- (43) Ghadwal, R. S.; Sen, S. S.; Roesky, H. W.; Tavcar, G.; Merkel, S.; Stalke, D. *Organometallics* **2009**, *28*, 6374–6377.
- (44) The NHC initiated ring-opening polymerization of the carbosiloxane TMOSC is quite sensitive to impurities. For a given highly purified batch of monomer, reproducible molecular weights and conversions were obtained, but some variations were noted in different monomer batches (see Figure S1, S2 of Supporting Information).
- (45) Kricheldorf, H. R. *Macromol. Rapid Commun.* **2009**, *30*, 1371–1381.
- (46) Clarson, S. J. In *Cyclic Polymers*; Second ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordrecht, 2000, p 161–183.
- (47) Lee, H. C.; Lee, H.; Lee, W.; Chang, T.; Roovers, J. *Macromolecules* **2000**, *33*, 8119–8121.
- (48) Kricheldorf, H. R.; Hachmann-Thiessen, H.; Schwarz, G. *Macromolecules* **2004**, *37*, 6340–6345.
- (49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.
- (50) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.
- (51) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669–681.