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Anionic Cyclopolymerization of Linked Bis(vinylsilyl) Monomers: Substituent Control over Polymer Structure

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ABSTRACT: The *n*-BuLi-initiated polymerization of $(CH_2{=}CHMe_2Si)_2NR$ (R = Me, **1**; R = $SiMe_3$, **2**) gave highly regular polymers **3** and **4** which consisted entirely of linked cyclic units with no detectable cross-links or linear segments. The substituent R profoundly affected the ring size found in the resulting cyclopolymer: monomer **2** gave only five-membered rings in the polymer backbone, while **1** formed both five- and six-membered rings. The stereochemistry of polymerization of **2** was found to be solvent-dependent: the ratio of cis to trans five-membered rings in **4** increased when the reaction was conducted in the presence of coordinating cosolvents (e.g., Et_3N). Polymers **3** and **4** could be cleanly ring opened with HF(aq) to give poly(vinyldimethylfluorosilanes) **7** and **8**. The synthetic utility of polymer **8** was demonstrated by its reaction with a variety of nucleophilic reagents to give highly regular, highly functionalized polymers of the type $(CH_2CHSi(CH_3)_2R')_n$.

Introduction

Cyclopolymerization[1,2] is a useful technique for controlling the regio- and stereochemistry of monomer additions, leading to polymers with well-defined microstructures.[3] Recently, we have been exploring the application of cyclopolymerization to generate polymers that incorporate reactive main-group functionalities such as organophosphorus ylides[4] and Si−X bonds.[5] The latter study involved the radical-initiated polymerizations of several bis(vinyldimethylsilyl) compounds, $(CH_2{=}CHMe_2Si)_2X$ (X = O, NH, NMe), to give soluble polymers with little residual unsaturation.[5] Although cyclopolymerization was successfully observed under these conditions, it was felt that better control over structure might be achieved by employing anionic initiation.

Anionic polymerization of vinylsilanes has been known for some time,[6−27] although only a few examples of anionic cyclopolymerization of bis(vinylsilyl) monomers have been reported.[17,18,20,27] In cases where both vinyl groups are attached to the same silicon atom, a cyclopolymerization mechanism is not strictly followed, leading to the presence of unreacted vinyl groups.[17,20] However, by including a spacer between the vinylsilyl groups, as in $(CH_2{=}CHMe_2Si)_2CH_2$, the propensity toward cyclopolymerization is increased, and complete reaction of the vinyl groups is observed.[18]

Bis(vinylsilyl) monomers employing amino groups as spacers should be suitable for anionic cyclopolymerization, since Si−N bonds are known to be stable to nucleophilic attack by alkyllithium reagents.[28,29] One attractive feature of these monomers is that once the polymerization is complete, the Si−N bonds can be cleaved by acids, HX, to form reactive Si−X bonds which then can be further derivatized.[29] In this way, monomers of the type $(CH_2{=}CHMe_2Si)_2NR$ ought to function as masked halosilanes, $CH_2{=}CHMe_2SiX$, the amino linking group NR serving both to protect the reactive Si−X functionality and to exert control over the regiochemistry of the polymerization.

The anionic cyclopolymerization of two amine-linked bis(vinylsilyl) monomers $(CH_2{=}CHMe_2Si)_2NR$ (R = Me, **1**; R = $SiMe_3$, **2**) was studied. Under standard anionic polymerization conditions these monomers gave soluble polymers with well-defined structures. The steric bulk of the amino linking group was found to exert a strong effect on the reactivity of the monomer, leading to marked changes in the microstructures of the resulting cyclopolymers. Cleavage of the Si−N bonds in the cyclopolymers with aqueous hydrofluoric acid gave highly functionalized poly(fluorosilanes), to which a variety of pendant groups could be attached through simple nucleophilic displacement reactions.

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Table 1. Molecular Weights[a] of the Cyclopolymers

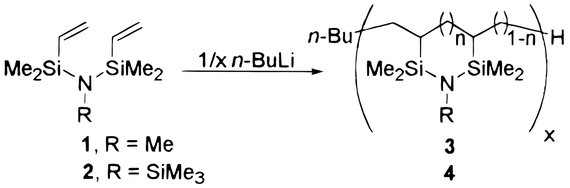
monomer	n-BuLi (mol %)	solvent(s)	polymer	yield	M_n	M_w	M_w/M_n
1	10	8:1 hexane/Et_3N	**3a**	$87^{b,c}$	4570^{c}	6870^{c}	1.51^{c}
1	5	8:1 hexane/Et_3N	**3b**	53^{d}	5060^{d}	10100^{d}	2.03^{d}
2	10	8:1 hexane/Et_3N	**4a**	92	6330	6940	1.10
2	5	8:1 hexane/Et_3N	**4b**	96^{e}	9440^{e}	10800^{e}	1.14^{e}
2	4	8:1 hexane/Et_3N	**4c**	97^{d}	10600^{d}	11400^{d}	1.08^{d}
2	2.2	8:1 hexane/Et_3N	**4d**	99	15000	17900	1.20
2	5	hexane	**4e**	99^{d}	11500^{d}	12900^{d}	1.12^{d}
2	5	8:1 hexane/THF	**4f**	97^{b}	6260	7740	1.24

[a] Determined by gel permeation chromatography (GPC) relative to polystyrene standards. [b] Incomplete consumption of monomer was observed. [c] Average of four experiments. [d] Average of two experiments. [e] Average of three experiments.

Results and Discussion

Synthesis and Characterization of Cyclopolymers. The n-BuLi-initiated polymerization of 1,3-divinylpentamethyldisilazane (**1**) was studied briefly by Stober, Michael, and Speier in the late 1960s.[27,30] They reported obtaining a soluble polymer with low residual unsaturation but were only able to characterize it by osmometry, combustion analysis, and infrared spectroscopy. We have reexamined the polymerization of **1** as well as that of bis(vinyldimethylsilyl)(trimethylsilyl)amine (**2**)[31] whose cyclopolymerization behavior had not been studied previously.

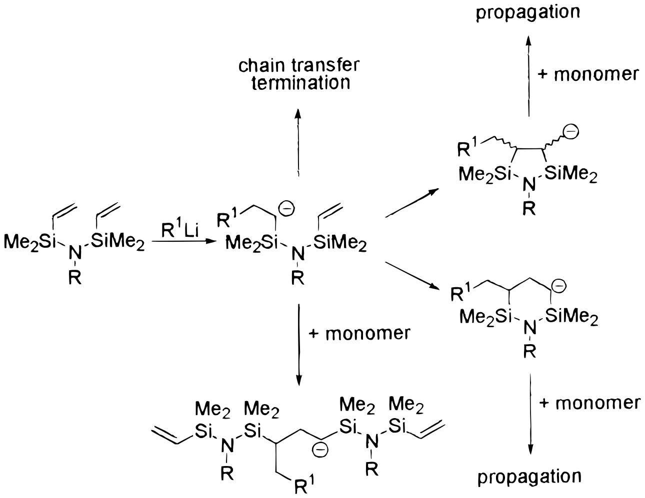
Monomer **1** reportedly formed only insoluble, cross-linked polymers when treated with n-BuLi in hydrocarbon solvent; however, when triethylamine was added as cosolvent, soluble polymers were obtained instead.[27,30] For this reason, we employed an 8:1 hexane/triethylamine solvent mixture for the n-BuLi-initiated polymerization of monomers **1** and **2** (eq 1). The reactions were allowed to proceed at ambient temperature for 3–5 days before quenching with methanol. The polymers thus formed were obtained by precipitation from toluene/methanol as white solids which were very soluble in common organic solvents. Results of the polymerizations of **1** and **2** carried out with different monomer/initiator ratios are compiled in Table 1.



(1)

From the data in Table 1, it can be seen that the polymerization of **1** terminated prior to complete conversion of the monomer. Reaction times in excess of 5 days did not increase the conversion, nor did further exhaustive purification of the monomer. In contrast, **2** quantitatively polymerized at a variety of monomer/initiator ratios to give polymers **4a**–**d** in high isolated yields. Monomer **2** also quantitatively polymerized in the absence of triethylamine cosolvent to give a completely soluble cyclopolymer **4e**. Substitution of THF for the triethylamine cosolvent led to incomplete conversion of **2**, presumably due to termination reactions involving reaction of the organolithium intermediates with THF.[32]

Scheme 1. Possible Reaction Pathways in the Cyclopolymerization of 1 and 2

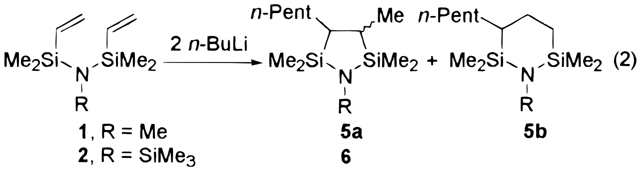


Scheme 1 illustrates the reaction pathways that are possible during the anionic polymerization of **1** and **2**. The alkyllithium initiator or growing polymer chain end (R^1Li) most likely adds to the terminal position of the vinyl group, yielding a stabilized carbanionic intermediate.[33] This intermediate may then react with the second vinylsilyl moiety in either an endo or exo fashion, leading to the formation of six- and five-membered ring repeat units, respectively, which further propagate the chain. The acyclic intermediate may also react in an intermolecular reaction with a second monomer unit, incorporating a SiNSi linkage into the polymer backbone and leaving a dangling vinyl group capable of forming cross-links with other growing polymer chains. Termination and/or chain transfer processes could also occur, as these are well-precedented in the anionic polymerization of vinylsilanes.[8,9,13,19,23,26,34]

Polymers **3a** and **3b** possessed monomodal, but somewhat broadened, molecular weight distributions (as measured by GPC; see Table 1). The molecular weight of **3b** was only slightly higher than that of **3a**, due to termination of the polymerization. Polymers **4a**–**f** gave monomodal GPC traces with polydispersities close to 1, reflecting a lack of significant termination reactions. The molecular weights of **4a**–**d** increased with increasing monomer/initiator ratios.

The high solubilities of **3** and **4** and their relatively narrow, monomodal molecular weight distributions suggested that these monomers polymerized predominantly through a cyclopolymerization mechanism without significant cross-linking reactions. The question still remained, however, as to the regioselectivity of the cyclization steps. To gain more insight into this question, **1** and **2** were reacted with initiator under conditions expected to favor the formation of monomolecular products. Such model cyclization reactions have proven to be useful tools for the structural characterization of cyclopolymers.[35]

When **1** and **2** were added dropwise to dilute solutions of excess n-BuLi, monomolecular cyclized products **5** and **6** were formed along with oligomeric byproducts (eq 2). Products **5** and **6** could be separated from the less-volatile byproducts by vacuum distillation and were isolated in low yields (14 and 11%, respectively) as colorless oils. These oils gave correct elemental analyses



(2)

for monomolecular adducts of the monomers with 1 equiv of *n*-butane but were shown by GC/MS to consist of mixtures of isomers (three for **5**, two for **6**).

Two isomers of **5** (designated **5a**) had similar mass spectra; these were separated from the third isomer (**5b**) by preparative GC, and both fractions were fully characterized by multinuclear NMR spectroscopy. The NMR spectra of **5a** and **5b** were consistent with those of previously synthesized products of radical cyclizations of **1**;[36] thus, the two isomers of **5a** were identified as five-membered rings, and the single isomer **5b** was identified as a six-membered ring. The ratio **5a**:**5b** was 1.3:1, and the two isomers (cis and trans) of **5a** were present in a 1.5:1 ratio. (The predominating stereoisomer was not identified.) A similar analysis showed that the two isomers of product **6** (present in a 1:1 ratio) were cis and trans five-membered rings. Thus, **2** cyclizes with a higher regioselectivity for the formation of five-membered rings than **1**, most likely as a result of its larger N substituent. Nearly identical regioselectivities were observed in the radical cyclizations of these two dienes.[36]

Assuming the cyclization steps of the polymerizations of **1** and **2** have regioselectivities similar to those of the model cyclizations discussed above, polymer **3** should consist of a mixture of five- and six-membered ring backbone units and polymer **4** of only five-membered rings. To test this hypothesis, polymers **3** and **4** were characterized by infrared (IR), ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies, and their spectra were compared to those of cyclic model compounds **5** and **6**. The spectra of **3** and **4** did not change with chain length (with the exception of the relative intensities of the end group signals).

The IR spectra of **3** and **4** indicated the absence of residual olefinic groups but otherwise provided no structural information. The ^{1}H NMR spectra of **3** and **4** (Table 2) also did not show residual vinyl resonances but instead displayed broad aliphatic signals, confirming that complete polymerization of the vinyl groups had taken place. The SiMe regions of both spectra were complex, with several sharp, overlapping signals. In addition to the aliphatic and SiMe signals, the spectrum of **3** contained a broad singlet at 2.39 ppm arising from the NMe group; the spectrum of **4** contained a sharp, intense singlet at 0.087 ppm arising from the pendant SiMe$_3$ group.

The ^{13}C NMR spectra of **3** and **4** were markedly different, particularly in the aliphatic region (Table 3). The spectrum of **3** contained four sets of broad polymer backbone resonances in the region 25−35 ppm and seven sharp aliphatic resonances. With the aid of a DEPT sequence and comparison with the spectra of **5a** and **5b**, four of the seven sharp signals were assigned to *n*-pentyl end group resonances and the other three to NMe signals. The chemical shifts of the three NMe signals were nearly identical to those of model compounds **5a** and **5b**, providing strong evidence that polymer **3** contained cyclic structures similar to **5a** and **5b** in its polymer backbone.

The aliphatic region of the ^{13}C NMR spectrum of **4** was considerably simpler than that of **3**, consisting of three sharp end group resonances and two broad backbone resonances. Interestingly, the relative intensities of the two backbone signals varied dramatically depending upon the reaction solvent (Figure 1). Based on the chemical shifts of model compound **6**, the downfield resonance (31.9 ppm) was assigned to trans five-membered rings in the polymer backbone and the upfield resonance (28 ppm) to cis five-membered rings.[37] The change in intensities of these two backbone resonances with reaction solvent suggested that the stereoselectivity of cyclization was solvent-dependent, favoring the formation of trans rings in the absence of coordinating cosolvents and cis rings in the presence of THF or Et$_3$N. The origin of this solvent effect is unclear but probably has to do with the state of aggregation and the coordination sphere of the cyclizing organolithium intermediate (Scheme 1).

Chemical shifts in ^{29}Si NMR spectroscopy are known to be very sensitive to factors such as ring size[38] and were thus expected to be useful for the characterization of polymers **3** and **4** (Table 4). In Figure 2, the ^{29}Si NMR spectrum of **3** is shown along with those of model compounds **5a** and **5b**. The two sets of resonances at 7 and 14 ppm in the spectrum of **3** corresponded well to those of the six- and five-membered ring model compounds **5b** and **5a**, respectively. Two distinct resonances at 14 ppm were observed, consistent with the presence of both cis and trans isomers of the five-membered ring repeat unit in the polymer backbone.

The ^{29}Si NMR of polymer **4** (Figure 3), like that of polymer **3**, exhibited two five-membered ring SiMe$_2$ resonances near 14 ppm. Two additional sharp SiMe$_3$ resonances were found near 0 ppm. The relative intensities of the two sets of SiMe$_2$ and SiMe$_3$ signals varied with the reaction solvent, showing the same trend as was observed for the ^{13}C NMR aliphatic backbone resonances. On this basis, the pair of resonances at 0.5 and 14 ppm could be assigned to cis five-membered ring repeat units and the pair at 0.2 and 14.7 ppm to trans rings.

Taken together, the GPC and spectroscopic evidence suggested that polymers **3** and **4** possessed highly regular structures, consisting entirely of linked cyclic units with no detectable cross-links or linear segments. In line with the results of the model anionic cyclization experiments, the spectroscopic studies indicated that **4** contained only five-membered rings in the polymer backbone, while **3** contained both five- and six-membered rings. The high exo-regioselectivity of cyclization of monomer **2** in the model studies and polymerization experiments was unexpected, given the usual preference for β-addition of anions to vinylsilanes.[33] In addition, this cyclization step was found to exhibit solvent-dependent stereochemistry: the ratio of cis to trans five-membered rings in polymer **4** increased when the reaction was conducted in the presence of polar cosolvents. Thus, by employing anionic initiation, significant control was achieved over both the regio- and stereochemistry of the polymerization reactions. Indeed, as evidenced primarily by the broadness and number of signals in the NMR spectra, polymer **3** contained a much more regular structure than the polymer previously prepared from **1** using radical initiators.[5]

Ring-Opening Reactions of Cyclopolymers. Cyclopolymers **3** and **4** were treated with aqueous HF in order to convert their Si−N bonds quantitatively to moisture-stable Si−F bonds.[5,29] These reactions were

Table 2. ^{1}H NMR Spectral Data ($CDCl_3$ Solution) for the Polymers Prepared in This Study

		$\delta_{aliphatic}$			
polymer	δ_{SiCH_3}	backbone		end group	δ_{other}
3	−0.1, −0.03, 0.05 (br) (12 H)	0.4−0.7, 0.8−2.0 (br)	(7 H)	0.87 (m, CH_3), 1.24 (br s, CH_2)	δ_{NCH_3} 2.39 (s) (3 H)
4	0.027, 0.19 (br, $SiMe_2$), 0.087 (s, $SiMe_3$) (21 H)	0.48, 1.10, 1.37, 1.64, 1.74 (br)	(6.5 H)	0.87 (m, CH_3), 1.25 (br, CH_2)	
7	0.20, 0.23 (br s) (6 H)	1.05 (br, CH), 1.55 (br; CH_2) (3.45 H)		0.87 (br t, CH_3), 1.24 (br, CH_2)	
8	0.23, 0.25 (d, $^3J_{HF} = 6$ Hz[a]) (6 H)	1.05 (br, CH), 1.55 (br, CH_2)	(3.2 H)	0.87 (br t, CH_3), 1.24 (br, CH_2)	
9	0.082 (d, $^3J = 4$ Hz) (6 H)	0.89 (br, CH), 1.42 (br s, CH_2)	(3.3 H)	0.89 (br, CH_3), 1.25 (br s, CH_2)	δ_{SiH} 3.90 (br s, $J_{SiH} =$ 182 Hz) (1 H)
10	−0.004, 0.012 (s) (9 H)	0.8 (br, CH), 1.35 (br, CH_2)	(3.3 H)	0.87 (br, CH_3), 1.24 (br, CH_2)	
11, 11′	0.081 (s) (6 H)	0.87 (br, CH), 1.4 (br, CH_2)	(3.3 H)	0.87 (br, CH_3), 1.24 (br, CH_2)	$\delta_{CH=CH_2}$ 5.63 (br d, $J =$ 19 Hz), 6.15 (br dd) $\delta_{CH=CH_2}$ 5.91 (br d, $J =$ 13 Hz) (3 H)
12	0.24 (br s) (6 H)	1.05 (br, CH), 1.55 (br, CH_2)	(3.3 H)	0.87 (m, CH_3), 1.24 (br s, CH_2)	$\delta_{C\equiv CH}$ 2.40 (br s) (1 H)

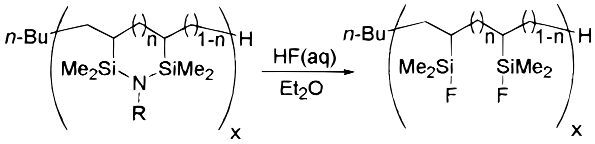
[a] Cf. $^3J_{H-F} = 7.2$ Hz in Me_3SiF.[40]

Table 3. ^{13}C NMR Spectral Data ($CDCl_3$ Solution) for the Polymers Prepared in This Study[a]

polymer	δ_{SiCH_3}	$\delta_{aliphatic}$	$\delta_{end\ group}$	δ_{other}
3	−5.23 (s), −3.41 (br), −2.0 (br), −0.9 (br), −0.06 (s)	25.5 (br), 28.0 (br), 31.5 (br), 34.8 (br)	14.2 (s, CH_3), 22.6, 22.7 (s, CH_3CH_2), 32.35 (s, $CH_3CH_2CH_2$)	δ_{NCH_3} 26.91, 27.02, 28.97
4	−0.3,1.2, 2.9, 4.2 (br, $SiMe_2$), 3.75 (s, $SiMe_3$)	25.5−30.0 (br, cis), 31.4−32.8 (br, trans)	14.2 (s, CH_3), 22.6 (s, CH_3CH_2), 32.3 (s, $CH_3CH_2CH_2$)	
7	−2.64, −0.93 (br s)	24.2, 26.3, 27.5, 28.6 (br, CH), 29.8 (br, CH_2)	14.14 (s, CH_3), 22.59 (s, CH_3CH_2), 32.07, 32.28, 32.4 (s, CH_2)	
8	−0.85 (br)	28.3 (br, CH), 29.4, 30.0 (br, CH_2)	14.2 (s, CH_3), 22.6 (s, CH_3CH_2), 32.0, 32.3 (s, CH_2)	
9	−3.91, −3.25 (s)	27.8 (br, CH), 29.8 (s), 30.6 (br), 31.2 (br) (CH_2)	14.2 (s, CH_3), 22.6 (s, CH_3CH_2)	
10	0.10 (br s)	27.8, 30.6 (br, CH), 31.5, 33.0 (br, CH_2)	14.2 (s, CH_3), 22.8 (s, CH_3CH_2)	
11, 11′	−1.88 (br s)	25.5−30.0 (br, CH), 31.4, 32.8 (br, CH_2)	14.2 (s, CH_3), 22.8 (s, CH_3CH_2), 26.5, 26.9, 29.8 (s, CH_2)	$\delta_{CH=CH_2}$131.28 (br s), $\delta_{CH=CH_2}$140.31 (br s)
12	−0.19 (br s)	25.5−30.0 (br, CH), 30.7, 32.0 (br, CH_2)	14.2 (s, CH_3), 22.6 (s, CH_3CH_2), 29.67, 34.3 (s, CH_2)	$\delta_{C\equiv CH}$ 90.23 (br s), $\delta_{C\equiv CH}$ 95.09 (br s)

[a] Signals designated as arising from CH, CH_2, or CH_3 groups were assigned with the help of DEPT sequences.

expected to be useful not only as a method of further derivatizing the polymer backbone but also as sensitive tests to detect acyclic SiNSi units in the original cyclopolymers, since such structures would lead to random chain ruptures which would be readily detectable by GPC.[39] The products of these reactions, **7** and **8**, were obtained in good yield as analytically pure, clear, colorless viscous oils after aqueous workup (eq 3, Table 5). Analysis of **7** and **8** by GPC showed a drop in both M_n and M_w when compared to the parent polymers, consistent with the expected drop in hydrodynamic volume upon conversion from cyclic to linear repeat units.[40] More importantly, however, the polydispersity indices (M_w/M_n) showed little to no change upon ring opening (Table 5), ruling out the presence of significant amounts of acyclic units in **3** and **4**.



(3)

3, R = Me; n = 0, 1
4, R = SiMe3, n = 0

7
8

Spectroscopic analysis of polymers **7** and **8** indicated that the ring-opening reaction was complete. The ^{1}H NMR spectrum of **7** lacked the NMe resonance found in the spectrum of **3**, and the spectra of **8a−f** lacked the $SiMe_3$ resonance found in the spectrum of **4** (Table 2). Overall, the ^{1}H NMR spectra of **7** and **8** were very similar to each other and greatly simplified compared

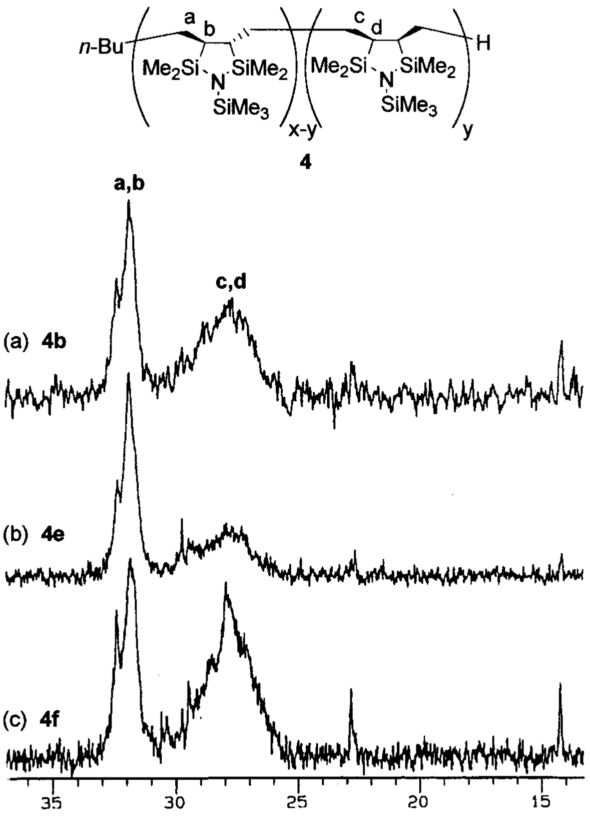


Figure 1. Aliphatic region of the ^{13}C NMR spectra of polymers (a) **4b**, (b) **4e**, and (c) **4f**.

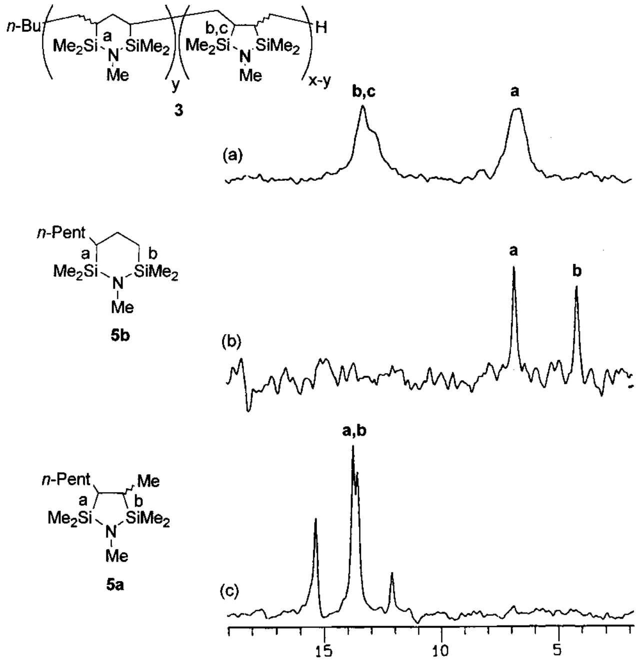


Figure 2. ^{29}Si NMR spectra of (a) polymer **3**, (b) compound **5b**, and (c) compound **5a**.

to the spectra of **3** and **4**. The broad, complex SiMe resonances of **3** and **4** were replaced with relatively sharp signals. In the aliphatic region, the backbone methylene and methine resonances were now well-resolved.

The structural differences between **7** and **8** were most readily apparent in the SiMe regions of their ^{13}C NMR spectra (Table 3). The spectrum of **7** displayed two broad, well-separated SiMe signals of roughly equal intensity at −2.64 and −0.93 ppm corresponding to respectively head-to-tail and head-to-head monomer sequences derived from six- and five-membered rings in **3**. The spectrum of **8**, on the other hand, contained only the head-to-head signal at −0.85 ppm, completely consistent with the previous formulation of **4** as consisting of only five-membered ring repeat units. The aliphatic regions of the ^{13}C NMR spectra of **7** and **8** exhibited clearly resolved methylene and methine resonances; the spectrum of **7** was more complex than that of **8**, consistent with its having a greater diversity of backbone sequences.

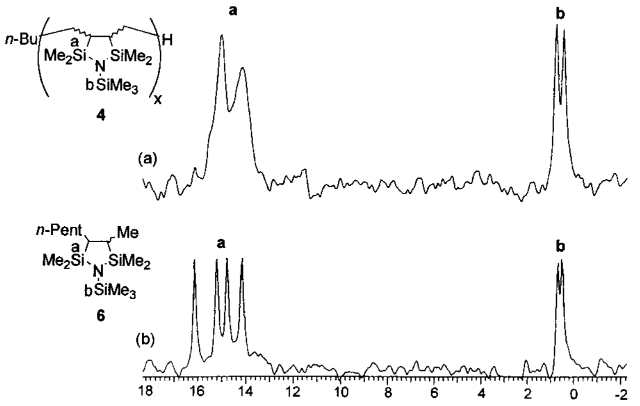


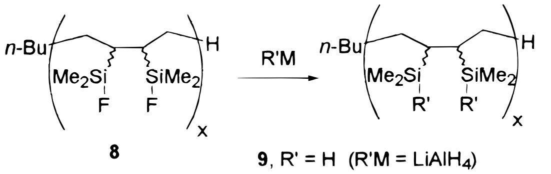
Figure 3. ^{29}Si NMR spectra of (a) polymer **4** and (b) compound **6**.

Table 4. ^{29}Si NMR Spectral Data (CDCl$_3$ Solution) for the Polymers Prepared in This Study

polymer	δ
3	six-membered rings: 7.4 (br s) (0.9 Si)
	five-membered rings: 13.7 (br s), 14.1 (br s) (1 Si)
4	0.2 (s, trans SiMe$_3$), 0.5 (s, cis SiMe$_3$) (1 Si)
	14.0 (br s, cis SiMe$_2$), 14.7 (s, trans SiMe$_2$) (2 Si)
7	32.83 (d, J_{SiF} = 285 Hz) (1 Si)
	33.92 (d, J_{SiF} = 287 Hz) (0.8 Si)
8	32.36 (br d, J_{SiF} = 287 Hz) (1 Si)
	33.61 (br d, J_{SiF} = 286 Hz) (0.4 Si)
9	−10.95, −10.63, −10.06, −9.43 (br, overlapped)
10	2.01, 2.36, 2.71 (s, overlapped), 4.61 (s)
11, 11′	−4.2 (br) (1.2 Si), −2.25 (s) (1 Si)
12	−13.27 (br), −11.29 (s) (overlapped)

The ^{29}Si NMR spectra of **7** and **8** (Table 4) contained no signals due to residual cyclic structures, but only sharp resonances, strongly coupled to fluorine, in the expected range for R$_3$SiF compounds.[38] In their ^{19}F NMR spectra, polymers **7** and **8** exhibited strong, somewhat complex signals in the region associated with R$_3$SiF compounds.[41]

Derivatization Reactions of Polymer 8. The reactive Si−F bonds of poly(vinyldimethylfluorosilane) (**8**) were easily derivatized using a variety of nucleophilic reagents (eq 4); the results are shown in Table 6.



(4)

9, R' = H (R'M = LiAlH$_4$)
10, R' = Me (R'M = MeLi)
11, R' = CH=CH$_2$ (R'M = CH$_2$=CHLi)
11', R' = CH=CH$_2$ (R'M = CH$_2$=CHMgBr)
12, R' = C≡CH (R'M = HC≡CMgBr)

As can be seen from Table 6, the derivatization reactions proceeded in good yield. All of the product

Table 5. Results of Ring-Opening Reactions of Polymers 3 and 4 with HF(aq)

reactant	product	yield	$M_n{}^a$ (Δ)^b	$M_w{}^a$ (Δ)	$M_w/M_n{}^a$ (Δ)
3a	**7a**	89^c	2890^c (−1680)	5010^c (−1860)	1.74^c (+0.23)
4a	**8a**	93	2250 (−4080)	2920 (−4020)	1.30 (+0.20)
4b	**8b**	89^c	6910^c (−2500)	7850^c (−2950)	1.16^c (+0.02)
4c	**8c**	89^c	5770^c (−4830)	6750^c (−4650)	1.18^c (+0.02)
4d	**8d**	93	8680 (−6320)	9790 (−8110)	1.13 (−0.07)
4e	**8e**	82	5920 (−5580)	6630 (−6270)	1.12 (0)
4f	**8f**	83	3780 (−2480)	4690 (−3050)	1.24 (0)

[a] Determined by gel permeation chromatography (GPC) relative to polystyrene standards. [b] Difference of average for ring-opened product polymer minus that of the parent polymer. [c] Average of two experiments.

Table 6. Derivatizations of Fluorosilane Polymer 8 with Nucleophilic Reagents

parent polymer	nucleophilic reagent	product	yield	$M_n{}^a$ (Δ)^b	$M_w{}^a$ (Δ)^b	$M_w/M_n{}^a$ (Δ)^b
8c	$LiAlH_4$	**9**	76	8230 (+3540)	8740 (+309)	1.06 (−0.15)
8b	MeLi	**10**	93	8390 (+30)	9160 (+80)	1.09 (0)
8b	$CH_2{=}CHLi$	**11**	88	13300^c (+7900)	23500^c (+16900)	1.76^c (+0.54)
8d	$CH_2{=}CHMgBr$	**11′**	64	15800^c (+7200)	26400^c (+16600)	1.67^c (+0.54)
8b	$HC{\equiv}CMgBr$	**12**	98	4220 (−1240)	5210 (−1410)	1.24 (+0.02)

[a] Determined by gel permeation chromatography (GPC) relative to polystyrene standards. [b] Difference of the value for the derivatized product polymer minus that of the parent polymer. [c] Multimodal distribution.

polymers except **12** were isolated as white powders by precipitation from methanol. Polymer **12**, due to its appreciable solubility in methanol, was isolated by precipitation from water. Polymers **9**, **10**, and **12** gave monomodal GPC traces with polydispersities essentially identical to those of the parent polymers, although the M_w and M_n values varied depending on the substituents (Table 6). Polymers **11** and **11′**, on the other hand, exhibited multimodal molecular weight distributions, indicating that some cross-linking had occurred during the functionalization reactions (perhaps involving radical or anionic additions to the pendant vinyl groups of the product polymers).

Spectroscopic and analytical data of polymers **9**−**12** were consistent with quantitative conversion of the Si−F groups of **8** to Si−R′ groups (Tables 2−6). Polymer **9** (R′ = H) exhibited spectroscopic signatures indicative of the presence of Si−H groups: an intense band at 2104 cm^{-1} in its IR spectrum and a singlet at 3.90 ppm in its ^{1}H NMR spectrum. For polymer **10** (R′ = Me), the SiMe signal in the ^{1}H NMR spectrum was shifted 0.23 ppm upfield from its position in the spectrum of **8**, consistent with the transformation of a $SiMe_2F$ to a $SiMe_3$ group. Polymers **11** and **11′** (R′ = $CH{=}CH_2$) gave identical IR and NMR spectra which contained characteristic absorptions for the pendant vinylsilane units: three multiplets in the range 5.5−6.5 ppm in the ^{1}H NMR spectra, two sharp signals at 131.28 and 140.31 ppm in the ^{13}C NMR spectra, and several diagnostic[42] bands (3045, 3007, 1898, 1590, 1009 cm^{-1}) in the IR spectra. For polymer **12** (R′ = $C{\equiv}CH$), the pendant ethynyl groups gave strong absorptions at 3290 and 2032 cm^{-1} in the IR spectrum, a broad singlet at 2.40 ppm in the ^{1}H NMR spectrum, and resonances at 90.23 and 95.09 ppm in the ^{13}C NMR spectrum.

The remainder of the spectroscopic data for polymers **9**−**12** were similar. The SiMe groups generally gave one or two sharp signals in the ^{1}H and ^{13}C NMR spectra. The methylene and methine backbone resonances were well-resolved in the ^{1}H and ^{13}C NMR spectra and were distinguishable by ^{13}C DEPT NMR sequences. The ^{29}Si NMR spectra of all of the derivatized polymers contained similar patterns of several closely spaced singlets (reflecting, most likely, the effect of backbone stereochemistry); the chemical shifts of these signals varied with the substituent R′.

These derivatization experiments demonstrated the usefulness of **8** as a starting point for the synthesis of a variety of polymers of the type $(CH_2CHSi(CH_3)_2R')_n$ with regular microstructures consisting of perfectly alternating head-to-head and tail-to-tail monomer sequences. The high degree of order in the polymer backbone of **8** and derivatives of **8** was a consequence of the $NSiMe_3$ linking group in monomer **2**, which functioned not only as a protecting group for the fluorosilane units but also as a directing group to control the regioselectivity of cyclization. Starting from polymer **8**, the syntheses of many interesting polymers with potentially useful applications should be possible.

Experimental Section

Measurements. ^{1}H, ^{19}F, ^{13}C, and ^{29}Si NMR spectra were obtained at 300, 282, 75.4, and 59.6 MHz, respectively, using chloroform-*d* ($CDCl_3$) as solvent. ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent (7.24 and 77.0 ppm, respectively). ^{29}Si and ^{19}F NMR spectra were referenced (0 ppm) to external standards (TMS and $CFCl_3$, respectively). Infrared spectra were obtained on a Perkin-Elmer 1600 series FTIR. GC/MS measurements were carried out on an HP 5890 GC (HP-1 silicone gum capillary column) with an HP 5971 MS detector. Preparative GC was performed on a Gow-Mac 69-350 GC (20% DC-710 on Chromasorb-P; thermal conductivity detector). GPC molecular weight determinations were made using a Waters Millipore 150-C ALC/GPC chromatograph equipped with either a three-column setup (Waters Ultrastyragel 10^4, 10^3 Å; Waters μPorasil GPC 60 Å; for polymers **4** and **8**−**12**) or a two-column setup (Waters Ultrastyragel 10^4, 10^3 Å; for polymers **3** and **7**) using toluene as the eluent. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Materials. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes and 1,3-divinyltetramethyldisilazane were purchased from United Chemical Technologies. Chlorosilanes were distilled from magnesium turnings before use. Organolithium and -magnesium reagents were purchased from Aldrich. 1,3-Divinylpentamethyldisilazane was prepared by the reaction of vinyldimethylchlorosilane with methylamine.[43] Vinyllithium was prepared by a literature method.[44]

Synthesis of Bis(vinyldimethylsilyl)(trimethylsilyl)amine (2).[31] A solution of 1,3-divinyltetramethyldisilazane (20.0 mL, 16.4 g, 88.3 mmol) in 150 mL of THF was treated with *n*-BuLi (18.0 mL, 2.50 M in hexanes, 45.0 mmol) at −78 °C. After warming to room temperature, the reaction was quenched with trimethylchlorosilane (11.4 mL, 9.76 g, 89.8 mmol). The reaction mixture was evaporated to dryness, extracted with hexanes, and filtered. Removal of hexanes at reduced pressure left a white solid which was purified by Kugelrohr distillation (0.01 mmHg, 55 °C), giving **2** as a clear, waxy solid (19.32 g, 85%), mp 63−65 °C. Anal. Calcd: C, 51.29; H, 10.56. Found: C, 51.48; H, 10.54. ^{1}H NMR: δ 0.17 (s, 9 H, $SiMe_3$), 0.22 (s, 12 H, $Si(CH_3)_2CH{=}CH_2$), 5.63 (dd, J_{cis} = 3.8 Hz, J_{gem} = 20.3 Hz, 2 H, $SiCH{=}CH_2$ (trans to Si)), 5.86 (dd, J_{cis} = 3.8 Hz, J_{trans} = 14.7 Hz, 2 H, $SiCH{=}CH_2$), 6.24 (dd, J_{trans} = 14.7 Hz, J_{gem} = 20.2 Hz, 2 H, $SiCH{=}CH_2$ (cis to Si)). ^{13}C NMR: δ 3.91 ($Si(CH_3)_2CH{=}CH_2$), 5.55 ($SiMe_3$), 130.33 ($SiCH{=}CH_2$), 143.44 ($SiCH{=}CH_2$). ^{29}Si NMR: δ −6.43 (2 Si, $SiMe_2$-$CH{=}CH_2$), 3.39 (1 Si, $SiMe_3$).

Model Cyclization Reactions. Reaction of $(CH_2{=}CHMe_2Si)_2NMe$ (1) with Excess *n*-BuLi. Hexane (350 mL), triethylamine (10 mL), and *n*-BuLi (20.0 mL; 2.0 M in cyclohexane; 40 mmol) were combined in a 500 mL Schlenk flask equipped with a stir bar and a rubber septum. Over the course of 2 days **1** (4.8 mL, 4.0 g, 20 mmol) was added to the mixture via syringe, one drop at a time. After the addition was complete, the reaction mixture was stirred for an additional 18 h before quenching with 1.7 mL (1.3 g, 42 mmol) of anhydrous methanol. The resulting mixture was filtered through a glass frit containing Celite, and the salts were washed with three 20 mL portions of hexane. The solvents were removed at reduced pressure, leaving a yellow oil which was distilled at 0.005 Torr. The desired monocyclic products **5a** and **5b** distilled together as a slightly yellow liquid boiling at 67.5 °C (0.73 g, 14%). By increasing the temperature, further fractions (total 2.69 g) could be obtained which were shown by GC/MS analysis to contain higher MW compounds that were not further identified. A viscous, yellow residue (1.79 g) remained in the distillation pot. By use of preparative GC (isothermal, column temperature = 200 °C), **5a** and **5b** could be separated for spectroscopic analysis. (It was not possible to separate the two stereoisomers of **5a**.) Anal. Calcd (mixture of isomers): C, 60.62; H, 12.18. Found: C, 60.98; H, 12.20.

cis/trans-3-Pentyl-1,2,2,4,5,5-hexamethyl-2,5-disila-1-azacyclopentane, ***5a***: ^{1}H NMR: δ −0.11 (s, 3 H, $SiCH_3$), −0.082 (s, 3 H, $SiCH_3$), −0.063 (s, 3 H, $SiCH_3$), −0.016 (s, 3 H, $SiCH_3$), 0.007 (br s, 6 H, $SiCH_3$), 0.040 (s, 3 H, $SiCH_3$), 0.071 (3 H, $SiCH_3$), 0.55 (br, 2 H, SiCH), 0.87 (br; 9 H; *n*-pentyl CH_3, $SiCHCH_3$), 0.95 (d, *J* = 7 Hz, 3 H, $SiCHCH_3$), 1.08 (m, 1 H, SiCH), 1.12−1.4 (br, 16 H; *n*-pentyl CH_2), 1.4 (br, 4 H, CH_2-$CH_2CH_2CH_2CH_3$), 1.7 (m, 1 H, SiCH), 2.41 (s, 6 H, NCH_3). ^{13}C DEPT NMR: δ −3.93, −3.80, −3.73, −2.20, −1.65, −1.56, −0.74, −0.27 ($SiCH_3$), 11.62 (cis $SiCHCH_3$), 14.33 (trans $SiCHCH_3$), 14.14, 14.20 (*n*-pentyl CH_3), 18.95 (cis $SiCHCH_3$), 22.80 (trans $SiCHCH_3$), 27.74 (cis $SiCHCH_2$), 31.36 (trans $SiCHCH_2$), 22.67, 22.77 ($CH_2CH_2CH_2CH_2CH_3$), 26.97, 27.03 (NCH_3), 29.31 (trans $CH_2CH_2CH_2CH_2CH_3$), 30.00, 30.53 ($CH_2CH_2CH_2CH_2CH_3$), 32.29, 32.45 ($CH_2CH_2CH_2CH_2CH_3$). ^{29}Si NMR: δ 12.09, 13.57, 13.75, 15.34. MS (EI): *m/z* = 257 {M^+; 24, 28}, 242 {$(M - CH_3)^+$; 81, 100}, 186 {$(M - C_5H_{11})^+$; 27, 37}, 146 {$(Me_2SiN(Me)SiMe_2H)^+$; 70, 75}, 130 {$(Me_2Si{=}NSiMe_2)^+$; 100, 96}, 73 {$(Me_3Si)^+$; 54, 57}, 59 {$(Me_2SiH)^+$; 55, 58}.

3-Pentyl-1,2,2,6,6-pentamethyl-2,6-disila-1-azacyclohexane, **5b**. ^{1}H NMR: δ −0.084 (s, 3 H, $SiCH_3$), −0.037 (s, 3 H, $SiCH_3$), −0.005 (s, 3 H, $SiCH_3$), 0.012 (s, 3 H, $SiCH_3$), 0.50 (br, 2 H, $SiCH_2$), 0.70 (m, 1 H, SiCH), 0.87 (t, 3 H, *n*-pentyl CH_3), 1.05−1.35 (br, 9 H, $SiCH_2CH_2$, *n*-pentyl CH_2), 1.41 (qm, J^1 = 13 Hz, J^2 = 2 Hz, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 1.87 (m, *J* = 3 Hz, 1 H), 2.37 (3 H, NCH_3). ^{13}C DEPT NMR: δ −4.97, −2.21, −1.90, −1.12 ($SiCH_3$), 14.14 (*n*-pentyl CH_3), 15.30 ($SiCH_2CH_2$-$CHSi$), 22.70 ($CH_2CH_2CH_2CH_2CH_3$), 23.82 ($SiCH_2CH_2CHSi$), 28.03 (SiCH), 28.69 ($CH_2CH_2CH_2CH_2CH_3$), 28.75 (NCH_3), 30.63 ($CH_2CH_2CH_2CH_2CH_3$), 32.14 ($CH_2CH_2CH_2CH_2CH_3$). ^{29}Si NMR: δ 4.16, 6.82. MS (EI): *m/z* = 257 {M^+, 20}, 242 {$(M - CH_3)^+$, 100}, 187 {$(M - C_5H_{10})^+$, 14}, 158 {$(M - C_7H_{15})^+$, 26}, 146 { $(Me_2SiN(Me)SiMe_2H)^+$, 55}, 132 {$(Me_2SiN(H)$-$SiMe_2H)^+$, 51}, 86 {21}, 73 {$(Me_3Si)^+$, 37}, 59 {$(Me_2SiH)^+$, 50}.

Reaction of $(CH_2{=}CHMe_2Si)_2NSiMe_3$ (2) with Excess *n*-BuLi: Synthesis of *cis/trans*-3-Pentyl-1-trimethylsilyl-2,2,4,5,5-pentamethyl-2,5-disila-1-azacyclopentane (6). The above procedure was followed, employing 17.4 mL of *n*-BuLi (2.0 M in cyclohexane; 34.8 mmol) dissolved in 350 mL of hexane and 10 mL of triethylamine. A solution of **2** (4.48 g, 17.4 mmol) in ca. 75 mL of hexane was added to the reaction mixture over the course of 8.5 h using a dropping funnel. Upon completion of the addition, the reaction mixture was stirred for 12 h before quenching with 1.5 mL (1.2 g, 37 mmol) of anhydrous methanol. The product was purified as in the above example. Compound **6** (mixture of cis and trans isomers) was obtained as a colorless liquid (0.59 g, 11%) boiling at 99−100 °C and 0.005 Torr. A second fraction (0.24 g) boiling at higher temperatures was shown by GC/MS analysis to contain higher MW compounds. A viscous, yellow residue (4.87 g) remained in the distillation pot. Anal. Calcd (mixture of isomers): C, 57.06; H, 11.81. Found: C, 57.25; H, 11.82. ^{1}H NMR: δ 0.016 (3 H, $SiCH_3$), 0.058 (3 H, $SiCH_3$), 0.064 (3 H, $SiCH_3$), 0.160 (3 H, $SiCH_3$), 0.211 (3 H, $SiCH_3$), 0.233 (3 H, $SiCH_3$), 0.132 (21 H, $SiMe_3$, $SiCH_3$), 0.57 (m, 2 H, SiCH), 0.87 (d, *J* = 7 Hz, 3 H, $SiCHCH_3$), 0.92 (br, 6 H, *n*-pentyl CH_3), 1.00 (d, *J* = 7 Hz, 3 H, $SiCHCH_3$), 1.08 (q, *J* = 7 Hz, 1 H, $SiCHCH_3$), 1.2−1.4 (br, 12 H, $CH_2CH_2CH_2CH_2CH_3$), 1.42 (br, 4 H, $CH_2CH_2CH_2CH_2$-CH_3), 1.72 (m, 1 H, SiCH). ^{13}C DEPT NMR: δ −0.89, −0.47, 0.30, 1.59, 1.73, 1.96, 3.43, 4.14 ($SiMe_2$), 3.65, 3.69 ($SiMe_3$), 11.11 (cis $SiCHCH_3$), 14.06 (trans $SiCHCH_3$), 14.29, 14.33 ($CH_2CH_2CH_2CH_2CH_3$), 19.63 (cis $SiCHCH_3$), 24.16 (trans $SiCHCH_3$), 28.52 (cis $SiCHCH_2$), 31.82 (trans $SiCHCH_2$), 22.82, 22.93 ($CH_2CH_2CH_2CH_2CH_3$), 26.32 (cis $CH_2CH_2CH_2CH_2CH_3$), 29.32 (trans $CH_2CH_2CH_2CH_2CH_3$), 30.12, 30.63 ($CH_2CH_2CH_2$-CH_2CH_3), 32.44, 32.73 ($CH_2CH_2CH_2CH_2CH_3$). ^{29}Si NMR: δ 0.53, 0.69, 14.15, 14.79, 15.20, 16.14. MS (EI): *m/z* = 315 {M^+; 13, 13}, 300 {$(M - CH_3)^+$; 100, 100}, 244 {$(M - C_5H_{11})^+$; 15, 14}, 202 {31, 37}, 188 {48, 67}, 130 {$(Me_2Si{=}NSiMe_2)^+$; 34, 49}, 100 {20, 30}, 73 {$(Me_3Si)^+$; 20, 29}.

Synthesis of Polymers. Details of characterization for polymers may be found in Tables 1−6. Calculated values for combustion analyses contain terms accounting for the end groups.

Cyclopolymerization of $(CH_2{=}CHMe_2Si)_2NMe$ (1) with 10 mol % *n*-BuLi. The monomer (2.03 g, 10.2 mmol) was vacuum-transferred from 0.4 mL of dibutylmagnesium (1.0 M in heptane)[45] into a 50 mL three-necked, round-bottomed flask equipped with a magnetic stir bar and two vacuum line adapters. Following this, a mixture of hexane (8 mL) and triethylamine (1 mL) was vacuum-transferred from *n*-BuLi (0.6 mL, 2.5 M in hexane) into the reaction vessel. The mixture was warmed to room temperature, and *n*-BuLi (0.40 mL, 2.5 M in hexane, 1.0 mmol, 10 mol %) was added via syringe, resulting in a light yellow solution. After 3 days of stirring at room temperature, the reaction was terminated with 0.5 mL of anhydrous methanol. All volatiles were removed at reduced pressure, leaving a white solid that was dissolved in ca. 8 mL of toluene and precipitated by adding this solution to 200 mL of well-stirred, anhydrous methanol. The product **3a**, a white powder, was collected by suction filtration and dried for 14 h at 0.005 Torr (1.83 g, 87%). Anal. Calcd for $C_9H_{21}NSi_2 + 0.1\ C_4H_{10}$: C, 55.01; H, 10.80. Found: C, 54.63; H, 10.74. IR (NaCl disk): 2950 (s), 2905 (s), 2856 (s), 2849 (m), 2805 (m), 1458 (w), 1405 (w), 1248 (vs), 1186 (w), 1142 (s), 1075 (s), 908 (vs), 882 (vs), 829 (vs), 790 (m), 767 (vs), 677 (w).

Cyclopolymerization of $(CH_2{=}CHMe_2Si)_2NSiMe_3$ (2). The previous procedure was used, except that the solid monomer (2.58 g, 10.0 mmol) was charged into the reaction vessel (a 100 mL Schlenk flask equipped with a magnetic stir bar and vacuum line adapter). The appropriate solvent or solvent mixture (8 mL of hexane and 1 mL of triethylamine for **4a**−**d**; 9 mL of hexane for **4e**; 8 mL of hexane and 1 mL of

THF for **4f**) was vacuum-transferred from *n*-BuLi (0.4 mL; 2.5 M in hexane) into the reaction vessel. The reaction was initiated with the appropriate amount of *n*-BuLi (2.5 M in hexane) added via syringe. After 3 days of stirring, the reaction was terminated with 0.5 mL of anhydrous methanol and the product **4** purified as in the above procedure. Anal. Calcd for $C_{11}H_{27}NSi_3 + 0.05\ C_4H_{10}$ (**4b**): C, 51.64; H, 10.64. Found: C, 51.70; H, 10.58. IR (NaCl disk): 2953 (s), 2905 (m), 2853 (m), 1405 (w), 1251 (vs), 964 (vs), 899 (vs), 836 (s), 795 (m), 771 (m), 679 (w).

Reaction of Cyclopolymer 3a with HF(aq). A solution of polymer **3a** (1.59 g, 7.75 mmol) in 30 mL of diethyl ether was added in 1 mL portions to a well-stirred mixture of 10 mL of diethyl ether and 6 mL of aqueous HF (49%) in a HDPE beaker with a Teflon-coated magnetic stir bar. (**Safety note**: extreme caution should be exercised when handling 49% aqueous HF.[46]) After stirring for 1 h, the reaction mixture was transferred to a separatory funnel where it was washed four times with 20 mL portions of saturated $NaHCO_3$(aq). The organic layer was separated, dried over anhydrous $MgSO_4$, and filtered. Removal of all volatiles at reduced pressure and drying for 15 h at 0.005 Torr left **7a** as a clear, colorless, viscous oil (1.51 g, 91%). Anal. Calcd for $C_4H_9FSi + 0.05\ C_4H_{10}$: C, 47.10; H, 8.94. Found: C, 47.69; H, 9.05. ^{19}F NMR: δ −161.43 (br), −158.97 (s), −157.69 (s). IR (NaCl disk): 2961 (s), 2920 (s), 2852 (s), 1454 (w), 1408 (w), 1256 (vs), 1059 (w), 864 (vs), 835 (vs), 784 (vs), 761 (s), 692 (m).

Reaction of Cyclopolymer 4c with HF(aq). Polymer **4c** (1.27 g, 4.89 mmol) was reacted with 5 mL of aqueous HF (49%) according to the procedure outlined above. The product **8c**, a clear, tacky solid, was dried for 13 h at 0.005 Torr (0.88 g, 85%). Anal. Calcd for $C_4H_9FSi + 0.02\ C_4H_{10}$: C, 46.51; H, 8.80. Found: C, 46.39; H, 8.80. ^{19}F NMR: δ −159.45 (br), −158.75 (br s), −157.64 (s), −157.17 (s). IR (NaCl disk): 2959 (m), 2925 (m), 2856 (m), 1463 (w), 1406 (w), 1256 (vs), 862 (vs), 840 (vs), 787 (s), 690 (m), 643 (m).

Reaction of Poly(vinyldimethylfluorosilane) (8c) with $LiAlH_4$. A solution of 1.356 g (12.87 mmol) of polymer **8c** in 20 mL of diethyl ether was added carefully via cannula to 1.45 g (38.2 mmol) of $LiAlH_4$ in a 50 mL three-necked, round-bottomed flask equipped with reflux condenser, stir bar, glass stopper, and rubber septum. An exothermic reaction ensued. Upon completion of the addition, another 10 mL of ether was added via cannula, and the reaction mixture was heated at reflux for 19 h. After cooling to room temperature, the reaction mixture was hydrolyzed carefully by the slow addition of water to the reaction flask. The organic layer was separated and washed twice with water, and the aqueous layer was back-extracted twice with ether. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. After removal of solvent at reduced pressure, the product **9**, a clear, colorless oil, was dried for 39.5 h on the vacuum line (0.853 g, 76%). Anal. Calcd for $C_4H_{10}Si + 0.02\ C_4H_{10}$: C, 56.09; H, 11.77. Found: C, 56.60; H, 11.69. IR (NaCl disk): 2954 (s), 2914 (s), 2850 (s), 2104 (vs), 1458 (w), 1416 (w), 1248 (vs), 885 (vs), 833 (s), 757 (s), 695 (m), 632 (w).

Reaction of Poly(vinyldimethylfluorosilane) (8b) with MeLi. Polymer **8b** (0.70 g, 6.6 mmol) was dissolved in 30 mL of diethyl ether in a 100 mL Schlenk flask and cooled to −17 °C in an ethylene glycol/dry ice bath. Methyllithium (5.3 mL; 1.4 M in diethyl ether; 7.4 mmol) was added slowly to the mixture via syringe. After completion of the addition, the reaction mixture was stirred for 4 h at −17 °C, followed by 21 h at room temperature. For workup, the reaction mixture was poured into 50 mL of saturated $NaHCO_3$(aq). The organic layer was separated, washed twice with distilled water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent at reduced pressure, the residue was purified by precipitation from toluene/methanol, giving **10** as a white powder which was dried in vacuo for 18 h (0.626 g, 93%). Anal. Calcd for $C_5H_{12}Si + 0.025\ C_4H_{10}$: C, 60.24; H, 12.14. Found: C, 60.12; H, 12.04. IR (NaCl disk): 2951 (s), 2852 (s), 1444 (m), 1404 (m), 1247 (s), 908 (s), 832 (s), 748 (s), 684 (s).

Reaction of Poly(vinyldimethylfluorosilane) (8b) with $CH_2{=}CHLi$. A solution of 12.1 mmol of freshly prepared vinyllithium in 60 mL of diethyl ether was added to a solution of 0.854 g (8.08 mmol) of **8b** in 20 mL of diethyl ether in a 200 mL Schlenk flask. The reaction mixture was stirred at room temperature for 2 days. The workup procedure used was the same as that in the previous example. The product **11**, a white powder, was dried for 29 h at 0.02 Torr (0.81 g, 88%). Anal. Calcd for $C_6H_{12}Si + 0.025\ C_4H_{10}$: C, 64.44; H, 10.86. Found: C, 64.21; H, 10.99. IR (NaCl disk): 3045 (m), 3007 (w), 2952 (s), 2852 (m), 1898 (w), 1590 (w), 1457 (w), 1403 (m), 1247 (s), 1009 (m), 948 (s), 828 (vs), 765 (s), 695 (m), 522 (w). Polymer **11′** was obtained similarly by heating **8d** (0.95 g, 9.1 mmol) and $CH_2{=}CHMgBr$ (36.2 mmol) at reflux for 5 days in ca. 40 mL of THF (yield 0.65 g, 64%), followed by the typical workup procedure.

Reaction of Poly(vinyldimethylfluorosilane) (8b) with $HC{\equiv}CMgBr$. A solution of **8b** (0.854 g, 8.08 mmol) in 10 mL of THF was combined with 46.0 mL of $HC{\equiv}CMgBr$ solution (0.53 M in THF, 24.4 mmol) in a 500 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar, and two rubber septa. The mixture was heated in an oil bath at reflux for 4 days. After cooling to room temperature, the reaction mixture was subjected to the usual aqueous workup conditions. Removal of all volatiles at reduced pressure left a brown solid that was dissolved in 20 mL of methanol and precipitated from 225 mL of well-stirred water. The product **12**, a tan powder, was collected by suction filtration and dried for 16.25 h at 0.02 Torr (0.88 g, 98%). Anal. Calcd for $C_6H_{10}Si + 0.025\ C_4H_{10}$: C, 65.60; H, 9.25. Found: C, 65.14; H, 9.40. IR (NaCl disk): 3290 (s), 2957 (s), 2922 (s), 2854 (s), 2032 (s), 1456 (w), 1409 (w), 1250 (s), 840 (vs), 774 (s), 672 (s), 576 (w).

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