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Organocatalytic Living Ring-Opening Polymerization of Cyclic Carbosiloxanes

Bas G. G. Lohmeijer,[†] Geraud Dubois,[†] Frank Leibfarth,[†] Russell C. Pratt,[†] Fredrik Nederberg,[†] Alshakim Nelson,[†] Robert M. Waymouth,*[,‡] Charles Wade,[†] and James L. Hedrick*[,†]

IBM Almaden Research Center, 650 Harry Road, San Jose California 95123, and Department of Chemistry, Stanford University, Stanford, California 94305

hedrick@almaden.ibm.com; waymouth@stanford.edu

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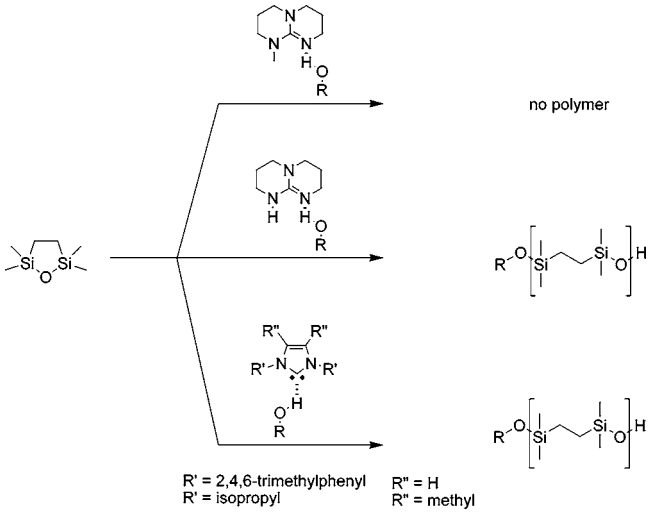
ABSTRACT



An organocatalytic route to narrowly dispersed poly(carbosiloxanes) of predictable molecular weight and end group fidelity is described. *N*-Heterocyclic carbenes (NHC) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalyze the ring opening of cyclic carbosiloxanes. The pK_b of the catalyst is important in preventing adverse transetherification reactions and obtaining well-defined polymers. Mechanistic studies indicate that hydrogen bonding to TBD or the NHC activates alcohols or silanols for ring-opening reactions.

Polysiloxanes and related structures have been widely used in a variety of applications, including medical, microelectronics, coatings, etc.[1] Polycarbosiloxanes (PCS) having carbosilane and siloxy linkages in the backbone are attractive materials by combining useful properties of polysiloxanes and polycarbosilanes.[2] PCS was first synthesized by the anionic ring-opening polymerization of cyclic carbosiloxanes (CCS) using alkali salts as initiators with only modest control of molecular weight and broad polydispersities.[3] This gives rise to a polymer composed of regular Si−O−Si−CH_2−CH_2 units. Interestingly, only recently the simplest example of this type of alternating copolymer with Si−CH_2−Si in the main chain has been synthesized.[4] Contrary to the linear polymers described above, cross-linked networks can be

[†] IBM Almaden Research Center.
[‡] Stanford University.

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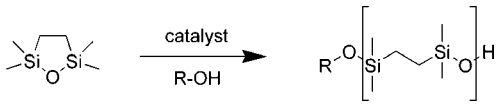
obtained through the ring-opening polymerization of bridged cyclic carbosiloxanes for applications as nonshrinking sol−gel systems.[5] In our own work, we have focused on the development of metal-free organocatalytic ring-opening polymerizations (ROP) of cyclic esters, which has led us to investigate the reactivity of known transesterification agents, such as DMAP,[6] phosphines,[7] *N*-heterocyclic carbenes[8] (NHCs), bifunctional amino-thioureas,[9] and guanidines.[10] Application of organocatalysis to the ring-opening polymerization (ROP) of cyclic carbosiloxanes would be highly desirable for emerging microelectronic applications (Scheme 1).

Scheme 1. Ring-Opening Polymerization of 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane

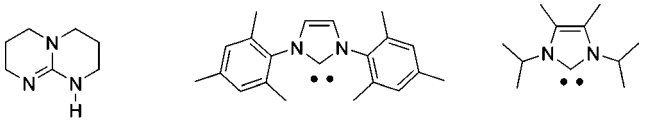


The demonstration by Breslow that stabilized singlet carbenes derived from thiamine cofactors are nucleophilic catalysts[11] and the pioneering work by Wanzlick,[12] Arduengo,[13] and Bertrand[14] in developing stable *N*-heterocyclic carbenes provided the inspiration for the development of *N*-heterocyclic carbenes as nucleophilic organic catalysts. Nucleophilic mechanisms have been proposed for NHC-catalyzed reactions, such as transesterification, ROP, benzoin-type condensations,[15,16] and Stetter reactions. However, NHCs are potent hydrogen bond acceptors and can activate alcohols for nucleophilic attack, as suggested by Movassaghi for the NHC-catalyzed amidation of unactivated esters with amino alcohols.[17] Arduengo[18] and Cowley[19] were among the first to report that NHCs form strong hydrogen bonds, and Clyburne[20] demonstrated the strong interactions between NHCs and organic acids. Clearly, these reports indicate another mode of activation for NHC that may have implications in other transformations.

Interesting similarities exist between the chemistry of catalysis by NHCs and another strongly basic organic molecule, the commercially available guanidine 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). First of all, the pK_a values of the conjugate acid of TBD in MeCN[21a] are close to those determined experimentally and computationally for those of the NHCs (pK_a = 26 vs 26−39).[19b] TBD has been applied as a strongly basic catalyst for a variety of reactions, including Michael additions,[22] Wittig reactions,[23] Henry reactions,[24] and transesterification reactions.[25] More importantly, Corey has shown that bicyclic guanidine catalysts exhibit bifunctional hydrogen bonding capabilities, including nucleophile activation, in the enantioselective Strecker synthesis of α-aminonitriles and α-amino acids.[26] De Mendoza used TBD in the design of artificial receptors that effectively mimic the catalytic activity of natural enzymes via hydrogen bonding complexes.[27] Recently, we have found TBD to be a very active catalyst for ROP of strained cyclic esters, providing polymers of controlled molecular weight and narrow polydispersities. While pseudo-anionic mechanisms are the most plausible, TBD appears to be also capable of activating the monomer via acyl−TBD intermediates.[10] Herein, we apply both NHCs and TBD to perform organocatalytic ROP of a cyclic carbosiloxane (2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (TMOSC)) to prepare polymers with predictable molecular weights, narrow polydispersities, and end group fidelity.

We have surveyed the catalytic activity of three representative organocatalysts in the ROP of TMOSC: TBD, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**1**) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**2**) (Scheme 2).[13,14]

Scheme 2. Organocatalysts for ROP of TMOSC



Conditions for the TBD- and NHC-catalyzed ROP of TMOSC were surveyed in solution using primary alcohols as initiators. Solution polymerizations in toluene ([CCS] = 2 M) generated narrowly dispersed polymers of predictable molecular weight, irrespective of the catalysts surveyed (Table 1).

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Table 1. Results of ROP of TMOSC by Different Organocatalysts

catalyst	$[M]_0/[I]_0$[a]	time	conversion (%)[b]	M_n (PDI)[c]
MTBD	100	48 h	0	
TBD	10	0.5 h	93	
	50	3 h	94	7300 (1.04)
	100	6 h	87	13100 (1.04)
	200	18 h	82	18300 (1.03)
	400	26 h	76	23400 (1.05)
1	100	0.5 h	80	12800 (1.14)
2	100	1 min	99	10200 (1.19)

[a] Initial monomer/alcohol ratio. [b] Determined by ^{1}H NMR. [c] Determined by GPC in THF equipped with an RI detector.

The polymerization of TMOSC by TBD was investigated in detail (Figure 1). Polymerizations proceed with a linear correlation between the molecular weight, as measured by gel permeation chromatography (GPC) and monomer conversion, as measured by ^{1}H NMR spectroscopy, an attribute consistent with a living polymerization. Furthermore, Figure 1 also shows the complete incorporation of the UV-active initiator, 4-pyrenebutan-1-ol, into the polymer backbone by overlaying the GPC traces as measured by both the RI and UV detector, demonstrating end group fidelity.

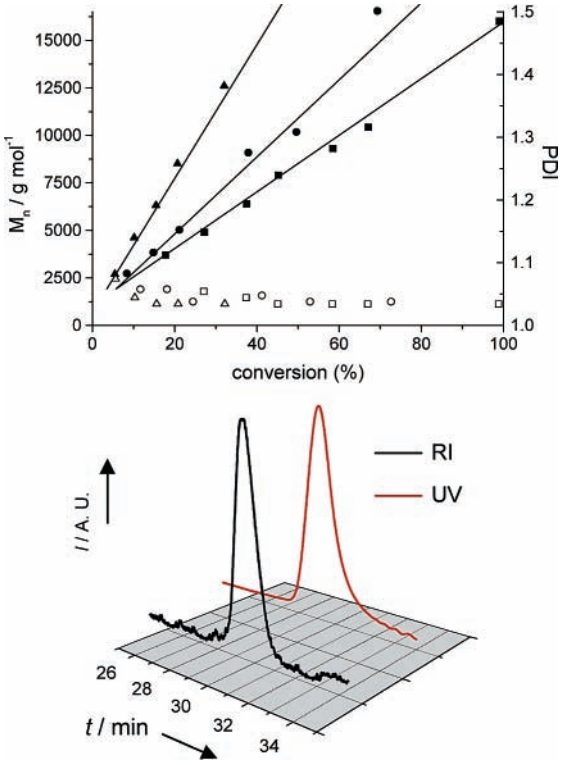

Figure 1. Polymerization of TMOSC initiated by pyrenebutanol using TBD as catalyst for targeted DPs of 100 (squares), 200 (circles), and 400 (triangles). Molecular weight is plotted as a function of conversion. Open symbols represent the obtained polydispersities (top). Overlay of the GPC traces by RI and UV detector (bottom).

Polydispersities (PDI = M_w/M_n) remain below 1.05 throughout the polymerization. Interestingly, the polymerization times are different for the different catalysts; **2** shows the highest activity, and polymerizations with a targeted degree of polymerization (DP) of 100 are completed within 1 min, whereas TBD requires 6 h to reach full conversion and **1** is between with 1 h. This relative reactivity parallels the relative pK_a's of the organocatalysts' conjugate acids (pK_a (TBD-H$^+$) = 26.0,[19a] pK_a (**1**-H$^+$) = 28.2,[19b] pK_a (**2**-H$^+$) = 35.7,[19b] CH_3CN). To the extent that hydrogen bonding activates the alcohol or silanol for ring opening, it might be expected that more basic catalysts would lead to faster rates, as observed. However, the slightly less basic *N*-methylated TBD (MTBD) (pK_a = 25.5)[19a] was inactive for ROP under these conditions, which implies that the basicity of the catalyst is not the only factor that influences catalytic activity. To investigate the influence of hydrogen bonding on the polymerization, ^{1}H NMR was used to probe the proton shift of the initiating alcohol and the propagating silanol. The 1:1 complexes of TBD, **1**, and **2** with pyrenebutanol and triethylsilanol, respectively, were prepared in C_6D_6 at 0.05 M.

The ^{1}H NMR spectra in C_6D_6 of TBD and pyrenebutanol and of TBD and triethylsilanol show clear shifts for the OH signal, from 2.0 to 5.3 ppm and from 2.3 to 6.5 ppm, providing clear evidence for hydrogen bonding. For catalysts **1** and **2**, these shifts are more pronounced, in line with their pK_a's (Table 2). MTBD showed a shift of the proton signal of pyrenebutanol to only 4.8 ppm.

Table 2. Proton Shifts for Hydrogen Bonded Complexes (0.05 M)

R−OH	shift (ppm)	complex	shift (ppm)
PyBu−OH	2.0	TBD	5.3
	2.0	**1**	5.5
	2.0	**2**	6.2
Et_3Si−OH	2.3	TBD	6.5
	2.3	**1**	6.7
	2.3	**2**	11.5

A complication that is usually encountered in the anionic polymerization of cyclic oxycarbosilanes is the equilibration of the polymer through silyl ether interchange reactions after monomer consumption. These adverse transetherification reactions lead to scrambling of the molecular weight and high polydispersities. This is normally circumvented by the addition of a terminating agent, such as trimethylchlorosilane, after a certain conversion to maintain narrow polydispersities under kinetic control. For catalysts **1** and **2**, we found indeed that after complete monomer conversion scrambling of the

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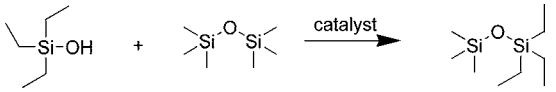
polymer takes place, judging from the increase in polydispersity (from 1.19 to 1.43 and 1.14 to 1.26 for **2** and **1** after 5 min and 1.5 h, respectively).

Remarkably though, when using TBD as the catalyst, no scrambling took place, and polydispersities were unchanged after allowing the reaction mixture to stand for 3 days. Apparently the level of activation of the terminal silanols through hydrogen bonding with TBD is not sufficient to promote transetherification of the polymer backbone. In case of the NHC catalysts **1** and **2**, that level of activation is sufficient, and adverse side reactions after polymerization occur. Addition of hexamethyldisiloxane to the 1:1 complexes of triethylsilanol and the three organocatalysts clearly showed the scrambling products for **2**, but no reaction in case of **1** and TBD, proving TBD's inability to transetherify (Scheme 3).

Scheme 3. Scrambling Products



The exquisite control of the TBD catalyst relative to the NHC is also manifested in the ROP of the commercially used hexamethylcyclotrisiloxane (D3) (Scheme 4). The

Scheme 4. ROP of Hexamethylcyclotrisiloxane (D3)

polymerization was surveyed in toluene ([D3] = 2.2 M) using pyrenebutanol as an initiator in the presence of either TBD or **2** with a targeted DP of 100. Using the UV detector of the GPC, narrowly dispersed products were obtained with the TBD catalyst (PDI < 1.2), while polymerization from **2** proceeded with considerably less control, as judged by the broader polydispersities (>1.4). To quantify this, D3 initiated from PEB−OH with a targeted DP of 150 yielded a narrowly dispersed block copolymer with a M_n of 33 000 g/mol and PDI of 1.26.

The ability to initiate from a wide variety of functional substrates will have enormous implications for tailor-made macromolecules in a variety of applications. We have surveyed hydroxy functional macroinitiators, diols, silanols, primary amines, secondary amines, and thiols as candidate initiators using TBD as the organocatalyst (Table 3).

Table 3. Effect of Different Initiators Using TBD

initiator	$[M]_0/[I]_0$[a]	time	conversion (%)[b]	M_n (PDI)[c]
$PEO_{120}-OH$[d]	50	2 h	81	8500 (1.08)
$PS_{35}-OH$[e]	50	2 h	93	8200 (1.14)
$PEB_{100}-OH$[f]	50	2 h	61	7800 (1.06)
$HO-C_2H_4-OH$	50	2 h	99	3800 (1.13)
Et_3Si-OH	100	6 h	95	12300 (1.04)
$(C_3H_7)_2-NH$	100	48 h	0	
$C_6H_{13}-NH_2$	100	48 h	0	
$C_{18}H_{37}-SH$	100	48 h	0	

[a] Initial monomer/alcohol ratio. [b] Determined by ^1H NMR. [c] Determined by GPC in THF equipped with an RI detector. [d] M_n = 5000 g mol^{-1}, PDI = 1.05. [e] Prepared by NMP, M_n = 3900 g mol^{-1}, PDI = 1.11. [f] M_n = 5600 g mol^{-1}, PDI = 1.04.

The efficiency of the initiation, tolerance of catalysts to functionality, and versatility and simplicity of polymerization allows for the facile synthesis of block copolymers. Monohydroxy functional oligomers of poly(poly(ethylene oxide)) (PEO), polystyrene (PS), and polybutadiene (PEB) all having molecular weights of approximately 5000 g/mol were used as macroinitiators for the ROP of TMOSC with a targeted DP of 50. Narrowly dispersed, monomodal block copolymers with no detectable homopolymer contamination were generated with high monomer conversion together with the expected increase in molecular weight. Polymerization of TMOSC initiated from ethylene glycol provides a facile route to dihydroxy-terminated oligomers (Table 3). Amines and thiols were ineffective as initiators for the ROP of TMOSC; this may reflect the lower pK_a's of these initiators.

Organocatalytic routes to poly(carbosiloxanes) using both guanidine and *N*-heterocyclic carbene catalysts in the presence of an alcoholic initiator are described. A linear correlation between molecular weight and conversion was demonstrated along with the initiation efficiency and end group fidelity. The versatility of this approach was demonstrated with functional initiators and block copolymers.

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Supporting Information Available: Experimental methods, procedures, and selected analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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