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Cyclopolymerization of Metalloid-Containing α,ω -Dienes. 1,3-Divinyltetramethyldisiloxane, 1,3-Divinyltetramethyldisilazane, and 1,3-Divinylpentamethyldisilazane

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ABSTRACT: The di-*tert*-butyl peroxide-initiated cyclopolymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{X}$ ($\text{X} = \text{O}, \text{NH}, \text{NMe}$) gives polymers of relatively low molecular weight. Their IR, ^1H NMR, and ^{29}Si NMR spectra provided some structural information when they were compared with spectroscopic data for model cyclic and acyclic organosilicon compounds. These studies indicated the presence of five- and six-membered cyclic units in the polymer chain, and possibly also of seven-membered cyclic and acyclic units. The Si-NH-Si functions in the cyclopolymer derived from $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ reacted readily with HF and HCl to open the ring and introduce SiMe_2F and SiMe_2Cl substituents, respectively, onto the polymer backbone. Reactions of the former with LiAlH_4 , MeLi , $n\text{-BuLi}$, and $\text{CH}_2=\text{CHMgBr}$ converted them to SiMe_2H , SiMe_3 , $\text{SiMe}_2\text{Bu-}n$, and $\text{SiMe}_2(\text{CH}=\text{CH}_2)$ substituents, respectively.

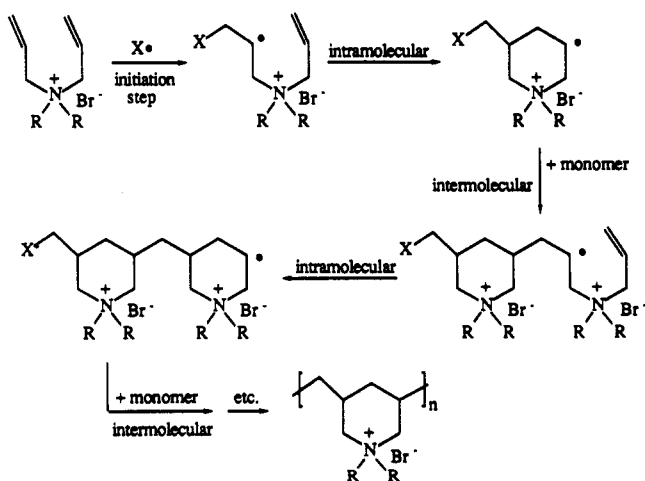
Introduction

Since early investigations by Butler and co-workers,¹ the polymerization of α,ω -dienes to form linear polymers that contain cyclic units has been the focus of numerous studies.² The scope of this polymerization, now known as cyclopolymerization, is broad, encompassing a large number of dienes and a variety of initiation modes, and has resulted in the formation of new polymers, including some of industrial and medical importance. Most commonly, 1,5- and 1,6-dienes have been investigated, but dienes separated by as many as 14 CH_2 units have been shown to undergo cyclopolymerization.³

Radical initiation has been the most widely employed method of promoting cyclopolymerization, and the mechanism has been studied extensively.²⁻⁴ Initially, cyclopolymer formed from radical-initiated polymerization of 1,6-dienes were assigned structures based upon a linear network of six-membered rings linked by methylene units. The mechanism for the formation of six-membered rings was based upon the hypothesis that the more stable intermediate radical during polymerization would be a secondary radical (see Scheme I). Therefore, radical initiation of a 1,6-diene would lead to formation of a secondary radical which then, through a series of alternating intra- and intermolecular steps, would result in a linear polymer containing six-membered rings.

Butler and co-workers proposed such a structure for the polymers produced from diallyl quaternary ammonium

Scheme I
Proposed Mechanism for Cyclopolymerization of Diallyl Quaternary Ammonium Salts



salts (Scheme I).^{1,5} The proposed structure of the cyclopolymer was consistent with the high solubility (hence linear nature) of the polymers which contained little or no residual unsaturation. Degradation of the polymers showed that cyclic structures were present along the polymer backbone but could not establish the ring size in the polymer. At the time of Butler's work, evidence obtained by other workers suggested that six-membered rings were formed during radical-induced cyclization of

α,ω -dienes.⁶ Numerous later studies, however, have shown that diene cyclopolymerization can lead to polymers containing a variety of ring sizes, including five-membered, six-membered and higher membered rings.⁷ (In fact, one study⁸ showed that the polymer prepared from diallyldimethylammonium chloride actually is composed of five-membered rings, rather than the six-membered rings proposed by Butler.) Therefore, other mechanistic pathways must be considered for cyclopolymerization which may depend upon a variety of reaction conditions.

While the scope of cyclopolymerization is broad, only a few polymers have been prepared from silicon-containing dienes. Polymers produced by the cyclopolymerization of dialkylsilanes have been formulated to contain six-membered-ring units.⁹ Polymers containing seven- and eight-membered rings have been prepared from allyl(3-butenyl)SiR₂ and bis(3-butenyl)SiR₂ (R = Me, Ph), respectively.¹⁰ Surprisingly, the cyclopolymerization of disilylated dienes has not been thoroughly investigated. Russian workers studied the γ -radiation and organic peroxide-initiated polymerization of two 1,3-divinylsiloxanes ([CH₂=CH(CH₃)(R)Si]₂O (R = CH₃, Ph)) and of CH₂=CH(CH₃)₂SiOSi(CH₃)(CH=CH₂)OSi(R)(CH₃)(CH=CH₂).^{11a,b} On the basis of IR studies of the disiloxane-derived polymers, it was concluded that cyclopolymerization had occurred in part and that six-membered siloxanes were present.^{11a,b} In a later study,^{11c} (CH₂=CHMe₂Si)₂X (X = O, NH, NCH₃) were reported to undergo di-*tert*-butyl peroxide-initiated polymerization of undetermined type, the disiloxane giving a gel.^{11c}

The potential to prepare linear polymers containing a large number of functionalized silicon substituents led us to investigate the polymerization of dienes of the type (CH₂=CHMe₂Si)₂X (X = O, NH, NCH₃). The polymers successfully prepared from these dienes by di-*tert*-butyl peroxide-initiated polymerization have been analyzed by a variety of spectroscopic methods, most notably ²⁹Si NMR spectroscopy, and information concerning the polymer structures has been obtained. In addition, the chemical reactions of the polymers clearly established the presence of cyclic units as well as of acyclic units along the polymer backbone. Both the cyclopolymers and the derived polymers have potential for a variety of applications because of the chemistry available through the silyl substituents in the polymers.

Results and Discussion

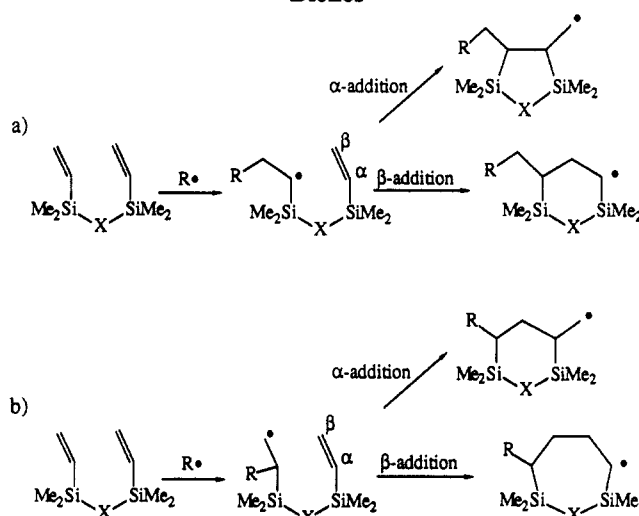
Preparation and Spectroscopic Analysis of Cyclopolymers. The polymerization of 1,6-dienes of the type (H₂C=CHMe₂Si)₂X (where X = O, NH, NCH₃) was investigated. Of the several initiator and solvent systems investigated, di-*tert*-butyl peroxide in chlorobenzene provided the best results. In a typical polymerization reaction, the monomer, catalyst, and solvent were charged into a flask equipped with a magnetic stirbar and a reflux condenser topped with a gas inlet/outlet tube connected to an argon bubbler on a Schlenk line. The mixture was freeze-thaw-degassed four times and then heated (170–215 °C) in a sand bath for 6–48 h. The solvent and any unreacted starting material subsequently were removed by vacuum distillation.

High temperatures were required to effect polymerization, as lower temperatures resulted in reduced polymer yields and polymeric products of lower molecular weight. At high temperatures the yields of the polymers 1–3 are between 66 and 77% (Table I). The polymers were glassy solids in the cases of 1 and 2 and a tacky solid in the case of 3. As anticipated, GPC revealed a broad molecular weight distribution for the polymers, and the values given

Table I
Reaction Conditions for the Polymerization of the Dienes

(H ₂ C=CHMe ₂ Si) ₂ X	<i>t</i> -BuOOBu- <i>t</i> , mol %	temp, °C (time, h)	% yield	<i>M</i> _n (Δ <i>F</i> _p)	<i>M</i> _w (GPC)
X = O	2.6	180–210 (44)	74 (1)	2310	3750
X = NH	2.6	215 (24)	66 (2)	1910	2628
X = NCH ₃	2.5	215 (24)	77 (3)	1190	

Scheme II
Possible Pathways in the Radical Polymerization of Dienes



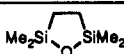
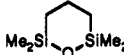

in Table I reflect the mean molecular weights.

During the radical-induced polymerization of the 1,6-dienes (where X = O, NH, NCH₃), several reaction pathways are possible. Reaction of the radical initiator with the diene is likely to occur to give the thermodynamically more stable secondary radical, as shown in Scheme IIa. Ring closure could occur either through an α - or a β -addition process to give either five- or six-membered rings. In addition to cyclization, other radical processes which would result in linear or cross-linked units are possible. Although less thermodynamically stable than a secondary radical, a primary radical could be formed upon radical initiation as shown in Scheme IIb. Ring-closure pathways could result in either six- or seven-membered rings.

To determine the nature of the structural components of the polymers, the polymers (1–3) were analyzed by infrared, ¹H NMR, ¹³C NMR, and ²⁹Si NMR spectroscopy and by elemental analysis. When appropriate, the spectroscopic data obtained for the polymers have been compared with spectroscopic data obtained for appropriate model compounds. Such comparisons provide important structural information regarding the composition of the polymers.

The infrared spectral data for the polymers provide only general structural information for the polymers (i.e., presence of SiCH₃ functional groups). However, for polymer 1 (X = O) the various Si–O functions present in the polymer can be detected. The Si–O region of the infrared spectrum of a dilute sample of 1 in CCl₄ consists of three bands at 1050 (broad, strong), 994 (sharp, medium), and 921 (sharp, medium) cm^{–1}. The ν (Si–O) bands for several model compounds are given in Table II. The band observed at 921 cm^{–1} in the infrared spectrum of 1 may be due to the presence of five-membered rings similar to that in 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane, which exhibits a ν (Si–O) band at 920 cm^{–1}.^{12a}

Table II
Infrared $\nu(\text{Si-O})$ Bands (cm^{-1}) of Model Siloxanes

polymer 1 (Si-O)	model compounds	
	structure	$\nu(\text{Si-O})$
921 (m)		920
994 (s)		987
1050 (s, broad)		1020
	$\text{R}_3\text{SiOSiR}_3$	1040-1080

Similarly, the band at 994 cm^{-1} in the infrared spectrum of 1 may be due to the presence of six-membered rings similar to that in the model compound 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane, which exhibits a $\nu(\text{Si-O})$ band at 987 cm^{-1} .¹³ The broad band at 1050 cm^{-1} in the infrared spectrum of 1 may be due to linear components ($\text{R}_3\text{SiOSiR}_3$, $\nu(\text{Si-O})$ at $1040\text{--}1080\text{ cm}^{-1}$) and/or to seven-membered cyclic components (2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane, $\nu(\text{Si-O})$ at 1020 cm^{-1}).^{12a,13}

The ^1H NMR spectral data for polymers 1-3 are given in Table III. In the ^1H NMR spectra of the polymers, weak resonances are observed in the olefinic region, most likely due to the presence of $\text{CH}_2=\text{CHSi}$ end groups in the polymer. The SiCH_3 regions of the spectra consist of broad, intense resonances. The aliphatic regions (including the NH region for the case where $\text{X} = \text{NH}$) are very broad, with no discrete multiplets. In the case where $\text{X} = \text{NCH}_3$, the NCH_3 protons appear as a broad singlet at 2.42 ppm. While the various regions of the spectra can be labeled as SiCH_3 , aliphatic, and SiCH_2Si , they overlap and are not distinct.

Due to the broadness of the resonances and to the overlap of the regions in the ^1H NMR spectra of the polymers 1-3, one cannot rely heavily upon the integrated areas of the regions to provide data for structural analysis of the polymers. They provide only an estimate of the ratios of the olefinic, SiCH_3 , aliphatic, NCH_3 , and SiCH_2Si protons in the polymers. Clearly, however, the degree of unsaturation in the polymers is low, as can be seen by comparison of the integrated values of the olefinic and SiCH_3 , aliphatic, and NCH_3 protons.

The ^{13}C NMR spectral data for the polymers are listed in Table IV. The ^{13}C NMR spectra of the polymers all exhibit broad resonances for the SiCH_3 and aliphatic carbon atoms. Due to the broadness and the number of resonances found in the SiCH_3 and aliphatic regions, one can conclude that the polymer chain is composed of rings of various sizes (and perhaps linear components).^{9f} The olefinic carbon signals, on the other hand, are much sharper, as would be expected for dangling vinyl groups on the polymers. Unfortunately, the broad resonances encountered in both the ^{13}C NMR and the ^1H NMR spectra of the polymers prevent structural determination of the ring sizes present in the polymer on the basis of these NMR spectral data alone.

Because ^{29}Si NMR chemical shifts are sensitive to structural factors such as electronegativity, steric interactions, and variation in bond angles, the data obtained from the ^{29}Si NMR spectra of the polymers offer important structural information about the polymers. As noted, various ring sizes can be formed during the polymerization process (Scheme II), and by comparing ^{29}Si NMR chemical shift data for the polymers with those of cyclic and linear model compounds, structural information about the units

in the polymers may be obtained. Therefore, a number of model compounds for polymers 1 and 2 were prepared and their ^{29}Si NMR spectra were obtained. The ^{29}Si NMR spectra of 1 and 2 along with spectral data for several model compounds, are given in Figures 1 and 2. In addition, the ^{29}Si NMR spectral data for polymers 1-3 are listed in Table V.

For polymer 1, strong, broad resonances centered at 7.8 and 13.2 ppm and two weaker resonances centered at -4 and 25.2 ppm are observed in the ^{29}Si NMR spectrum. By comparison with the vinyl-containing model compound ($\text{CH}_2=\text{CHMe}_2\text{Si}$)₂O ($\delta_{\text{Si}} = -3.1\text{ ppm}$), the resonance in the spectrum of 1 centered at -4 ppm can be attributed to $\text{CH}_2=\text{CHSi}$ groups in the polymer (Figure 1). The five-membered-ring compound, 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane, has a δ_{Si} of 24.3 ppm, so the resonance centered at 25.2 ppm in the spectrum of 1 can be attributed to five-membered-ring species in the polymer. The six-membered-ring compound, 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane, has a $\delta_{\text{Si}} = 12.62\text{ ppm}$, and the seven-membered-ring compound, 2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane, has a $\delta_{\text{Si}} = 12.74\text{ ppm}$. Thus the resonance centered at 13.2 ppm could be due to the presence of the six-membered cyclosiloxane unit with, possibly, some contribution of the seven-membered cyclosiloxane unit as well. The 7.8 ppm resonance could arise from the presence of saturated, cyclic disiloxane groupings. Acyclic disiloxanes generally exhibit ^{29}Si NMR chemical shifts in the 6-10 ppm range (for example, 6.86 ppm for $\text{Me}_3\text{SiOSiMe}_3$).^{12b}

The integration of the area of the resonances in the ^{29}Si NMR spectrum of 1 could provide information about the relative number of $\text{CH}_2=\text{CHSi}$ groups, five- and six-membered rings, and other units. However, as one can see from the spectrum (Figure 1), the resonances centered at 7.8 and 13.2 ppm overlap, making integration inexact. To increase the resolution of these resonances, both low-temperature solution ^{29}Si NMR and solid-state ^{29}Si NMR (MAS) spectra for 1 were obtained. Figure 3 shows the solution ^{29}Si NMR spectrum of 1 at -67.6°C (toluene- d_6). However, no significant sharpening of the overlapping resonances was observed at this lower temperature. Because 1 is a glassy solid at room temperature, it is a suitable candidate for solid-state NMR spectroscopy, which often affords high resolution. The solid-state ^{29}Si NMR (MAS) spectrum of 1 is shown in Figure 4. While the signal to noise ratio is much improved over that obtained by solution methods, resolution of the overlapping resonances is not improved. Because of the overlap in the resonances in the ^{29}Si NMR spectra (both variable-temperature solution and solid state), integration of the area of the resonances can only result in an approximate estimation of the number of the various components in the polymer. Based upon the integration of the resonances in the various regions, the basic units of the polymer can be roughly formulated as having 1.1 SiOSi in five-membered rings, 3.9 SiOSi in six- and, possibly, seven-membered rings, and 3.6 SiOSi in acyclic units, relative to $\text{SiCH}=\text{CH}_2 = 1$.

The ^{29}Si NMR spectrum of polymer 2 ($\text{X} = \text{NH}$) and those of several model compounds are given in Figure 2. In the spectrum of 2, a broad resonance from 0 to 7 ppm and a broad resonance from 10 to 17 ppm are observed. The resonance from 10 to 17 ppm may be attributed to five-membered-ring species, as the chemical shift is similar to that for 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane ($\delta_{\text{Si}} = 13.10\text{ ppm}$). The six- and seven-membered-ring model compounds (2,2,6,6-tetramethyl-1-aza-2,6-disila-

Table III
¹H NMR Spectral Data (CDCl₃ Solution) for the Polymers Prepared in This Study

polymer	δ _{SiCH₃}	δ _{aliphatic}	δ _{olefinic}	δ _{other}
1 (X = O)	-0.3 to +0.3 (40.8 H)	0.3-2.3 (13 H)	5.3-6.2 (1 H)	
2 (X = NH)	-0.15 to +0.25 (35.3 H)	0.25-2.2 (16.6 H)	5.2-6.2 (1 H)	
3 (X = NCH ₃)	-0.2 to +0.2 (72.5 H)	0.2-2.3 (30.8 H)	4.3-6.0 (1 H)	δ _{NCH₃} 2.42 (10.8 H)
4	0-0.4 (1.6 H)	0.4-2.5 (1 H)		
5	0-0.9 (2.6 H)	0.9-2.5 (1 H)		
6	-0.1 to +0.2 (6.8 H)	0.2-2.2 (3.3 H)		δ _{SiH} 3.7-4.1 (1 H)
7	-0.2 to +0.2 (3.7 H)	0.2-2.1 (1 H)		
8	-0.1 to +0.15 (2.1 H)	0.15-0.4 (1 H, SiCH ₂ CH ₂ CH ₂ CH ₃) 0.4-0.6 (1 H, SiCH ₂ CH ₂ CH ₂ CH ₃) 0.6-1.1 (1.2 H, SiCH ₂ CH ₂ CH ₂ CH ₃) 1.1-1.7 (1.7 H, SiCH ₂ CH ₂ CH ₂ CH ₃)		
9	-0.2 to +0.4 (2.5 H)	0.4-2.3 (2 H)		δ _{CH=CH₂} 5.5-6.3 (1 H)
10	-0.1 to +0.4 (20 H)	0.4-2.3 (5.5 H)		δ _{SiH} 4.4-4.7 (1 H, SiH)

Table IV
¹³C NMR Spectral Data (CDCl₃ Solution) for Polymers Prepared in This Study

polymer	δ _{SiCH₃}	δ _{aliphatic}	δ _{olefinic}	δ _{other}
1 (X = O)	-4 to +3.5	10-38	131.57, 139.68	
2 (X = NH)	-2 to +7	8-40	131.31, 141.34	
3 (X = NCH ₃)	-5.5 to +5	11-42		δ _{NCH₃} 27.04 (q, <i>J</i> = 134.2 Hz) 28.55 (q, <i>J</i> = 132.0 Hz) 28.70 (q, <i>J</i> = 132.0 Hz)
4	-4 to +2	10-44		
5	-2 to +7.5	7.5-37		
6	-4 to 0	0-44		
7	-4 to +3	8-42		
8	-0.4 to +1	13-17 13.91 (q, <i>J</i> = 124.4 Hz, CH ₃) 26.28 (t, <i>J</i> = 122.4 Hz, CH ₂) 26.72 (t, <i>J</i> = 125.4 Hz, CH ₂) 26.88 (t, <i>J</i> = 125.4 Hz, CH ₂)		
9	-7 to +2	8-45		δ _{CH=CH₂} 124-125 130-133 138-142
10	-2 to +5	7-40		

cyclohexane and 2,2,7,7-tetramethyl-1-aza-2,7-disilacycloheptane) have δ_{Si} of 3.04 and 4.74 ppm, respectively. These values correspond well with the most intense portion of the broad resonance between 0 and 7 ppm. Again, linear units are possible in the polymer, and the chemical shifts for such units are anticipated in this region (for example, Me₃SiNHSiMe₃ has a δ_{Si} = 0.2 ppm^{12b}). Because the resonances for six- and seven-membered-ring units in the polymer would be expected to overlap with resonances for linear units, integration to provide structural information is only approximate. Based upon the integration of the resonances in the various regions, the basic units of the polymer can be roughly formulated as one five-membered-ring unit to 2.9 six- and seven-membered-ring and linear units.

Comparison of the ²⁹Si NMR spectral data for 1 and 2 with those of various model compounds provides a means of obtaining only qualitative structural information at best about the polymers. The presence of five- and larger-membered rings is confirmed by comparison of chemical shift data of the resonances in NMR spectra of the polymers with those for model cyclic compounds. Because the chemical shifts for five- and six-, and seven-membered

rings and for acyclic compounds often are very similar and because the resonances in the spectra of the polymers are broad, the presence of seven-membered rings and of acyclic units in the polymers cannot with certainty be confirmed or ruled out.

Chemical Transformations of the Cyclopolymers 1 and 2. One of the motivations behind preparing cyclopolymers containing a large number of functionalized silicon groups (Si-X-Si groups) is that such polymers should be amenable to chemical transformations. In fact, we can take advantage of the known chemistry of the Si-X-Si units in the cyclopolymers to prepare a variety of new polymers. In addition, reactions of the polymers that result in cleavage of the Si-X-Si units in the cyclopolymers would provide useful information concerning the structure of the polymers.

Cleavage of R₃Si-O-SiR₃ species with electrophiles such as BF₃ to give R₃SiF is well known.¹⁵ However, reaction of the cyclopolymer 1 (X = O) with an excess of BF₃·OEt₂ (under vigorous conditions) led to only partial cleavage of the Si-O-Si groups in the cyclopolymer. The polymeric product was analyzed by ¹H, ¹³C, and ²⁹Si NMR spectroscopy as well as by IR spectroscopy and elemental

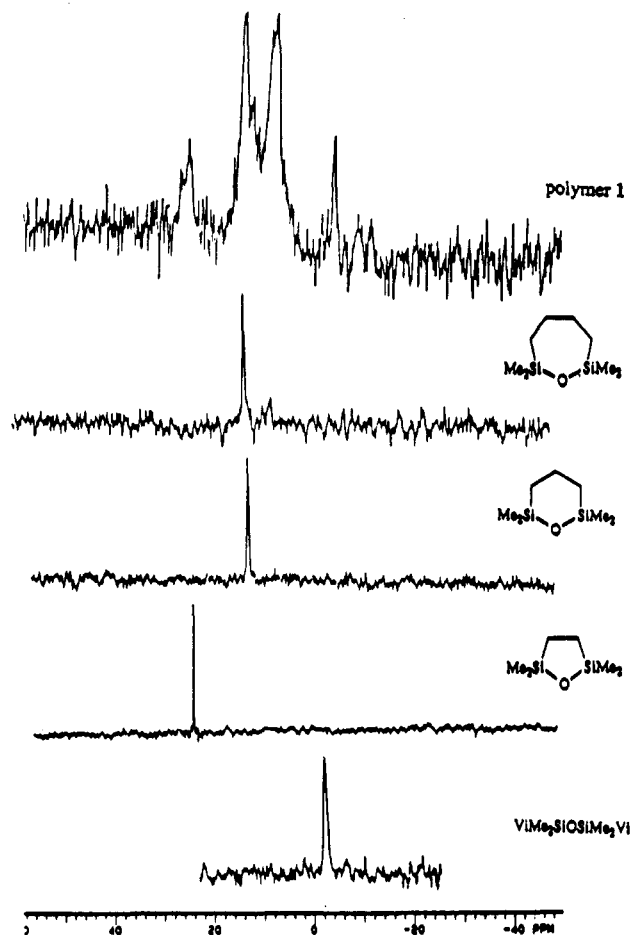


Figure 1. ^{29}Si NMR spectra of polymer 1 ($\text{X} = \text{O}$) and model compounds.

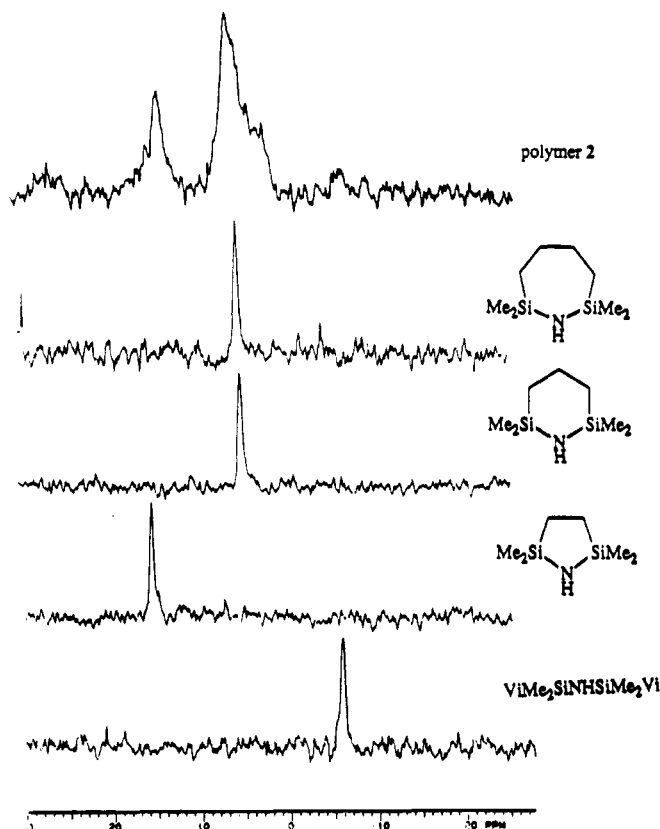


Figure 2. ^{29}Si NMR spectra of polymer 2 ($\text{X} = \text{NH}$) and model compounds.

analysis. Little structural information was obtained from the ^1H and ^{13}C NMR spectra, but the IR spectrum and the

Table V
 ^{29}Si NMR Spectral Data (CDCl_3 Solution) for Polymers Prepared in This Study

polymer	δ (integral)
1 ($\text{X} = \text{O}$)	-4 (1 Si), 7.8 (b, 7.2 Si), 13.2 (b, 7.5 Si), 25.2 (b, 2.25 Si)
2 ($\text{X} = \text{NH}$)	0-7 (vb, 2.9 Si), 10-17 (vb, 1 Si)
3 ($\text{X} = \text{NCH}_3$)	0-9 (b, 1.3 Si), 11-18 (b, 1 Si)
4	33.2 (d, $J = 288$ Hz)
5	28-37 (b)
6	-17 to -6 (vb)
7	0-6 (b)
8	2.5 (b, 1 Si), 5.0 (b, 1 Si)
9	-7 to -5 (b, 1 Si), -5 to -1 (b, 1.7 Si)
10	-14.1 (d, $J = 191$ Hz, 1 Si, SiH) -12.8 (d, $J = 197$ Hz, 2 Si, SiH) 2-8 (b, 4 Si, SiCH ₃) 14-19 (b, 2 Si, SiCH ₃)

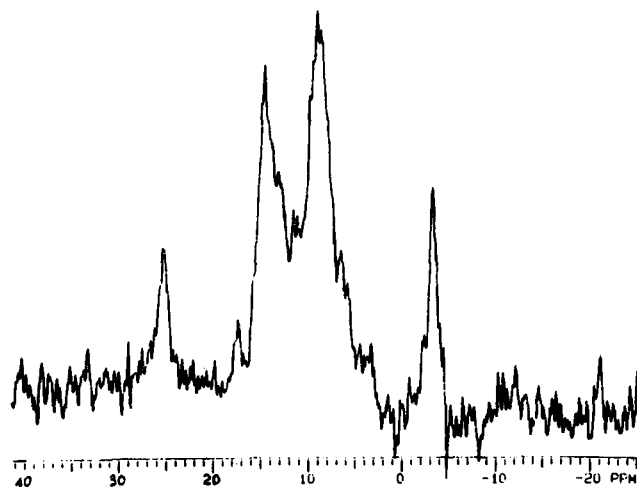


Figure 3. Low-temperature ^{29}Si NMR spectrum of polymer 1 ($\text{X} = \text{O}$).

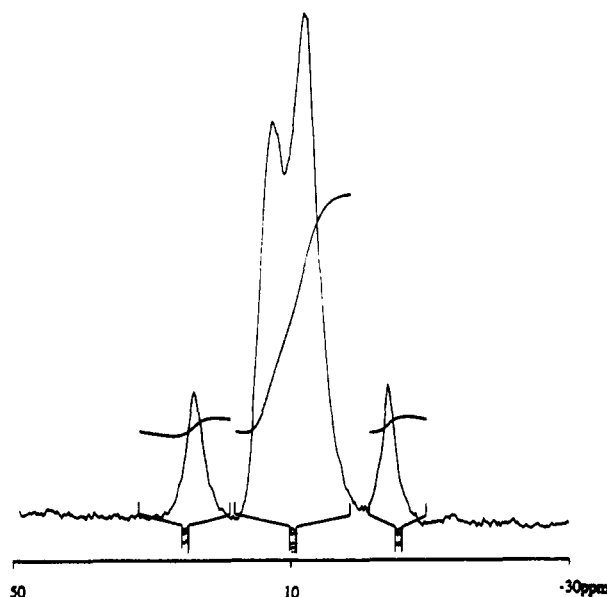
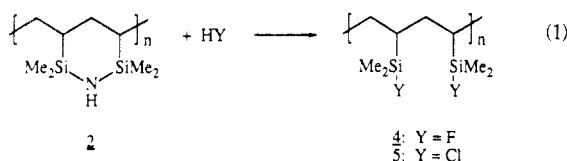


Figure 4. Solid-state ^{29}Si NMR spectrum of polymer 1 ($\text{X} = \text{O}$).

^{29}Si NMR spectral data revealed the presence of residual disiloxane functional groups in addition to Si-F functions. In the IR spectrum a medium-intensity band indicative of the presence of disiloxane functionality is observed at 997 cm^{-1} . The presence of the Si-O-Si function also was confirmed by the ^{29}Si NMR spectrum, which consisted of medium-intensity resonances from 5 to 18 ppm and a strong doublet at 33.2 ppm ($J = 285$ Hz). The broad resonances between 5 and 18 ppm were assumed to be due to unreacted Si-O-Si groups of the parent cyclopolymer

1. The doublet pattern at 33.2 ppm is indicative of Si-F bonds introduced into the polymer, and both the chemical shift and the coupling constant are consistent with the formation of RMe_2SiF species in the polymer. For example, Me_3SiF has a ^{29}Si NMR chemical shift of 35.4 ppm with $J_{\text{Si-F}} = 279.8 \text{ Hz}$.¹⁶

The high reactivity of disilazanes, $\text{R}_3\text{SiN(R')SiR}_3$, led us to concentrate on ring-cleavage reactions of the cyclopolymer 2 (X = NH). Acids such as HF and HCl readily cleave the Si-N-Si bonds in disilazanes to give two Si-F or Si-Cl bonds and ammonium salts.^{17,18} Reaction of cyclopolymer 2 (X = NH) with both aqueous HF and anhydrous HCl led to ring-opened polymers 4 and 5, that contained no residual Si-N-Si bonds (eq 1). In eq 1, the cyclopolymer 2 is represented, for simplicity, as a linear polymer comprised of six-membered rings although, as discussed previously, the polymer is of more complicated structure, containing cyclic and acyclic units.



The ring-opened polymers 4 and 5 were characterized by ^1H , ^{13}C , ^{19}F (in the case of 4), and ^{29}Si NMR spectroscopy, in addition to IR spectroscopy and elemental analysis. The ^1H NMR spectra of 4 and 5 (Table III) contain broad resonances in the SiCH_3 and aliphatic regions. As discussed previously, the parent cyclopolymer 2 contains a small number of Si-Vi groups, presumably present as terminal (or dangling) $\text{Me}_2\text{SiN(H)SiMe}_2\text{Vi}$ groups in the cyclopolymer. Reaction of these groups with the protic acids HF and HCl would result in Si-N cleavage to give an Me_2SiF or Me_2SiCl end group in the polymer and release of the corresponding $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiF}$. Therefore, polymers 4 and 5 are not expected to contain any Si-Vi groups, and this is confirmed by their ^1H NMR spectra. As in the parent cyclopolymer 2, the overlap of the resonances of the SiCH_3 and aliphatic regions in the spectra prevents precise integration of the areas of the regions. The integrated areas, therefore, provide only an estimate of the ratios of the various regions.

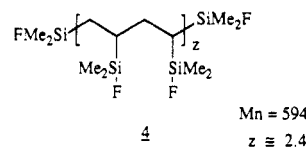
Little structural information could be gained from the ^{13}C NMR spectra of polymers 4 and 5 (Table IV), as they consisted of broad multiplets in the SiCH_3 and aliphatic regions. The ^{19}F NMR spectrum of 4 confirmed the existence of Si-F functional groups in the polymer. The spectrum consists of two broad, overlapping resonances at -157.5 and -162.2 ppm. These chemical shifts lie in the expected region for R_3SiF compounds (for example, Me_3SiF has $\delta_{\text{F}} = -156.5 \text{ ppm}$).¹⁹

The ^{29}Si NMR spectra for 4 and 5 clearly showed that the disilazane functions in the parent cyclopolymer 2 have been completely cleaved to give Si-F and Si-Cl bonds. For 4, the ^{29}Si NMR spectrum consists of a strong doublet ($J = 288 \text{ Hz}$) at 33.2 ppm, indicative of the Si-F bonds in the polymer, and both the chemical shift and the coupling constant are consistent with the formation of RMe_2SiF species. No residual resonances were observed in the spectrum of 4 for the Si-N-Si groups of 2 (δ_{Si} from -0.15 and 2.2 ppm), indicating that complete cleavage had occurred. For 5, the ^{29}Si NMR spectrum consists of a broad resonance from 28 to 37 ppm. The chemical shift is consistent with the formation of RMe_2SiCl species in the polymer. For example, Me_3SiCl has a ^{29}Si NMR

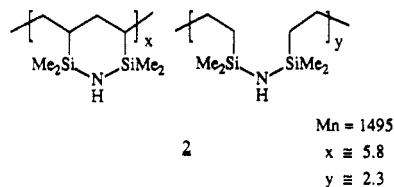
chemical shift of 30.2 ppm.¹⁶ Again, no residual resonances for Si-N-Si units of 2 are observed.

Molecular weight data for polymer 4 provide important information concerning not only the structure of 4 but also the structure of the parent polymer 2. The molecular weight values determined by GPC for 4 were $M_w = 819$ and $M_n = 594$ with $D = 1.34$ (where the polydispersity, D , is defined as the values of M_w/M_n). If the parent polymer 2 consisted only of acyclic disilazane units with the Si-N-Si bonds in the polymer backbone, cleavage of the units by HF would result in low molecular weight, volatile Si-F-containing species. Since a polymeric residue (4) was isolated from the reaction of 2 with HF, cyclic species must be present in the parent polymer 2. However, isolation of polymer 4 does not rule out the possibility that the parent polymer 2 contains some acyclic species, and a comparison of the molecular weights of polymers 4 and 2 should provide an indication of the presence of acyclic species in 2.

If we assume that polymer 4 has two Me_2SiF end groups and repeat units of the general form $-\text{[CH}_2\text{CH}(\text{SiMe}_2\text{F})\text{CH}_2\text{CH}(\text{SiMe}_2\text{F})\text{]}_z-$, then the number of repeat units, z , is calculated to be approximately 2.4 (using $M_n = 594$).



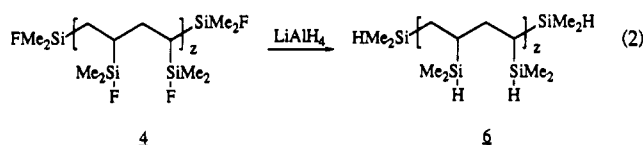
The molecular weight of the parent polymer 2 is $M_n = 1495$. Excluding the dangling Si-Vi groups in 2 (which are present in very low concentration as determined by ^1H and ^{29}Si NMR spectroscopy), the total number of repeat units, both cyclic and acyclic, in 2 can be calculated to be approximately 8.1. Since the cleaved polymer 4 (really an oligomer) contains approximately 2.4 repeat units, the parent polymer 2 must contain some acyclic species which are cleaved during reaction with HF. The number of cyclic and acyclic units in 2 can therefore be calculated to be approximately 5.8 and 2.3, respectively. Note that in 2 the cyclic species are represented as six-membered rings for simplicity.



However, reliable quantitative conclusions cannot be drawn from these GPC-derived molecular weights since the molecular weights are calculated by comparing the retention time of the polymer with those of polystyrene standards. Interaction of the silicon-containing polymers of this study with the GPC column material will be different than the interaction of polystyrene with the GPC column material. Therefore, the molecular weight values determined by GPC cannot be taken as absolute. Another, equally problematic method for determining molecular weights of the polymers is cryoscopy in benzene. Molecular weight values determined by this procedure for polymers 4 and 2 are $M_n = 1910$ and $M_n = 910$, respectively. Based upon the arguments presented above, it is clear then that both cyclic and acyclic species are present in the parent polymer 2. Further molecular weight studies for variants of polymers 2 and 4 are presented later in this discussion.

Polymer 4 serves as a useful precursor for the preparation of a second generation of organosilicon functionalized polymers. The Si-F groups in 4 react readily with a variety of reagents, such as LiAlH_4 , RLi , and RMgBr , to give Si-H and Si-R containing polymers.

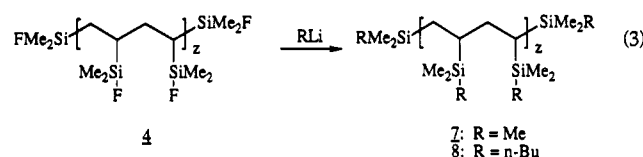
The reaction of 4 with LiAlH_4 in diethyl ether gave an Si-H-containing polymer, 6 (eq 2). Polymer 6 was



characterized by the usual spectroscopic techniques. The IR spectrum of 6 confirmed the presence of Si-H groups, as the characteristic Si-H absorption appears at 2112 cm^{-1} . The ^1H and ^{13}C NMR spectral data for 6 are given in Tables III and IV. The ^1H NMR spectrum consists of broad SiCH_3 (-0.1 to $+0.2$ ppm), aliphatic (0.2 – 2.2 ppm), and Si-H (3.7 – 4.1 ppm) resonances.

The ^{13}C NMR spectrum offered little structural information, as it consists of broad resonances in the SiCH_3 and aliphatic regions. However, the ^{29}Si NMR spectrum of 6, a broad resonance between -17 and -6 ppm, clearly showed that complete reaction of Si-F groups to give Si-H groups had occurred. This resonance is in the region anticipated for R_3SiH species (for example, Me_3SiH has a $\delta_{\text{Si}} = -16.34\text{ ppm}^{12b}$). No resonances were observed at 33.2 ppm , where the Si-F functional groups of the parent polymer 4 appear.

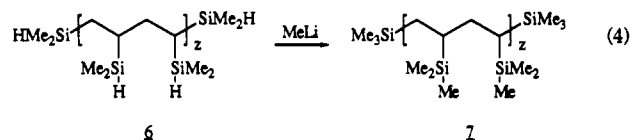
The reaction of 4 with the alkyllithium reagents MeLi and $n\text{-BuLi}$ gave Si-Me and Si- $n\text{-Bu}$ containing polymers 7 and 8 (eq 3). Polymer 4 reacted readily with MeLi in



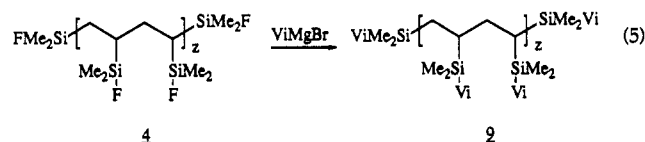
diethyl ether, and complete substitution of Si-F groups was effected by stirring the mixture at room temperature for 2 h. Reaction of 4 with $n\text{-BuLi}$ in hexane was less facile, and stirring of the mixture at room temperature for 20 h was required to ensure complete substitution of the Si-F groups.

Polymers 7 and 8 were characterized by the usual spectroscopic techniques. The ^1H NMR spectral data for 7 and 8 are given in Table III. The ^1H NMR spectrum of 7 consists of broad SiCH_3 and aliphatic regions. For 8, the ^1H NMR spectrum shows a broad resonance in the SiCH_3 region and overlapping resonances in the regions associated with the aliphatic protons of the $n\text{-Bu}$ groups. The ^{13}C NMR spectral data for 7 and 8 are given in Table IV. The ^{13}C NMR spectrum of 7 consists of broad resonances in the SiCH_3 and aliphatic regions. In addition to broad resonances in the SiCH_3 and aliphatic regions, the ^{13}C NMR spectrum of 8 contains sharper resonances between 13.91 and 26.88 ppm which can be associated with the $n\text{-Bu}$ groups in the polymer. The ^{29}Si NMR spectra of 7 and 8 confirm that complete substitution of the Si-F groups had occurred. For 7, the ^{29}Si NMR spectrum shows a broad resonance between 0 and 6 ppm , with no resonances observed in the Si-F region. Similarly, the ^{29}Si NMR spectrum of 8 consists of broad resonances at 2.5 and 5 ppm , with no resonances observed in the Si-F region.

The Si-H containing polymer 6 also can be alkylated by RLi species. Substitution of the Si-H groups in 6 was complete after heating a solution of 6 and MeLi in diethyl ether at reflux for 24 h (eq 4). The ^1H , ^{13}C , and ^{29}Si NMR spectral data obtained for this polymer are identical to those obtained for the Si-Me containing polymer prepared from polymer 4.

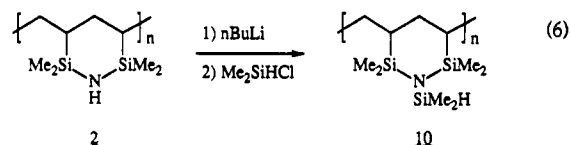


Polymer 4 also reacts with the Grignard reagent $\text{CH}_2=\text{CHMgBr}$ in tetrahydrofuran over 3.5 days to give a $\text{SiCH}=\text{CH}_2$ -containing polymer, 9 (eq 5). Character-



ization of 9 included the ^1H NMR and ^{13}C NMR spectral data given in Tables III and IV. The ^1H NMR spectrum of 9 contains broad resonances for the SiCH_3 and aliphatic regions as well as multiplets in the vinyl region between 5.5 and 6.3 ppm . The ^{13}C NMR spectrum of 9 also contains broad resonances for the SiCH_3 and aliphatic regions and several resonances between 124 and 142 ppm in the $\text{CH}=\text{CH}_2$ region. Evidence that complete substitution of the Si-F groups had occurred was given by the ^{29}Si NMR spectrum of 9 (Table V). The spectrum consists of two broad resonances from -7 to -5 ppm and from -5 to -1 ppm . No resonances are observed downfield in the Si-F region of the spectrum.

One final example of a chemical conversion of cyclopolymer 2 is given. The amine proton in cyclopolymer 2 can be readily substituted to give N-R-containing cyclopolymer. Reaction of 2 with $n\text{-BuLi}$, followed by quenching with Me_2SiHCl , gave an NSiMe_2H -containing cyclopolymer 10 (eq 6). The IR spectrum of 10 confirmed



the presence of SiMe_2H groups, as the characteristic Si-H absorption appeared at 2116 cm^{-1} . The ^1H NMR spectrum of 10 (Table III) consists of a broad SiCH_3 (-0.1 to $+0.4\text{ ppm}$), aliphatic (0.4 – 2.3 ppm), and Si-H (4.4 – 4.7 ppm) resonances. Integration of the areas of the regions suggests a SiCH_3 :aliphatic:Si-H proton ratio of approximately $20:5.5:1$. This is consistent with the proposed structure of the polymer, as shown in eq 6, which should have a SiCH_3 :aliphatic:Si-H proton ratio of $18:6:1$ in the ^1H NMR spectrum. The ^{13}C NMR spectrum (Table IV) offers little structural information. The ^{29}Si NMR spectrum of 10 (Table V) also confirms the presence of the Si-H bond in the cyclopolymer. Two doublets appear in the $\text{R}_3\text{Si-H}$ region of the spectrum at -14.1 ppm ($J = 191\text{ Hz}$) and -12.8 ppm ($J = 197\text{ Hz}$), which correspond to the exocyclic SiMe_2H groups in the polymer. The endocyclic SiMe_2 group signals appear further downfield as broad resonances from 2 to 8 ppm and from 14 to 19 ppm .

Concentration Effect on the Polymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$. As discussed earlier, cyclopoly-

Table VI
Molecular Weight Data for Polymers 2-2e and 4-4e

cyclopolymer (conc'n time)	mol wt	Si-F- containing polymer	mol wt
2 (3.5 M, 24 h)	$M_w = 2628$ $M_n = 1495$ $D = 1.76$	4	$M_w = 819$ $M_n = 594$ $D = 1.34$
2b (0.9 M, 24 h)	$M_w = 1720$ $M_n = 1248$ $D = 1.38$	4b	$M_w = 660$ $M_n = 535$ $D = 1.23$
2c (0.2 M, 24 h)	$M_w = 1120$ $M_n = 960$ $D = 1.16$	4c	$M_w = 553$ $M_n = 465$ $D = 1.20$
2d (0.9 M, 6 h)	$M_w = 1706$ $M_n = 1311$ $D = 1.30$	4d	$M_w = 678$ $M_n = 528$ $D = 1.28$
2e (0.9 M, 48 h)	$M_w = 3052$ $M_n = 1549$ $D = 1.97$	4e	$M_w = 646$ $M_n = 586$ $D = 1.10$

mer 2 contains both cyclic and acyclic units in the polymer backbone. The acyclic units are sites for polymer chain cleavage during the reaction of 2 with reagents that cleave the Si-N bonds of the Si-N-Si unit. Therefore, derivatives of lower molecular weight of polymers 2 are obtained when 2 is treated with such cleavage reagents. If the polymerization is kinetically controlled, a lower monomer concentration should favor intramolecular cyclization over intermolecular attack (which results in the formation of acyclic species). Thus, in an attempt to prepare cyclopolymer with a lower number of acyclic units, a series of polymerizations of $(CH_2=CHMe_2Si)_2NH$ was carried out at different concentrations. The standard polymerization procedure was employed in each case using 2.6 mol % of di-*tert*-butyl peroxide catalyst with heating to 215 °C for various times. The cyclopolymer designated as 2, 2b, and 2c were prepared at 3.5, 0.9, and 0.2 M monomer concentration, respectively, with heating for 24 h. The cyclopolymer designated as 2d and 2e were prepared at 0.9 M monomer concentration, with heating for 6 and 48 h, respectively. To determine the number of acyclic units present in the polymer, cleavage reactions with HF were performed to give Si-F-containing polymers 4-4e. A comparison of the molecular weights of the series of polymers provided information regarding the acyclic units present in the parent cyclopolymer. Molecular weight data for the polymers are presented in Table VI.

Initially, as the concentration of monomer was decreased, the molecular weight of the parent cyclopolymer 2 decreased. The weight-average molecular weights, M_w , for polymers 2, 2b, and 2c are 2628, 1720, and 1120, respectively. Because chain growth occurs through an intermolecular process, decreasing concentration leads to slower propagation, and lower molecular weight polymers were formed. However, with longer reaction times molecular weights should increase. Therefore, additional polymerization reactions were performed (2d and 2e) in which the monomer concentration was held constant (0.9 M) but reaction times were varied. When the reaction times were increased from 6 to 24 to 48 h, M_w values increased from 1706 to 1720 to 3052, respectively.

While these experiments have shown how concentration and reaction time affect molecular weights of the cyclopolymer, how these factors affect the number of acyclic units present in the polymers is of primary interest. To determine this, an examination of the number-average molecular weights for the cleaved polymers 4-4e is necessary. The M_n values for Si-F-containing polymers 4, 4b, and 4c are 594, 535, and 465, respectively. The polymers all have similar molecular weights, indicating

Table VII
 1H NMR Spectral Data and Molecular Weight Data for Polymers 1a-c

polymer	δ_{SiCH_3}	$\delta_{aliphatic}$	δ_{olefin}	$M_n(\Delta Fp)$
1a	-0.2 to +0.3 (14.5 H)	0.3-2.2 (6.7 H)	5.3-6.3 (1 H)	694
1b	-0.2 to +0.3 (28.0 H)	0.3-2.3 (13.6 H)	5.3-6.3 (1 H)	2703
1c	-0.2 to +0.3 (34.0 H)	0.3-2.3 (14.6 H)	5.2-6.2 (1 H)	3410

that the relative concentration of acyclic units in the corresponding parent cyclopolymer 2, 2b, and 2c is similar. Therefore, changing monomer concentration from 3.5 to 0.9 to 0.2 M has little effect upon the relative concentration of acyclic species in the cyclopolymer.

The M_n values for cleaved polymers 4d, 4b, and 4e are 528, 535, and 586. Again, the polymers all have similar molecular weights, indicating that the concentration of acyclic units in the corresponding parent cyclopolymer 2d, 2b, and 2e are similar. Therefore, changing reaction times from 6 to 24 to 48 h had little effect upon the relative concentration of acyclic species in the cyclopolymer. Overall, neither concentration nor reaction time appreciably affects the relative number of acyclic units present in the cyclopolymer 2-2e. Such evidence leads us to conclude that the polymerization of $(CH_2=CHMe_2Si)_2NH$ is thermodynamically controlled, rather than kinetically controlled.

Increasing Cyclopolymer Molecular Weights by Stepwise Addition of Initiator. A series of reactions was performed to determine if cyclopolymer of increased molecular weights could be prepared through stepwise addition of di-*tert*-butyl peroxide. In the first reaction of the series, $(CH_2=CHMe_2Si)_2O$ and 2.6 mol % of *tert*-butyl peroxide were heated in chlorobenzene for 2 days at 140-170 °C and then stirred at room temperature for 1 day (polymer 1a). In the second reaction of the series, the same procedure was used as in the first, but after heating for 2 days and then stirring at room temperature for 1 day, an additional 2.6 mol % of di-*tert*-butyl peroxide was added and the mixture was heated a second time to 140-170 °C for 2 days and then stirred at room temperature for 1 day. At this point, a measured aliquot of the reaction mixture was removed for analysis (polymer 1b). Lastly, a third addition of di-*tert*-butyl peroxide was made to the remaining portion of the reaction mixture, and again the mixture was heated to 140-170 °C for 2 days (polymer 1c). The polymers prepared in these reactions were analyzed by 1H NMR spectroscopy, and the molecular weights of the polymers were determined by cryoscopy in benzene (Table VII).

As can be seen from the molecular weight data in Table VII, as the amount of di-*tert*-butyl peroxide was increased, the molecular weights of the resulting polymers increased. This is anticipated since the cyclopolymer contains residual $CH_2=CHSi$ groups which can undergo further polymerization with unreacted monomer in the reaction mixtures. A comparison of the integrated areas of the $CH_2=CHSi$ proton resonances with the integrated areas of the resonances for the aliphatic and $SiCH_3$ protons in the 1H NMR spectra of the polymers also supports the molecular weight data. An increase in molecular weight is reflected in the decrease in the ratio of the dangling $CH_2=CHSi$ groups to the aliphatic and $SiCH_3$ groups.

Conclusion

A general synthetic route for the preparation of cyclopolymer from dienes of the type $(CH_2=CHMe_2Si)_2X$ was accomplished. Structural features of the polymers, such

as the presence of various cyclic and acyclic species, were determined through spectroscopic analysis and through chemical modification reactions. Due to the rich chemistry available through the Si-X-Si functional groups in the polymers, a variety of polymer derivatives can be prepared.

Experimental Section

General Comments. All reactions, unless otherwise noted, were performed under an argon atmosphere using standard Schlenk techniques. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from Hls America or Silar and distilled from magnesium chips before use. Grignard and alkyllithium reagents were purchased from Aldrich and used as received.

Proton NMR spectra were obtained on a Varian XL-300 NMR spectrometer using $\text{CDCl}_3/\text{CHCl}_3$ unless otherwise noted as a reference at 7.24 ppm downfield from tetramethylsilane. ^{13}C NMR spectra, both proton coupled and decoupled, were obtained using a Varian XL-300 NMR spectrometer operating at 75.4 MHz in CDCl_3 or C_6D_6 . ^{19}F NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 282.2 MHz in CDCl_3 using CFCl_3 (0.0 ppm) as the external standard. ^{29}Si NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 59.59 MHz in CDCl_3 or C_6D_6 using tetramethylsilane (0.00 ppm) as the external standard. Solid-state ^{29}Si NMR (MAS) spectra were obtained using a Bruker/IBM 250 NMR spectrometer operating at 59.59 MHz using coarse magic angle spinning cross polarization.

Molecular weights (ΔFp) were determined using the technique of cryoscopy in benzene. GPC molecular weight determinations were made using either a Waters Millipore GPCII Model 590 chromatograph equipped with Waters Millipore Ultrastaygel 10^4 -Å and 10^3 -Å columns with THF solvent or a Waters Millipore 150-C ALC/GPC chromatograph equipped with a Waters Millipore Ultrastaygel 10^3 -Å column with toluene solvent.

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Preparation of Monomers. $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}$ was purchased from Hls and used as received. $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ was prepared by the ammonolysis of $\text{H}_2\text{C}=\text{CHMe}_2\text{SiCl}$,¹¹ and $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NCH}_3$ was prepared by the reaction of H_2NCH_3 with $\text{CH}_2=\text{CHMe}_2\text{SiCl}$.¹¹

Standard Cyclopolymerization Procedure. The monomer, chlorobenzene, and di-*tert*-butyl peroxide were placed together in a round-bottomed flask equipped with a magnetic stirbar and a reflux condenser with a gas inlet/outlet tube connected to an oil bubbler on a Schlenk line. The mixture was freeze-thaw-degassed four times and then heated in a sand bath. After the heating was discontinued, volatiles were removed by trap-to-trap distillation under vacuum into a cold trap.

Cyclopolymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}$. The following quantities were used: 161.1 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}$ (860 mmol), 4.1 mL of di-*tert*-butyl peroxide (22 mmol, 2.6 mol %), and 230 mL of chlorobenzene.

The standard procedure was employed (500-mL flask) with heating to 180 °C for 8 h and then 210 °C for 36 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg into a cold trap and the residue was dried under vacuum (120 °C, 0.05 mmHg, 3.5 days). Upon cooling, a glassy, nearly clear solid (1) was obtained (119 g, 74%). Anal. Calcd: C, 51.59; H, 9.74. Found: C, 51.73; H, 9.85. ^{29}Si NMR (−67.6 °C, toluene- d_6): δ_{Si} −3.7 (1 Si), 8.6 (b, 7.5 Si), 14.0 (b, 7.5 Si), 24.8 (b, 1.5 Si). ^{29}Si NMR (MAS, CDCl_3): δ_{Si} −4.0 (1 Si), 8.2 and 12.6 (b, 11 Si), 23.7 (b, 1 Si). IR (in CCl_4 , cm^{-1}): 2956 (s), 2901 (m), 1600 (w), 1442 (w), 1407 (w), 1253 (s), 1050 (s, br), 994 (s), 921 (m), 836 (s). Molecular weight: ΔFp , M_n = 2310; GPC, M_w = 3750.

Cyclopolymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$. The following quantities were used: 72.1 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ (389 mmol), 1.86 mL of di-*tert*-butyl peroxide (10.1 mmol, 2.6 mol %), and 110 mL of chlorobenzene.

A 500-mL flask equipped with a magnetic stirbar and a Claisen adapter with a reflux condenser and gas inlet/outlet tube was evacuated and backfilled with argon before introduction of reagents. The standard procedure then was followed, with heating to 215 °C for 24 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg into a cold trap, and the residue was

dried under vacuum (room temperature for 24 h, then 50 °C for 48 h, 0.05 mmHg). Upon cooling, a cloudy, glassy solid (2) was obtained (47.5 g, 66%). Anal. Calcd: C, 51.81; H, 10.32. Found: C, 50.73; H, 10.04. IR (in CCl_4 , cm^{-1}): 3435 (w), 3384 (w), 2952 (s), 2898 (s), 1548 (s), 1406 (w), 1250 (s), 1156 (m), 1005 (m), 978 (m), 913 (s), 860–804 (s, br). Molecular weight: ΔFp , M_n = 1910; GPC, M_w = 2628, M_n = 1495, D = 1.76.

Cyclopolymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NCH}_3$. The following quantities were used: 4.82 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NCH}_3$ (24 mmol), 0.11 mL of di-*tert*-butyl peroxide (0.60 mmol, 2.5 mol %), and 7 mL of chlorobenzene.

The standard procedure was employed (100-mL flask) with heating to 215 °C for 24 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature for 16 h, then 80 °C for 4 h, 0.05 mmHg). Upon cooling, a faint yellow, glassy solid (3) was obtained (3.70 g, 77%). Anal. Calcd: C, 54.19; H, 10.61. Found: C, 53.34; H, 10.37. IR (in CCl_4 , cm^{-1}): 3435 (vw), 3385 (vw), 2951 (s), 2891 (s), 2806 (m), 1617 (w), 1461 (m), 1406 (m), 1374 (m), 1249 (s), 1182 (m), 1142 (s), 1076 (s), 990 (w), 882 (s), 837 (s). Molecular weight: ΔFp , M_n = 1188.

Polymer Functional Group Reactions. Reaction of Polymer 1 with $\text{BF}_3\cdot\text{OEt}_2$. A two-necked 100-mL round-bottomed flask equipped with a magnetic stirbar, a reflux condenser with a gas inlet/outlet tube connected to an oil bubbler on a Schlenk line, and a rubber septum was charged with 0.8 g of 1, 4 mL of $\text{BF}_3\cdot\text{OEt}_2$ (0.033 mol), and 15 mL each of diethyl ether and benzene. The mixture was stirred and heated to a vigorous reflux for 28 h. After cooling to room temperature, volatiles were removed from the mixture by trap-to-trap distillation (60 °C/0.05 mmHg). Hexane (25 mL) was added, and the mixture was stirred for an additional 10 h. A water workup was performed. Water was added until the organic layer cleared. After separation from the aqueous layer, the organic layer was dried over anhydrous MgSO_4 and then filtered. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 24 h). A viscous, slightly cloudy, light yellow oil was obtained (0.71 g). Anal. Calcd for complete conversion of SiOSi to 2 SiF : C, 46.10; H, 8.70. Found: C, 49.76; H, 9.20. ^{29}Si NMR (CDCl_3): δ_{Si} 5–18 (b, residual SiOSi , 1 Si), 33.2 (d, J = 285 Hz, 2.2 SiF). IR (thin film, cm^{-1}): 2960 (m), 1454 (w), 1409 (w), 1257 (s), 997 (m), 862 (s, br).

From the IR and ^{29}Si NMR spectra and from the analysis it is clear that unreacted SiOSi groups are present.

Reaction of Polymer 2 with HF. A solution of 13.0 g of 2 in 50 mL of diethyl ether was added in small portions over 5 min to 32 mL of HF (48% in H_2O) in a 250-mL plastic beaker in air. Bubbling and heat evolution were observed. The beaker was covered with aluminum foil, and the solution was stirred at room temperature for 40 min. A water workup was performed as usual. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 24 h). A viscous, light tan-yellow oil (4) was obtained (12.4 g). Anal. Calcd: C, 46.10; H, 8.70. Found: C, 46.68; H, 8.79. ^{19}F NMR (CDCl_3): δ_{F} −157.5 (b), −162.2 (b). IR (thin film, cm^{-1}): 2961 (m), 2916 (m), 1458 (w), 1408 (w), 1257 (s), 1019 (w), 862 (s), 789 (s), 764 (s). Molecular weight: ΔFp , M_n = 910; GPC, M_w = 819, M_n = 594, D = 1.34.

This procedure was used for the reactions of the other polymers of the 2 series with HF.

Reaction of Polymer 2 with Gaseous HCl. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stirbar, two rubber septa, and a liquid nitrogen reflux condenser connected to an oil bubbler on a Schlenk line was charged with 5.0 g of 2 and 75 mL of diethyl ether. Gaseous HCl was passed over the rapidly stirred solution for 4.5 h, during which time the solution became cloudy and a slight exotherm was noted. The gas was introduced over approximately 1-min intervals in which the HCl was turned on for 1 min and then turned off for 1 min and then turned back on and back off, etc. This allowed for complete reaction of the HCl between additions. After the HCl addition was complete, hexane (10 mL) was added and the mixture was filtered two times over Celite on a Schlenk frit to give a clear yellow solution. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 14 h). A very viscous, light

tan-yellow oil (5) was obtained (6.1 g). Anal. Calcd: C, 39.82; H, 7.52. Found: C, 40.94; H, 7.85. IR (thin film, cm^{-1}): 3650 (w), 2930 (s), 1600 (w), 1454 (m), 1407 (s), 1260 (s), 1040–995 (m, br), 850–730 (s, br). Molecular weight: ΔF_p , $M_n = 784$.

Reaction of 2 with HF and Then LiAlH_4 . A solution of 13.6 g of 2 in 100 mL of diethyl ether was added, as described above, to 35 mL of HF (48% in H_2O). Pentane (50 mL) was added, and then a water workup was performed as usual. The organic layer was transferred to a 1-L flask equipped with a magnetic stirbar and a septum. A slurry of 2.1 g of LiAlH_4 (0.055 mol) in 50 mL of diethyl ether was slowly added to the polymer solution by cannula. Bubbling and an exotherm were noted. The mixture was stirred at room temperature for 1.5 h before careful addition of H_2O to quench the excess LiAlH_4 . A water workup was performed as usual. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 14 h). A viscous, clear oil (6) was obtained (12.8 g). (Note: 6 can also be prepared by treatment of isolated 4 with LiAlH_4 in a similar manner to that described above.) Anal. Calcd: C, 55.72; H, 11.69. Found: C, 55.26; H, 11.42. IR (thin film, cm^{-1}): 2956 (s), 2902 (s), 2112 (s), 1453 (w), 1417 (w), 1249 (s), 1060 (w, br), 889 (s, br), 834 (s), 758 (m). Molecular weight: ΔF_p , $M_n = 876$; GPC, $M_w = 584$.

Reaction of Polymer 4 with MeLi. A 100-mL Schlenk flask equipped with a magnetic stirbar and a septum was charged with 0.642 g of 4 and 2 mL of diethyl ether. MeLi (9 mL, 1 M in diethyl ether, 9 mmol) was added to the solution by syringe. Bubbling and an exotherm were noted. The mixture was stirred for 2 h at room temperature, and then a water workup was performed as usual. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 24 h). A viscous, light yellow oil (7) was obtained (0.630 g). Anal. Calcd: C, 59.90; H, 12.07. Found: C, 59.83; H, 11.77. IR (thin film, cm^{-1}): 2946 (s), 2163 (w), 1931 (w), 1599 (m), 1447 (s), 1410 (s), 1340 (m), 1254 (s), 1044 (w), 854 (s), 748 (s). Molecular weight: ΔF_p , $M_n = 1317$.

Reaction of Polymer 4 with $n\text{-BuLi}$. A 100-mL Schlenk flask equipped with a magnetic stirbar and a septum was charged with 1.688 g of 4 and 20 mL of hexane. The solution was cooled in a water bath, and then $n\text{-BuLi}$ (10.5 mL, 2 M in hexane, 0.021 mol) was added to the solution by syringe. Slight clouding and an exotherm were noted. The mixture was stirred for 1 h at room temperature, and then a water workup was performed as usual. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 24 h). A viscous, but mobile, clear oil was obtained (2.04 g). By ^{29}Si NMR, weak peaks in the SiF region were still observed, indicating the reaction was not quite complete. Therefore, 1.664 g of the isolated polymer and 10 mL of hexane were placed in a flask as above. $n\text{-BuLi}$ (2.5 mL, 2 M, 0.005 mol) was added by syringe, and the reaction mixture was stirred at room temperature for 18 h. Water workup, removal of solvents, and drying under vacuum (room temperature, 0.05 mmHg, 24 h) resulted in 1.641 g of a clear oil (8). Anal. Calcd: C, 67.50; H, 12.75. Found: C, 67.03; H, 12.36. IR (thin film, cm^{-1}): 2958 (s), 2872 (s), 1465 (m), 1376 (w), 1341 (m), 1296 (w), 1247 (s), 1190 (m), 1080 (m), 1024 (w), 946 (w), 840 (s, br). Molecular weight: ΔF_p , $M_n = 2117$.

Reaction of Polymer 4 with ViMgBr . A 250-mL three-necked, round-bottomed flask equipped with a magnetic stirbar, two rubber septa, and a reflux condenser with a gas inlet/outlet tube connected to an oil bubbler on a Schlenk line was charged with 1.297 g of 4 and 20 mL of THF. ViMgBr (60 mL, 0.9 M in THF, 0.056 mol) was added by syringe, and a slight exotherm was noted. The reaction mixture was stirred at room temperature for 3.5 days. Pentane (50 mL) was added and a H_2O workup was performed as usual. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 14 h). A viscous, slightly cloudy, light yellow oil (9) was obtained (1.507 g). Anal. Calcd: C, 63.07; H, 10.59. Found: C, 63.43; H, 10.77. IR (thin film, cm^{-1}): 3015 (m), 2954 (s), 2980 (m), 1641 (w), 1405 (m), 1252 (s), 1009 (m, br), 950 (m), 920 (m), 834 (s, br), 692 (m). Molecular weight: ΔF_p , $M_n = 642$.

Reaction of Polymer 6 with MeLi. A 250-mL three-necked, round-bottomed flask equipped as above was charged with 0.803 g of 6 and 10 mL of diethyl ether. MeLi (13.3 mL, 1.4 M in diethyl ether, 0.019 mol) was added by syringe. The reaction mixture was refluxed for 8 h and then stirred at room temperature for 10 h. Pentane (50 mL) was added and a H_2O workup was performed. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (0.05 mmHg) for 14 h. A light yellow oil was obtained, but the ^1H NMR revealed that a small amount of Si–H units were still present. Therefore, another 13.3 mL of MeLi (1.4 M in diethyl ether, 0.019 mol) and 10 mL of diethyl ether were added, and the mixture was refluxed for an additional 16 h. Pentane (20 mL) was added and a H_2O workup was performed. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg for 24 h). A light yellow oil was obtained (0.802 g). The ^1H , ^{13}C , and ^{29}Si NMR spectral data obtained for this polymer are identical to those for 7 prepared by the reaction of 4 with MeLi, as described above.

Reaction of Polymer 2 with $n\text{-BuLi}$ and Me_3SiHCl . A 100-mL Schlenk flask equipped with a magnetic stirbar and a rubber septum was charged with 0.844 g of 2 and 40 mL of THF. The solution was cooled to -78°C (dry ice/acetone bath) and $n\text{-BuLi}$ (4.5 mL, 2.0 M in pentane, 9 mmol) was added by syringe. The cold bath was removed and the mixture was slowly warmed to room temperature, where stirring was continued for 1 h. The solution was slightly cloudy. Me_3SiHCl (1 mL, 9 mmol) was added dropwise and the solution turned clear and slightly yellow. The rubber septum on the flask was replaced with a reflux condenser with a gas inlet/outlet tube connected to an oil bubbler on a Schlenk line, and the mixture was refluxed for 6 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg and then hexane (20 mL) was added to precipitate LiCl. The mixture was filtered over a Schlenk frit, washing the salts several times with small portions of hexane. Volatiles were removed from the filtrate at 0.05 mmHg, and the residue was dried under vacuum (60°C for 3 h, then room temperature for 24 h, 0.05 mmHg). A slightly cloudy, light yellow, tacky solid (10) was obtained (1.051 g). Anal. Calcd: C, 49.30; H, 10.34. Found: C, 49.57; H, 10.39. IR (in CCl_4 , cm^{-1}): 2956 (s), 2918 (m), 2116 (m), 1408 (w), 1254 (s), 980 (s), 923 (s). Molecular weight: ΔF_p , $M_n = 2040$.

Concentration Effect on the Polymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$. Cyclopolymerization of a 0.9 M Solution of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$. The following quantities were used: 5.017 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ (27.0 mmol), 0.13 mL of di-*tert*-butyl peroxide (0.71 mmol, 2.6 mol %), and 30.6 mL of chlorobenzene.

A 100-mL Schlenk flask equipped with a magnetic stirbar and a reflux condenser with a gas inlet/outlet tube was charged with the reagents. The standard procedure was then followed, with heating to 215°C for 24 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature for 24 h, then 50°C for 24 h, 0.05 mmHg). Upon cooling, a cloudy, glassy solid (2b) was obtained (2.708 g, 54%). ^1H NMR (CDCl_3): δ –0.15 to +0.25 (b, 69.2 H, SiCH_3), 0.25–2.2 (vb, 26.4 H, aliph), 5.2–6.2 (b, 1 H, SiVi). ^{13}C NMR (CDCl_3): δ_{C} –2 to +7 (b, SiCH_3), 8–40 (vb, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} 0–8 (vb, 2.5 Si), 10–14 (vb, 1 Si). Molecular weight: ΔF_p , $M_n = 1624$; GPC, $M_w = 1720$, $M_n = 1248$, $D = 1.38$.

Cyclopolymerization of a 0.2 M Solution of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$. The following quantities were used: 5.499 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ (29.6 mmol), 0.14 mL of di-*tert*-butyl peroxide (0.76 mmol, 2.6 mol %), and 134 mL of chlorobenzene.

The standard apparatus was charged with the reactants. The standard procedure was then followed, with heating to 215°C for 24 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature for 24 h). Upon cooling, a cloudy, slightly mobile oil (2c) was obtained (2.356 g, 43%). ^1H NMR (CDCl_3): δ –0.15 to +0.25 (b, 55.7 H, SiCH_3), 0.25–2.2 (vb, 24.3 H, aliph), 5.2–6.2 (b, 1 H, SiVi). ^{13}C NMR (CDCl_3): δ_{C} –2 to +7 (b, SiCH_3), 8–40 (vb, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} –1 to +8 (vb, 2.4 Si), 10–15 (vb, 1 Si). Molecular weight: ΔF_p , $M_n = 1434$; GPC, $M_w = 1120$, $M_n = 960$, $D = 1.16$.

Cyclopolymerization of a 0.9 M Solution of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ (6-h Reaction Time). The following quantities were used: 4.642 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ (25.0 mmol), 0.12 mL of di-*tert*-butyl peroxide (0.65 mmol, 2.6 mol %), and 28.4 mL of chlorobenzene.

The standard apparatus was charged with the reactants. The standard procedure was then followed, with heating to 215 °C for 6 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature for 24 h). Upon cooling, a cloudy, slightly mobile oil (2d) was obtained (1.395 g, 30%). ^1H NMR (CDCl_3): δ -0.15 to +0.25 (b, 56 H, SiCH_3), 0.25–2.2 (vb, 23.7 H, aliph), 5.2–6.2 (b, 1 H, SiVi). ^{13}C NMR (CDCl_3): δ -2 to +7 (b, SiCH_3), 8–40 (vb, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} -1 to +8 (vb, 2.0 Si), 10–16 (vb, 1 Si). Molecular weight: ΔFp , $M_n = 1666$; GPC, $M_w = 1706$, $M_n = 1311$, $D = 1.30$.

Cyclopolymerization of a 0.9 M Solution of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ (48-h Reaction Time). The following quantities were used: 4.590 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{NH}$ (24.7 mmol), 0.12 mL of di-*tert*-butyl peroxide (0.65 mmol, 2.6 mol %), and 28 mL of chlorobenzene.

The standard apparatus was charged with the reactants. The standard procedure was then followed, with heating to 215 °C for 48 h. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature for 24 h, then 50 °C for 24 h, 0.05 mmHg). Upon cooling, a cloudy, nearly glassy solid (2e) was obtained (2.75 g, 60%). ^1H NMR (CDCl_3): δ -0.15 to +0.25 (b, 52 H, SiCH_3), 0.25–2.2 (vb, 24.7 H, aliph), 5.2–6.2 (b, 1 H, SiVi). ^{13}C NMR (CDCl_3): δ -2 to +7 (b, SiCH_3), 8–40 (vb, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} 0–8 (vb, 3.5 Si), 10–15 (vb, 1 Si). Molecular weight: ΔFp , $M_n = 1786$; GPC, $M_w = 3052$, $M_n = 1549$, $D = 1.97$.

Reaction of Polymer 2b with HF. A solution of 0.592 g of 2b in 10 mL of diethyl ether was treated with 1.5 mL of HF (48% in H_2O) and 50 mL of diethyl ether using the procedure described for 2a (above). A clear oil (4b) was obtained (0.456 g). ^1H NMR (CDCl_3): δ -0.1 to +0.4 (b, 1.9 H, SiCH_3), 0.4–2.2 (vb, 1 H, aliph). ^{13}C NMR (CDCl_3): δ -4 to +3 (b, SiCH_3), 8–44 (vb, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} 33 (d, $J \approx 288$ Hz, SiF). Molecular weight: ΔFp , $M_n = 895$; GPC, $M_w = 660$, $M_n = 535$, $D = 1.23$.

Reaction of Polymer 2c with HF. A solution of 0.553 g of 2c in 10 mL of diethyl ether was treated with 1.5 mL of HF (48% in H_2O) and 50 mL of diethyl ether as above. A clear oil (4c) was obtained. ^1H NMR (CDCl_3): δ -0.1 to +0.4 (b, 1.8 H, SiCH_3), 0.4–2.2 (vb, 1 H, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} 33 (d, $J \approx 288$ Hz, SiF). Molecular weight: ΔFp , $M_n = 658$; GPC, $M_w = 553$, $M_n = 465$, $D = 1.20$.

Reaction of Polymer 2d with HF. A solution of 1.091 g of 2d in 10 mL of diethyl ether was treated with 3.5 mL of HF (48% in H_2O) and 50 mL of diethyl ether as above. A clear oil (4d) was obtained (0.721 g). ^1H NMR (CDCl_3): δ -0.1 to +0.4 (b, 1.7 H, SiCH_3), 0.4–2.2 (vb, 1 H, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} 33 (d, $J \approx 288$ Hz, SiF). Molecular weight: ΔFp , $M_n = 631$; GPC, $M_w = 678$, $M_n = 528$, $D = 1.28$.

Reaction of Polymer 2e with HF. A solution of 1.538 g of 2e in 10 mL of diethyl ether was treated with 3.8 mL of HF (48% in H_2O) and 20 mL of diethyl ether as above. A clear oil (4e) was obtained (1.414 g). ^1H NMR (CDCl_3): δ 0–0.4 (b, 1.3 H, SiCH_3), 0.4–2.2 (vb, 1 H, aliph). ^{13}C NMR (CDCl_3): δ -4 to +3 (b, SiCH_3), 8–44 (vb, aliph). ^{29}Si NMR (CDCl_3): δ_{Si} 33 (d, $J \approx 288$ Hz, SiF). Molecular weight: ΔFp , $M_n = 859$; GPC, $M_w = 646$, $M_n = 586$, $D = 1.10$.

Increasing Cyclopolymer Molecular Weights by Stepwise Addition of Initiator. Cyclopolymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}$. **Control Experiment.** The following quantities were used: 3.897 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}$ (20.9 mmol), 0.100 mL of di-*tert*-butyl peroxide (0.54 mmol, 2.6 mol %), and 6 mL of chlorobenzene.

The standard procedure was employed (100-mL flask) with heating to 140–170 °C for 2 days followed by stirring at room temperature for 1 day. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg, 2 days). Upon cooling, a viscous oil (1a) was obtained (2.879 g, 74%) (Table VII).

Cyclopolymerization of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}$ (Incremental Addition of Catalyst). The following quantities were used:

3.763 g of $(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}$ (20.0 mmol), 0.096 mL of di-*tert*-butyl peroxide (0.52 mmol, 2.6 mol %), and 6 mL of chlorobenzene.

The standard procedure was employed (100-mL flask) with heating to 140–170 °C for 2 days followed by stirring at room temperature for 1 day. A 1.5-mL aliquot of the solution was removed and volatiles were removed from this aliquot by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg, 2 days). Upon cooling, a very viscous oil (1b) was obtained.

An aliquot (0.072 mL, 0.39 mmol) of di-*tert*-butyl peroxide was added to the remaining solution from above, and the mixture was freeze-thaw-degassed four times before heating to 140–170 °C for 2 days and stirring at room temperature for 1 day. Volatiles were removed by trap-to-trap distillation at 0.05 mmHg, and the residue was dried under vacuum (room temperature, 0.05 mmHg, 2 days). Upon cooling, a glassy solid, polymer 1c was obtained (Table VII).

Preparation of Model Compounds. 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane. This compound was prepared by a literature method.²⁰ ^1H NMR (CDCl_3): δ 0.13 (s, 12 H, SiCH_3), 0.73 (s, 4 H, CH_2). ^{13}C NMR (CDCl_3): δ 0.1 (s, SiCH_3), 8.9 (s, CH_2). ^{29}Si NMR (CDCl_3): δ_{Si} 24.3.

2,2,6,6-Tetramethyl-1-oxa-2,6-disilacyclohexane. $\text{ClMe}_2\text{Si}(\text{CH}_2)_2\text{SiMe}_2\text{Cl}$ (prepared by hydrosilylation of allyl- Me_2SiCl with HMe_2SiCl in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$)²¹ (4.09 g, 18 mmol) was added dropwise over 4 min to a solution of diethyl ether (25 mL) and H_2O (25 mL) which was cooled in a room temperature water bath. After stirring for 40 min the organic layer was separated from the aqueous layer (washing several times with 5-mL portions of hexane) and dried over MgSO_4 . After filtration, distillation afforded a pure fraction of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (1 g, 32%) at 140 °C (lit.²² 146 °C). The ^1H NMR spectrum matched that reported in the literature.²³ A large amount of viscous residue remained in the pot after distillation. ^1H NMR (CDCl_3): δ 0.04 (s, 6 H, SiCH_3), 0.54 (m, 2 H, SiCH_2CH_2), 1.80 (m, 1 H, SiCH_2CH_2). ^{13}C NMR (CDCl_3): δ 0.62 (q, $J = 118.1$ Hz, SiCH_3), 17.15 (t, $J = 118.0$ Hz, SiCH_2CH_2), 17.69 (tt, $^1J = 127.2$ Hz, $^2J = 4.7$ Hz, SiCH_2CH_2). ^{29}Si NMR (CDCl_3): δ_{Si} 12.70 (s).

2,2,7,7-Tetramethyl-1-oxa-2,7-disilacycloheptane. In a three-necked 50-mL round-bottomed flask equipped with a magnetic stir bar, rubber septum, glass stopper, and reflux condenser with a gas inlet/outlet tube connected to an oil bubbler on a Schlenk line were placed 1.3 g (7.5 mmol) of 1,1,6,6-tetramethyl-1,6-disilacyclohexane (prepared by reaction of $\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ with $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$ ²⁴) and 8 mL of diethyl ether. The flask was cooled in a room temperature water bath, and then Br_2 (0.45 mL, 8.7 mmol) was added dropwise over 30 min. After stirring for 1 h, the solution was added dropwise with a fine cannula to a solution of diethyl ether (5 mL) and H_2O (5 mL) in a reaction flask equipped as described above. After stirring for 1 h, the organic layer was separated, dried, and filtered as described above. Distillation at 20 mmHg afforded a fraction at 48–52 °C (lit.²⁵ 66–68 °C, 35 mmHg) of 2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane (0.2 g, 14%). A large amount of viscous residue remained in the pot after distillation. ^1H NMR (CDCl_3): δ 0.01 (s, 1.5 H, SiCH_3), 0.05 (s, 1.5 H, SiCH_3), 0.48 (m, 1 H, SiCH_2CH_2), 1.3 (m, 1 H, SiCH_2CH_2). ^{13}C NMR (CDCl_3): δ 0.04 (q, $J = 118.1$ Hz, SiCH_3), 18.61 (t, $J = 11.45$ Hz, SiCH_2CH_2), 25.01 (tm, $^1J = 130.9$ Hz, $^2J = 4.7$ Hz, SiCH_2CH_2). ^{29}Si NMR (CDCl_3): δ_{Si} 12.74 (s).

2,2,5,5-Tetramethyl-1-aza-2,5-disilacyclopentane. A 1-L three-necked round-bottomed flask equipped with a magnetic stirbar, two septa, and a dry ice/acetone reflux condenser was charged with $\text{ClMe}_2\text{Si}(\text{CH}_2)_2\text{SiMe}_2\text{Cl}$ (3 g, 13.9 mmol) and diethyl ether (200 mL). NH_3 was passed through a KOH drying column and then bubbled into the solution. After about 1 h the reaction appeared complete (excess NH_3 began rapidly refluxing). The reaction mixture was stirred for 2 h and then 200 mL of hexane was added. The solution then was filtered over Celite in a Schlenk frit, washing the salts three times with 20-mL portions of hexane. Volatiles were removed by vacuum trap distillation at 30 mmHg, and then distillation at 30 mmHg afforded 1 g (45%) of 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane at 66–68 °C (lit.²⁶ 67 °C/35 mmHg). A large amount of viscous residue remained in the pot after distillation. ^1H NMR (CDCl_3): δ 0.04 (s, 12 H,

SiCH₃), 0.15 (bs, 1 H, NH), 0.69 (s, 4 H, CH₂). ¹³C NMR (CDCl₃): δ_C 1.72 (q, *J* = 118.1 Hz, SiCH₃), 8.89 (t, *J* = 122.8 Hz, CH₂). ²⁹Si NMR (CDCl₃): δ_{Si} 13.10 (s).

2,2,6,6-Tetramethyl-1-aza-2,6-disilacyclohexane. The same procedure was employed as in the preparation of 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane given above using 5 g of ClMe₂Si(CH₂)₃SiMe₂Cl (21.8 mmol) in 300 mL of diethyl ether. Distillation afforded 0.4 g (11%) of 2,2,6,6-tetramethyl-1-aza-2,6-disilacyclohexane at 153 °C (lit.²⁷ 158–160 °C). A large amount of viscous residue remained in the pot after distillation. ¹H NMR (CDCl₃): δ 0.02 (s, 12 H, SiCH₃), 0.11 (s, 1 H, NH), 0.57 (m, 4 H, SiCH₂), 1.87 (m, 2 H, SiCH₂CH₂). ¹³C NMR (CDCl₃): δ_C 2.12 (q, *J* = 117.7 Hz, SiCH₃), 16.73 (t, *J* = 116.4, SiCH₂), 18.00 (tt, ¹*J* = 126.6 Hz, ²*J* = 4.7 Hz, SiCH₂CH₂). ²⁹Si NMR (CDCl₃): δ_{Si} 2.83 (s).

2,2,7,7-Tetramethyl-1-aza-2,7-disilacycloheptane. The same procedure was employed as in the preparation of 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane given above using 2.5 g (21.8 mmol) of ClMe₂Si(CH₂)₄SiMe₂Cl (prepared from the hydrosilylation of H₂C=CHCH₂CH₂Me₂SiCl with HMe₂SiCl in the presence of H₂PtCl₆·6H₂O²¹) in 70 mL of diethyl ether. Volatiles were removed by vacuum trap distillation at 30 mmHg, and then distillation at 30 mmHg afforded (0.9 g, 47%) 2,2,7,7-tetramethyl-1-aza-2,7-disilacycloheptane at 78–80 °C (lit.²⁸ 63 °C/4 mmHg). The ¹H NMR spectrum matched that reported in the literature.²⁸ A large amount of viscous residue remained in the pot after distillation. ¹H NMR (CDCl₃): δ 0.01 (s, 12 H, SiCH₃), 0.07 (s, 1 H, NH), 0.62 (m, 4 H, SiCH₂), 1.67 (m, 4 H, SiCH₂CH₂). ¹³C NMR (CDCl₃): δ_C 1.37 (q, *J* = 118.3 Hz, SiCH₃), 17.42 (t, *J* = 113.1 Hz, SiCH₂CH₂), 25.04 (t, *J* = 127.0 Hz, SiCH₂CH₂). ²⁹Si NMR (CDCl₃): δ_{Si} 4.74 (s).

1,2,2,5,5-Pentamethyl-1-aza-2,5-disilacyclopentane. A 1-L three-necked, round-bottomed flask equipped with a magnetic stirbar, two septa, and a dry ice/acetone reflux condenser was charged with ClMe₂Si(CH₂)₂SiMe₂Cl (12 g, 56 mmol) and diethyl ether (400 mL). MeNH₂ was slowly passed over the solution, with rapid stirring, for 6 h. Volatiles were removed by vacuum trap distillation at 50 mmHg, and then hexane (400 mL) was added to precipitate the salts. The solution was then filtered through Celite in a Schlenk frit, washing the salts three times with 50-mL portions of hexane. Volatiles were removed from the filtrate by vacuum trap distillation at 40 mmHg, and then distillation at 60 mmHg afforded 6.5 g (67%) of 1,2,2,5,5-pentamethyl-1-aza-2,5-disilacyclopentane at 66–68 °C (lit.²⁹ 145–149 °C at atmospheric pressure). A viscous residue remained in the pot after distillation. ¹H NMR (CDCl₃): δ 0.02 (s, 12 H, SiCH₃), 0.70 (s, 3 H, NCH₃), 2.46 (s, 4 H, SiCH₂). ¹³C NMR (CDCl₃): δ_C -1.21 (q, *J* = 118.3 Hz, SiCH₃), 7.95 (t, *J* = 123.0 Hz, CH₂), 26.73 (q, *J* = 134.4 Hz, NCH₃). ²⁹Si NMR (CDCl₃): δ_{Si} 13.58 (s).

1,2,2,6,6-Pentamethyl-1-aza-2,6-disilacyclohexane. A 1-L three-necked, round-bottomed flask equipped with a magnetic stirbar, two septa, and a dry ice/acetone reflux condenser was charged with ClMe₂Si(CH₂)₃SiMe₂Cl (3.1 g, 13 mmol) and diethyl ether (300 mL). MeNH₂ was slowly passed over the solution, with rapid stirring, for 5 h. Volatiles were removed by vacuum trap distillation at 50 mmHg, and then hexane (400 mL) was added to precipitate the salts. The solution was then filtered over Celite in a Schlenk frit, washing the salts three times with 50-mL portions of hexane. Volatiles were removed from the filtrate by vacuum trap distillation at 40 mmHg, and then distillation at 20 mmHg afforded 0.3 g (12%) of 1,2,2,6,6-pentamethyl-1-aza-2,6-disilacyclohexane at 82–84 °C (lit.²⁷ 51–53 °C/2 mmHg). The ¹H NMR spectrum resembled that reported in the literature,²⁷ except all chemical shifts were ~0.6 ppm downfield from those reported. A viscous residue remained in the pot after distillation. ¹H NMR (CDCl₃): δ 0.57 (s, 12 H, SiCH₃), 1.17 (m, *J* = 2.1 Hz, 4 H, SiCH₂CH₂), 2.33 (m, *J* = 2.4 Hz, 2 H, SiCH₂CH₂), 2.96 (s, 3 H, NCH₃). ¹³C NMR (CDCl₃): δ_C -1.55 (q, *J* = 117.8 Hz, SiCH₃), 17.33 (t, *J* = 118.0 Hz, SiCH₂CH₂), 17.68 (tt, ¹*J* = 128.0 Hz, ²*J* = 4.8 Hz, SiCH₂CH₂), 28.56 (q, *J* = 134.2 Hz, NCH₃). ²⁹Si NMR (CDCl₃): δ_{Si} 4.70 (s).

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