# Regio- and Stereospecific Cyclopolymerization of Bis(2-propenyl)diorganosilanes and the Two-State Stereoengineering of 3,5-*cis,isotactic* Poly(3,5-methylene-1-silacyclohexane)s

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S *Supporting Information*

ABSTRACT: Transition-metal-mediated coordination cyclopolymerization of bis(2-propenyl)dimethylsilane (**1a**) using the C_1-symmetric, group 4 metal preinitiator, $(\eta^5\text{-}C_5Me_5)Zr\text{-}(Me)_2[N(Et)C(Me)N(^tBu)]$ (**I**), in combination with 1 equiv of the borate coinitiator, $[PhNHMe_2][B(C_6F_5)_4]$ (**II**), proceeds in a regio- and stereospecific manner to provide highly stereoregular 3,5-*cis,isotactic* poly(3,5-methylene-1,1-dimethyl-1-silacyclohexane) (**2a**). Successful stereoengineering of **2a** to eliminate undesirable crystallinity while preserving a high T_g value of >120 °C was subsequently accomplished by employing a "two-state" propagation system that uniquely produces an isotactic stereoblock microstructure of decreasing stereoblock length with decreasing percent level of "activation" of **I** with **II**. The controlled character of cyclopolymerization of **1a** using the less sterically encumbered preinitiator, $(\eta^5\text{-}C_5Me_5)Hf(Me)_2[N(Et)C(Me)N(Et)]$ (**III**), and 1 equiv of **II** was used to prepare well-defined poly(1-hexene)-*b*-poly(3,5-methylene-1-silacyclohexane) block copolymers through sequential monomer additions.
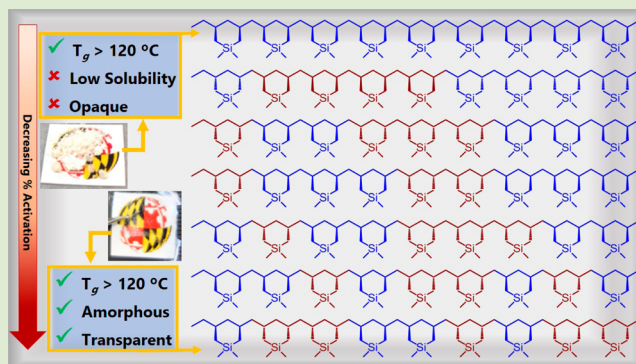
P olycarbosilanes, which encompass a large variety of extended arrays of carbon–carbon and carbon–silicon bonded macromolecular frameworks, have become increasingly attractive for use in a range of advanced technological applications.[1,2] The further design, synthesis, and evaluation of new fundamental forms of polycarbosilanes, however, is still severely hampered by the limited set of synthetic and polymerization methodologies that are available.[1] Herein, we now present a preliminary account of the successful development of a new category of polycarbosilane that is readily accessible through the regio- and stereospecific cyclopolymerization of bis(2-propenyl)diorganosilanes (**1**) to provide highly stereoregular 3,5-*cis,isotactic* poly(3,5-methylene-1-silacyclohexane)s (**2**), as depicted in Scheme 1. We further demonstrate that by employing a "two-state" propagation mechanism, the programmed stereoengineering of **2** can be accomplished as a means by which to modify and optimize the solid-state bulk properties of this unique class of material. Given

the incredible range of derivatives for **1** that are readily available with different R^1 and R^2 substituents, the present report serves to establish a highly versatile new polycarbosilane platform for materials research and applications.

Recently, we reported the living regio- and stereoselective coordination cyclopolymerization of 1,6-heptadiene using the C_1- symmetric cationic group 4 metal initiator, $\{Cp*Zr[N(Et)C(Me)N(^tBu)](Me)\}[B(C_6F_5)_4]$ ($Cp* = \eta^5\text{-}C_5Me_5$), that is generated in situ in solution through "activation" of the neutral preinitiator, $Cp*Zr(Me)_2[N(Et)C(Me)N(^tBu)]$ (**I**) with a stoichiometric amount of the borate coinitiator, $[PhNHMe_2]\text{-}[B(C_6F_5)_4]$ (**II**), to provide highly stereoregular and crystalline 1,3-*cis,isotactic* poly(1,3-methylenecyclohexane) (PMCH); a unique polyolefin that is characterized by possessing both high glass transition and melt temperatures of $T_g = 95$ °C and $T_m = 208$ °C, respectively.[3–5] Subsequent stereoengineering of the stereochemical microstructure of 1,3-*cis,isotactic* PMCH, using a previously reported two-state stereomodulation process that is based on activation of **I** with varying substoichiometric amounts of **II** (e.g., [**II**]/[**I**] = 0.95, 0.90, 0.85, 0.80, 0.75, and 0.50),[3,6] further provided an extended family of 1,3-*cis,isotactic* stereoblock PMCH materials of decreasing stereoblock length that were now shown to be amorphous in the solid state by

Scheme 1
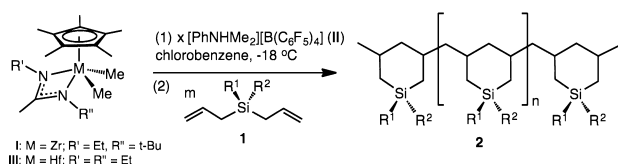
wide-angle X-ray diffraction (WAXD), but for which a desired high T_g value of >95 °C was still retained according to differential scanning calorimetry (DSC). Finally, the living character of these cyclopolymerizations provided access to novel "hard"−"soft" PMCH-poly(1-hexene) polyolefin diblock copolymers that were shown to adopt microphase-separated morphologies in the solid state.[7]

With the above results in hand, we next targeted the development of a corresponding class of high T_g polycarbosilanes based on the cyclopolymerization of **1** to **2** according to Scheme 1 that could also conceivably provide microphase-separated polycarbosilane-polyolefin block copolymers that retain high dimensional stability at elevated temperatures for use in certain advanced applications, such as nanolithography.[2a,b] In this regard, although the commercially available bis(2-propenyl)diorganosilane **1a** ($R^1 = R^2 = Me$) has been the subject of several previous attempts to prepare structurally well-defined polycarbosilane materials though transition-metal coordination polymerization, to date, only poor and inconclusive results have been obtained, and to the best of our knowledge, neither the molecular structure nor the dependence of solid-state physical properties on stereochemical microstructure have ever been clearly established for a poly(3,5-methylene-1-silacyclohexane) homopolymer based on **2**.[8−10]

In the present study, the coordinative cyclopolymerization of **1a** was successfully achieved according to Scheme 1 and Table 1.[11] More specifically, upon addition of 100 equiv of **1a** to the

Table 1. Coordination Cyclopolymerization of 1a[a]

run	Pre[a]	[II]/[Pre]	$M_n{}^{b}$ (kDa)	Đ	$T_g{}^{c}$ (°C)	$T_m{}^{c}$ (°C)
1	I	1.00	14.8	1.52	123	264
2	I	0.75	14.8	1.41	125	
3	I	0.65	18.5	1.38	125	
4	I	0.50	13.4	1.34	126	
5	I	0.30	13.6	1.20	127	
6	III	1.00	11.8	1.13	115	

[a]Polymerization conditions: Pre = preinitiator; [Pre] = 30 μmol in 15 mL of PhCl; [**1a**] = 3 mmol (100 equiv), t_p = 1−8 h, T_p = −18 °C. [b]Determined by GPC (THF, 25 °C, polystyrene standards). [c]Determined by DSC.

active cationic initiator generated in situ using a [II]/[I] ratio of 1.0 in chlorobenzene (PhCl) at −18 °C, a semicrystalline polymeric material corresponding to **2a** (vide infra) was obtained in 3 h after the usual work-up and purification (run 1, Table 1).[11] In similar fashion, several additional samples of **2a** were prepared by systematically decreasing the amount of the borate **II** used to activate the preinitiator **I** (runs 2−5, Table 1). Finally, in order to investigate the dependence of the stereochemical microstructure of **2a** on the gross symmetry properties of the active transition-metal propagating species, the closely related C_s-symmetric preinitiator, Cp*Hf(Me₂)[N-(Et)C(Me)N(Et)] (**III**),[12] was used in place of **I** while employing a full equivalent of **II** (run 6, Table 1).

The collection of different samples of **2a** prepared according to the conditions of Table 1 each displayed distinct differences in stereochemical microstructure, as characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and that were further found to correlate with changes in the solid-state bulk properties. To begin, Figure 1a,b compare the ^{13}C{^{1}H} NMR (200 MHz, TCE-d_2, 110 °C; TCE = 1,1,2,2-tetrachloroethane) spectra for **2a**, as obtained from the preinitiators **I** and **III**, respectively (cf.,
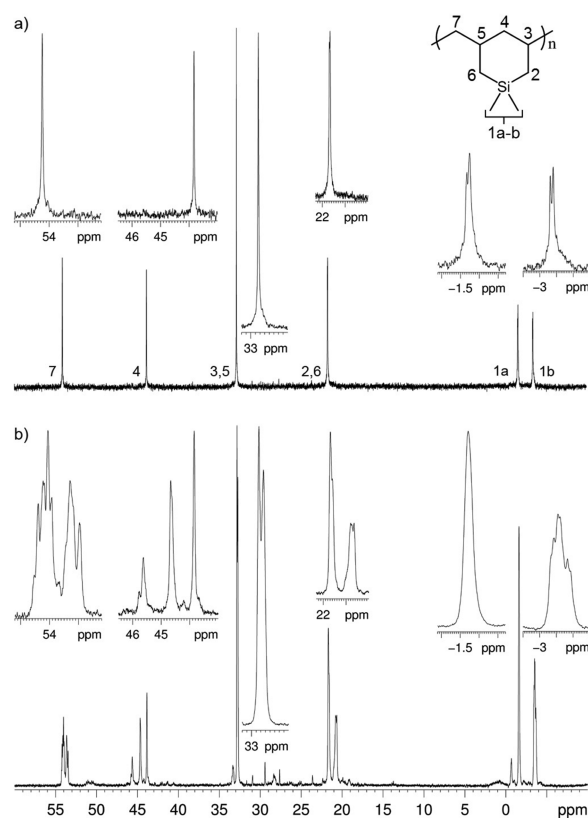

Figure 1. ^{13}C{^{1}H} NMR (200 MHz, TCE-d_2, 110 °C) spectra of (a) **2a** from run 1, Table 1 and (b) **2a** from run 6, Table 1.

runs 1 and 6 in Table 1). As shown, these data are consistent with a stereospecific cyclopolymerization occurring with use of the former preinitiator to provide a highly stereoregular 3,5-*cis,isotactic* poly(3,5-methylene-1-silacyclohexane) microstructure in which the six-membered ring is conformationally "locked in place", as evidenced by the separate resonances being observed for the two methyl groups attached to silicon (cf., resonances *1a* and *1b* in Figure 1a). In keeping with its highly stereoregular nature, this sample of **2a** is semicrystalline, as supported by WAXD data,[11] and a DSC analysis reveals a distinct T_g value of 123 °C and a T_m value of 264 °C (see run 1, Table 1). In contrast, the ^{13}C NMR spectrum for **2a** obtained using **III** clearly shows the result of a much reduced degree of stereoselectivity occurring during cyclopolymerization of **1a** that gives rise to an increase in the number and complexity of resonances attributed to the 3,5-*cis* ring structure due to loss of long-range isotacticity and a small degree of 3,5-*trans* ring stereochemistry. As the data in Table 1 further reveal, the more random stereochemical microstructure of this **2a** sample also gives rise to an amorphous solid state that is now lacking a distinct T_m, but, interestingly, one that still retains a high T_g value of 115 °C by DSC.

The inter-relationship between stereoregularity and crystallinity for **2a** can be further probed through a similar analysis of sets of data obtained for samples prepared with various levels of activation of **I** by the coinitiator **II** (runs 2−5 in Table 1). Importantly, as is readily apparent from the collection of ^{13}C and ^{29}Si NMR spectra presented in Figure 2, a steady decrease in the ratio of [II] to [I] tracks with an increasing probability of stereoinversion of configuration at the metal center of the propagating species via rapid dynamic methyl group exchange with a configurationally unstable inactive dormant state, that, in
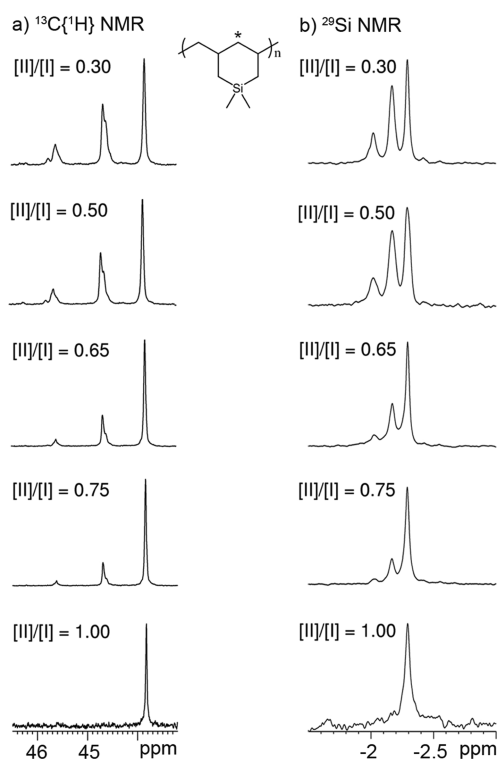
a) ^{13}C{^{1}H} NMR

[II]/[I] = 0.30

b) ^{29}Si NMR

[II]/[I] = 0.30

[II]/[I] = 0.50

[II]/[I] = 0.50

[II]/[I] = 0.65

[II]/[I] = 0.65

[II]/[I] = 0.75

[II]/[I] = 0.75

[II]/[I] = 1.00

[II]/[I] = 1.00

46   45   ppm

-2   -2.5 ppm

Figure 2. (a) Partial ^{13}C{^{1}H} NMR depicting the carbon atom at position 4 (200 MHz, TCE-d_2, 110 °C) and (b) ^{29}Si{^{1}H} NMR (100 MHz, TCE-d_2, 90 °C) spectra for **2a** obtained from (bottom to top) runs 1−5, Table 1.

turn, gives rise to an isotactic stereoblock microstructure of decreasing stereoblock length for **2a** with a concomitant increase in the level of *disyndiotactic* MrM tetrad incorporation, as depicted in Scheme 2.[3,4,13] Gratifyingly, as with 1,3-

Scheme 2
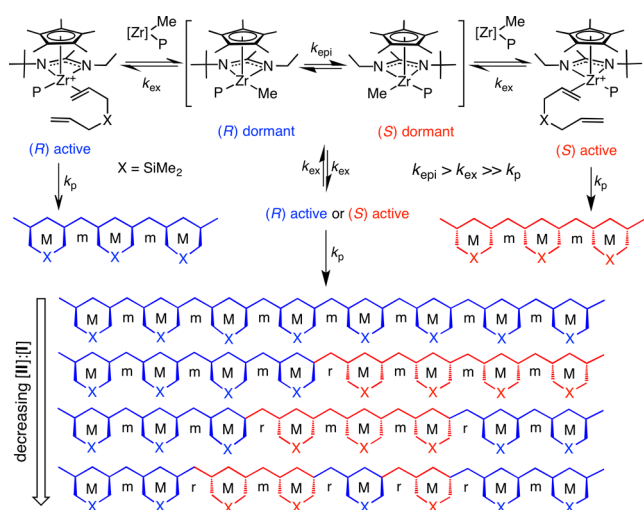
cis,isotactic PMCH,[4] the isotactic stereoblock microstructures of these different amorphous grades of **2a** appear to be sufficient for disrupting the propensity of polymer chain packing and crystallization in the solid state, as evidenced by the disappearance of a discernible T_m by DSC.[11] However, the geometrically constrained six-membered rings that comprise the backbone of **2a** ensure that a high T_g value of 125 °C is

maintained. It is also important to note that these amorphous grades of **2a** are freely soluble in hydrocarbon-based solvents such as toluene or chlorobenzene.

Through a number of previous studies, the living character of coordination polymerizations and copolymerizations of ethene, α-olefins, and α,ω-nonconjugated dienes using the initiator derived from 100% activation of **I** by **II** has been firmly established through several analytical (kinetic) and spectroscopic means.[3] In the present work, exhaustive end-group analysis of a low molecular weight sample (e.g., M_n = 2500 Da) by 1D and 2D ^{1}H and ^{13}C{^{1}H} NMR (800 and 200 MHz, respectively) showed only resonances expected for the 3-methyl-1-silacyclohexyl end groups of **2a** shown in Scheme 1 and with no evidence being obtained for vinylic resonances that might arise by chain-termination of the propagating species through β-hydrogen transfer processes. However, kinetic analysis of polymerizations conducted with 100% activation of **I** using the conditions provided in Table 1 clearly reveal a nonlinear dependence of M_n as a function of monomer conversion, as well as a steady increase in the polydispersity index, Đ ($=M_w/M_n$), as determined by gel permeation chromatography (GPC).[14] Upon further close inspection of ^{1}H NMR (800 MHz) spectra of either commercially obtained or independently synthesized samples of the monomer **1a**, it could be determined that these materials invariably contain 1−2% of isomeric 1-propenyl groups in place of the desired 2-propenyl substituents. Accordingly, given the inability to purify **1a** to a higher extent using conventional methods, it is likely that undesirable insertion of 1-propenyl end-groups leads to chain-termination. It also appears that the relative rates for propagation versus such a chain-termination event can be significantly influenced by the structure of the initiator, and the Đ value of 1.13 obtained using the preinitiator **III** in combination with **II** suggests that the *controlled* cyclo-polymerization of **1a** can be achieved under the conditions investigated (cf., run 6).[14] At the present time, however, we cannot account for the curious trend in the GPC data for the collection of samples of **2a** in which the relatively large Đ value of 1.52 obtained at 100% activation of **I** steadily decreases in magnitude as the ratio of [**II**]/[**I**] decreases and reaching a Đ value of 1.20 at 30% activation (cf., runs 1−5 in Table 1). Further investigations of the origin(s) of this phenomenon using different derivatives of **1** and polymerization conditions are currently in progress.

Based on the above preliminary findings, the next consideration was to determine if well-defined (high T_g) "hard"−(amorphous) "soft" polyolefin-*b*-poly(3,5-methylene-1-silacyclohexane) block copolymers could be prepared through sequential addition of an α-olefin (e.g., propene or 1-hexene) followed by that of **1a** or vice versa. For this study, the preinitiator **III** was chosen over **I** given the more favorable cyclopolymerization kinetics displayed by the former, and gratifyingly, sequential addition of 200 equiv of 1-hexene (t_p = 2 h) followed by 120 equiv of **1a** (t_p = 2 h) provided a poly(1-hexene)-*b*-poly(3,5-methylene-1-silacyclohexane) diblock co-polymer (**3**) for which the ^{13}C NMR spectrum shown in Figure 3a and GPC data (cf., M_n = 24.8 kDa; Đ = 1.20) were fully consistent with a targeted well-defined block architecture with a polycarbosilane mole fraction of 33% (by ^{1}H NMR).[11]

A final important question addressed in the present work is whether successful coordination cyclopolymerization of bis(2-propenyl)diorganosilanes using **I** or **III** can be extended to a larger set of different derivatives of **1**, including where $R^1 \neq R^2$,
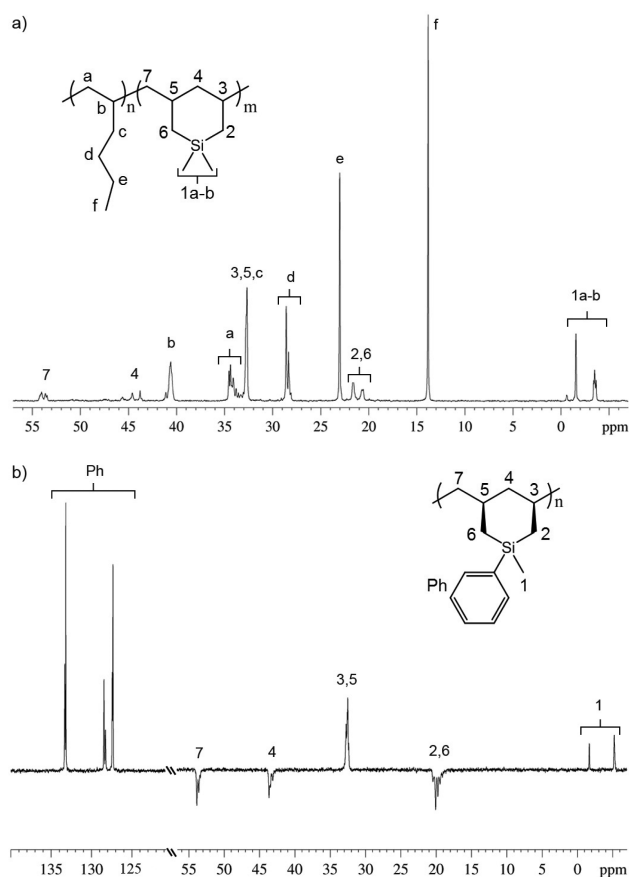
Figure 3. (a) $^{13}C\{^1H\}$ NMR spectra (100 MHz, TCE-d_2, 90 °C) of the block copolymer **3** and (b) $^{13}C\{^1H\}$ DEPT-135 spectrum of **2b**.

given the ease of synthesis of these compounds from commercially available precursors. Thus, in a preliminary study, both **I** and **III** were successful as preinitiators for the cyclopolymerization of **1b**, where R^1 = Me and R^2 = Ph to provide a polymeric material for which spectroscopic and analytical analyses are all fully consistent with a structure corresponding to that expected for **2b**, albeit, one with a more complex stereochemical microstructure as evidenced by the $^{13}C\{^1H\}$ DEPT-135 NMR spectrum shown in Figure 3b.[11,15] Details of a more thorough investigation of the synthesis, structures, and properties for this new class of polycarbosilane represented by **2**, and potential applications, will be reported in due course.

ASSOCIATED CONTENT

S Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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