I. Cyclization and Cyclopolymerization of Silicon-Containing Dienes
II. Functionalization of Carbosilane Dendrimers

by

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Professor Gregory C. Fu _____

This dissertation is dedicated to

my loving wife, Jee-Hoon,

and to my parents, Julene and William Krska.

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Submitted to the Department of Chemistry on April 24, 1997 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Chapter One. Radical-Initiated Hydrosilylation-Cyclization Reactions of Bis(vinyldimethylsilyl) Compounds $CH_2=CH(CH_3)_2SiXSi(CH_3)_2CH=CH_2$ (X = O, CH_2, NH, NCH_3, $NSi(CH_3)_3$)

The di-*tert*-butyl peroxide-initiated reactions of triethyl- and tri-*n*-propylsilane with bis(vinyldimethylsilyl) compounds $CH_2=CH(CH_3)_2SiXSi(CH_3)_2CH=CH_2$ (X = O, CH_2, NH, NCH_3, $NSi(CH_3)_3$) resulted in hydrosilylation-cyclization to give mixtures of trialkylsilylmethyl-substituted disilacyclohexanes and trialkylsilylmethyl-substituted disilacyclopentanes. The ratio of six-membered to five-membered ring products obtained was dependent on the linking group X and decreased in the order X = O > CH_2, NH > NCH_3. For X = $NSi(CH_3)_3$, only a mixture of the *cis* and *trans* isomers of the five-membered ring product was obtained. Explanations for these results and their implications for the structures of cyclopolymers generated from these dienes using radical initiators are discussed.

Chapter Two. Anionic Cyclopolymerization of 1,3-Divinylpentamethyldisilazane and Bis(vinyldimethylsilyl)(trimethylsilyl)amine

The anionic polymerizations of 1,3-divinylpentamethyldisilazane and bis(vinyldimethylsilyl)(trimethylsilyl)amine gave highly regular polymers which consisted completely of linked cyclic units with no detectable cross-links or linear segments. Detailed spectroscopic studies elucidated the influence of the reaction solvent and the substituent of the nitrogen linking group of the diene on the stereoselectivity of the ring-forming step. The resulting cyclopolymers could be ring-opened with aqueous hydrofluoric acid to give poly(vinyldimethylfluorosilanes) which demonstrated tacticities consistent with those of the parent cyclopolymers. Reactions of the Si-F bonds in these polymers with nucleophilic reagents gave highly regular, highly functionalized polymers of the type $(CH_2CHSi(CH_3)_2R)_n$.

Chapter Three. New Approaches to the Functionalization of Carbosilane Dendrimers

A new method was developed for attaching synthetically versatile (chloromethyl)silyl substituents to the branch terminii of carbosilane dendrimers via hydrosilylation. Dendrimers functionalized in this way exhibited both nucleophilic and electrophilic reaction chemistry, leading to heretofore unknown derivatives. During the course of these studies, many of the subtleties concerning the synthesis of carbosilane dendrimers were brought to light, in particular the types and amounts of defects produced during divergent growth sequences as well as methods for their elimination. As a result of these discoveries, the purities of various types of carbosilane dendrimers (e.g. vinyl- or allylsilane-based; with two- or three-fold branch multiplicities) could be accurately assessed, and a critical comparison of the various methods for their generation could be made.

Chapter Four. Synthesis and Characterization of Amphiphilic Carbosilane Dendrimers

A new method was developed for the attachment of amphiphilic groups to the terminal branches of hydrophobic dendrimers to give molecules whose structures mimicked those of micelles. This method employed nucleophilic reactions of variously substituted thiolate anions with carbosilane dendrimers bearing chloromethyl groups on their terminal branches. In this manner, dendrimers with four, eight and sixteen terminal alcohol, dimethylamino, trimethylammonium halide and sodium sulfonate groups were prepared in high yields. These new amphiphilic dendrimers were characterized by spectroscopic and mass spectrometric techniques. Their similarities to micelles were explored through studying their interactions with lipophilic compounds in aqueous solution.

Thesis Supervisor: Dietmar Seyferth
Title: Professor of Chemistry

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CHAPTER ONE

Radical-Initiated Hydrosilylation-Cyclization Reactions of Bis(vinyldimethylsilyl) Compounds, $CH_2=CH(CH_3)_2SiXSi(CH_3)_2CH=CH_2$ (X = O, CH_2, NH, NCH_3, $NSi(CH_3)_3$)

Adapted, in part, from Seyferth, D.; Friedrich, H.; Krska, S.W. Z. *Naturforsch.* **1994**, *49b*, 1818-26.

INTRODUCTION

Since the beginning of the 1980s the use of radicals in organic synthesis has increased dramatically. In particular, carbacycle formation by means of organotin reagents has played an important role in natural product synthesis.[1,2] This methodology has most often been applied to the synthesis of five-membered rings, since such cyclizations generally proceed more rapidly and with higher regio- and stereoselectivity than cyclizations forming larger rings. However, the formation of six-membered and larger rings using radical methods is also known.

The organic radical intermediate in such syntheses usually is generated by the abstraction of an appropriate group, e.g., the halogen atom of a carbon-halogen bond, by an organotin radical.[1,2] In a subsequent step the organic radical thus generated reacts with a C=C or C≡C bond within the molecule to form a cyclic radical intermediate which then abstracts a hydrogen atom from the organotin hydride to give the final product. Tandem cyclizations, in which bicyclic systems are formed, are also known.[1-3]

Recent research has focused on the use of organosilicon hydrides to replace organotin hydrides as mediators in radical reactions. Such reagents are attractive because of their lower toxicity and greater ease of removal during workup.[4-8]

Radical cyclization reactions play an important role in the cyclopolymerization of α,ω-dienes. Many examples of this process, which was pioneered by G.B. Butler and his coworkers, have been reported.[9] Radical cyclopolymerization of silicon-containing α,ω-unsaturated compounds, mostly diallylsilanes, has been studied over the years.[10-13] Recent work in this laboratory has explored the radical cyclopolymerization of

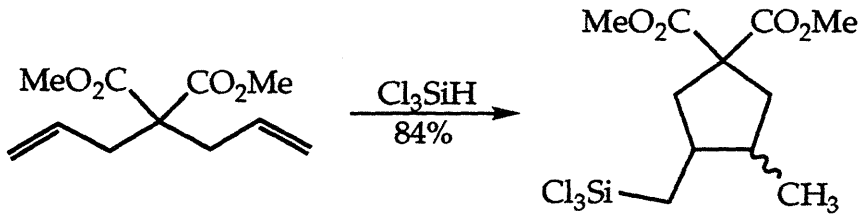
bis(vinyldimethylsilyl) compounds $CH_2=CH(CH_3)_2SiXSi(CH_3)_2CH=CH_2$ (X = O, CH_2, NH, NCH_3).[14,15]

Important to the understanding of the mechanism of any cyclopolymerization reaction is the determination of the size and relative abundance of rings in the cyclopolymer backbone. Spectroscopic studies, particularly ^{29}Si NMR, on the cyclopolymers derived from the radical polymerization of bis(vinyldimethylsilyl) compounds indicated the presence of more than one ring size in the polymer backbone.[14,15] However, due to the complexity and broad linewidths of the spectra, an unequivocal description of the microstructure of the cyclopolymers could not be determined. Compounding this problem was the lack of suitable means to prepare cyclic spectroscopic model compounds bearing alkyl substituents on the ring carbons α to the silicon atoms. Such compounds should more closely model the environment of the silicon atoms in the cyclic repeat units of the polymer backbone, an important consideration given the known sensitivity of ^{29}Si NMR shifts to the degree of β-substitution.[16]

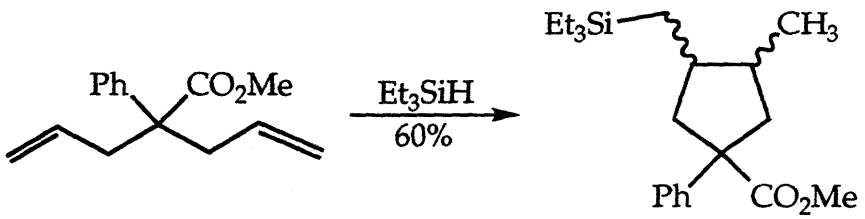
Considerable understanding of the microstructure of the cyclopolymers derived from bis(vinyldimethylsilyl) compounds could be gained by carrying out the radical cyclization of these monomers in such a way as to obtain easily isolable and characterizable monomolecular, cyclized products. Such a reaction would directly model the cyclization step of the cyclopolymerization reaction sequence while at the same time providing improved spectroscopic model compounds.

There are very few reports of radical cyclizations of isolated dienes leading to monomolecular, monocyclic products. Kraus and Liras employed triethyl- and trichlorosilyl radicals to obtain the first examples of radical cyclizations of isolated dienes, some of which are shown in eq. 1-3.[17] These

reactions differ from the organotin radical-induced cyclizations described earlier in that the organic radical intermediate is generated by the radical hydrosilylation of one of the C=C bonds (rather than by halide abstraction). Similar reactions employing the $(Me_3Si)_3Si\cdot$ radical were later described by Miura, et. al.[18] Hanessian has recently announced the first examples of a hydrostannation-cyclization reaction of isolated dienes employing $Me_3Sn\cdot$ radicals.[3,19]



(1)



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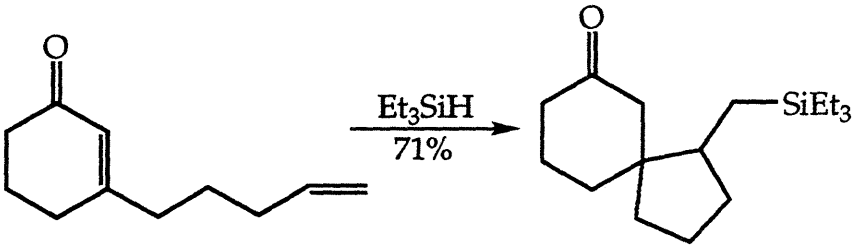


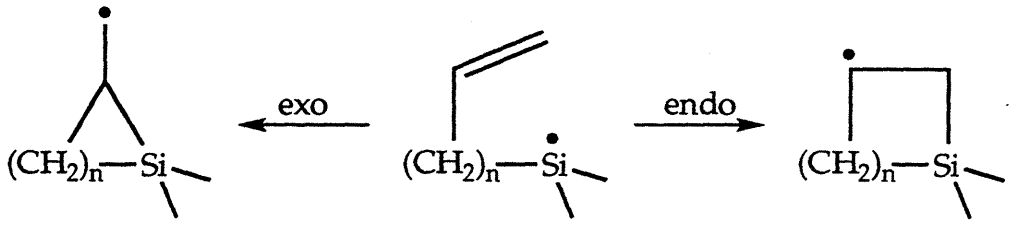
(3)

In the radical cyclization of bis(vinyldimethylsilyl) compounds, the presence of various silicon-heteroatom linkages in the cyclizing radical intermediate raises the interesting question of what effects such structural features will have on the regioselectivity of the cyclization. Since radical cyclization reactions are so important to organic synthesis, significant efforts

have been made over the years toward understanding the origins of their regio- and stereoselectivities.

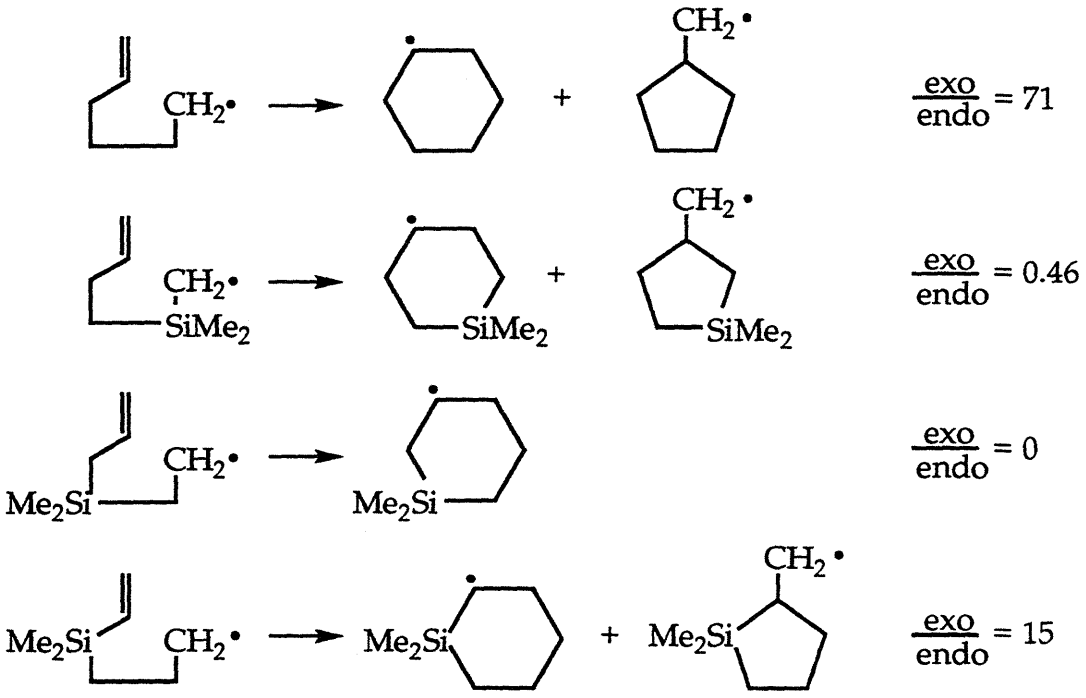
Building on the Baldwin rules for ring closure,[20] Beckwith described guidelines governing the regio- and stereochemistry of radical cyclizations in 1980.[21] Further computational work supported his hypothesis, now known as the Baldwin-Beckwith rules for radical cyclizations, that the selectivities of radical cyclizations under kinetic control are governed mainly by strain energies in the cyclic transition state. Computational studies have now progressed to the point that regio- and stereochemical outcomes of radical cyclizations can be predicted with some degree of quantitative accuracy for systems containing first row elements.[22-24]

Interestingly, in his seminal paper on cyclization regio- and stereoselectivities, Baldwin stated that his rules for ring closure were likely to fail when applied to systems containing a second row or higher element as a result of the larger atomic radii and bond distances involved.[20] Several papers have addressed the question of whether silicon-containing alkenyl radical cyclizations obey the Baldwin-Beckwith rules. Studies by Chatgilialoglu, Woynar, Ingold and Davies[25] and Barton and Revis[26] showed that alkenylsilyl radicals derived from hydrogen abstraction from a butenylsilane, an allyldisilane, a pentenylsilane and a butenyldisilane all undergo endo cyclizations, in contrast to the behavior of systems containing only first row elements which overwhelmingly favor exo cyclizations (Scheme 1). The reasons for this are uncertain, but explanations in terms of the longer Si-C bonds (vs. C-C bonds) and the pyramidal configuration of silyl radicals (vs. the planarity of carbon radicals) were discussed.



Scheme 1

The results of a separate series of studies by Wilt showed the regioselectivity of cyclization of silicon-containing 5-hexen-1-yl carbon-centered radicals varies according to the relative position of the silicon atom (Scheme 2).[27-29] The rates of endo cyclization were similar for the silicon-containing and the all-carbon system.[29] In contrast, the rates of exo cyclization for silicon-containing radicals were lower than that for the all-carbon system, likely due to the added difficulty of approach of the radical center to the CCH end of the C=C bond as a result of the longer Si-C bonds (vs. C-C bonds). The further suppression of exo cyclization rates found in the α- and β-silyl carbinyl radicals was thought to arise from subtle polar and/or conformational effects. The net result of all these factors is an erosion, and in two cases, reversal, of the normally observed selectivity for exo cyclization.



Scheme 2

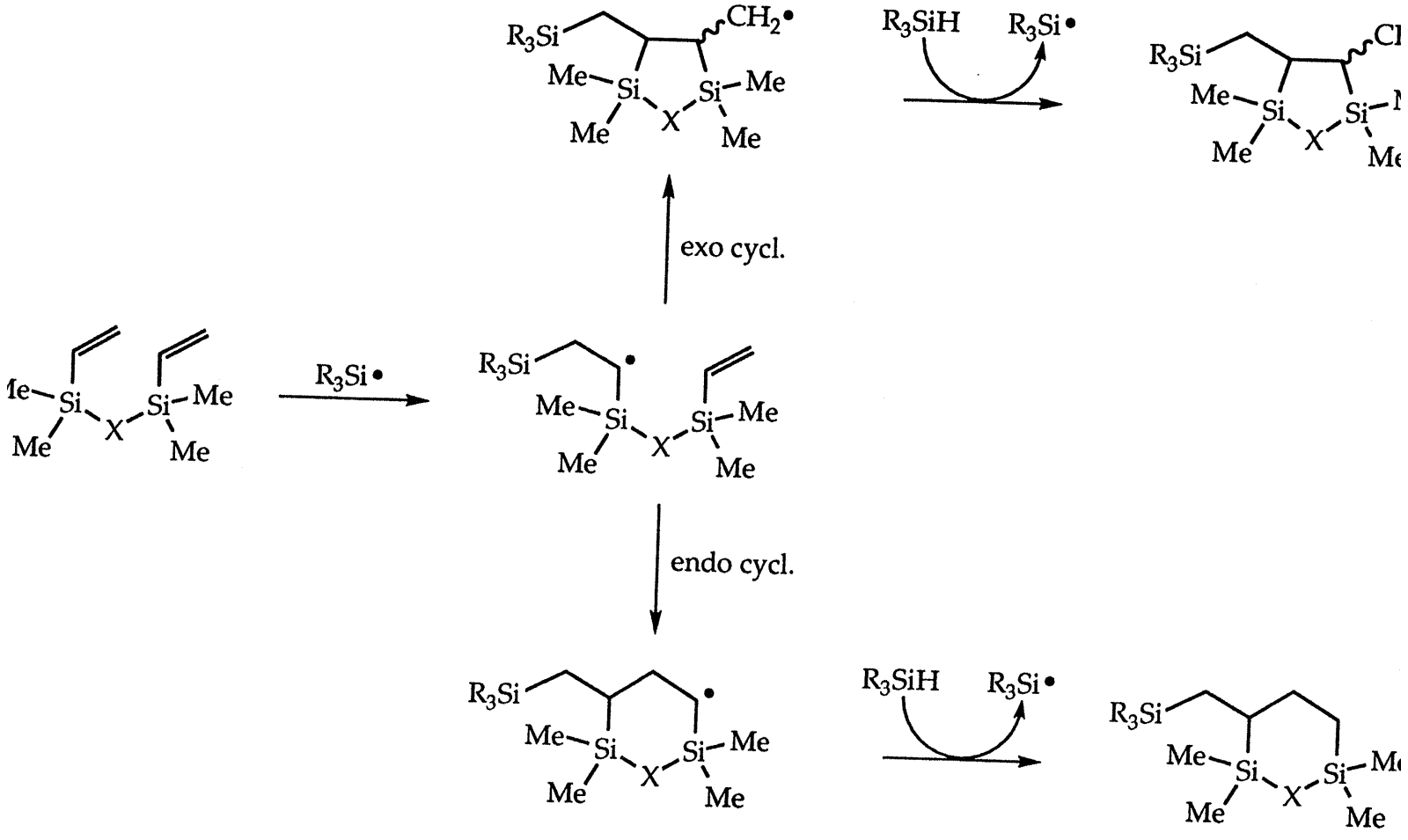
In order to model the reactivity of bis(vinyldimethylsilyl) compounds CH_2=CH$(CH_3)_2$SiXSi$(CH_3)_2$CH=CH_2 under conditions similar to those encountered during radical cyclopolymerizations, the X = O, CH_2, NH, NCH_3 and $NSi(CH_3)_3$ derivatives were reacted with trialkylsilyl radicals generated from trialkylsilanes R_3SiH (R = C_2H_5, *n*-C_3H_7) and peroxide initiators at elevated temperatures. These radical-initiated hydrosilylation-cyclization reactions were expected to demonstrate the stereoelectronic effects of incorporation of various silicon-heteroatom linkages into a cyclizing 5-hexenyl radical intermediate. The cyclic products of these reactions would function as model compounds whose spectra could be compared to those of the cyclopolymers generated from these monomers in order to gain further insight into the microstructures of the polymers.

RESULTS

Radical-initiated hydrosilylations of olefins and acetylenes are well-known reactions.[30] The reaction conditions chosen for the hydrosilylation-cyclization of bis(vinyldimethylsilyl) compounds $CH_2=CH(CH_3)_2SiXSi(CH_3)_2CH=CH_2$ (X = O, CH_2, NH, NCH_3, $NSi(CH_3)_3$) were similar to those used by El-Durini and Jackson for the radical addition of trialkylsilanes to simple olefins.[31] These authors found that di-*tert*-butyl peroxide was superior to dibenzoyl peroxide and azobisisobutyronitrile as an initiator of the radical hydrosilylation reaction. In our reactions, one molar equivalent of the bis(vinyldimethylsilyl) compound, mixed with 0.2 molar equivalents of di-*tert*-butyl peroxide, was added slowly, over a period of one to several days, to 12 - 20 molar equivalents of refluxing triethylsilane (b.p. 107°C) or tri-*n*-propylsilane (b.p. 171°C) under an argon atmosphere . Following the example of El-Durini and Jackson and using only 6 molar equivalents of trialkylsilane resulted in low cyclization product yields (<25%), and the starting diene mainly polymerized, leaving no unconverted diene. Adding the diene/peroxide mixture too quickly to the trialkylsilane had a similar effect on product yield. The expected chemistry is illustrated in Scheme 3.

The products of these reactions, obtained in moderate to high yield after distillation, had the expected elemental compositions (*via* C,H analysis) for the postulated cyclic compounds (Table 1), but GC/MS investigations demonstrated that more than one isomer was obtained in each case (three main isomers for products **1 - 7**, and two main isomers for product **8**).

While the ^1H NMR spectra of the products were uninformative other than to show the absence of residual C=C bonds, the ^{13}C and ^{29}Si NMR spectra were very useful in the identification of the isomers present. Comparison of



Scheme 3. Possible Reaction Pathways in the Hydrosilylation-Cyclization of Silicon-Containing Dienes.

e 1. Results of the Cyclization Reactions.

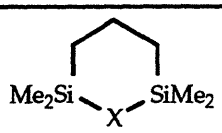
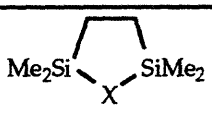
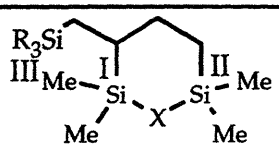
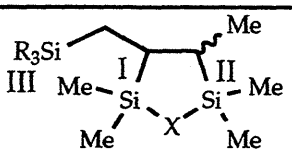
trate unt used)	Reagent (amount used) /react. time[a]	Product number	Yield (g / %)	Boiling point (°C/mm Hg)	Emp. Formula / Calcd. MW (g/mol)	C (%)[c] calcd./found	H (%)[c] calcd./found	Noteboo Referenc
Divinyltetramethyl- oxane (3.87 g)	*n*-Pr_3SiH (37 g) 1 day[b]	1	4.4 / 61	98-102 / 0.2	$C_{17}H_{40}OSi_3$ 344.760	59.22/59.47	11.70/11.75	HF[d]
Divinyltetramethyl- oxane (3.87 g)	Et_3SiH (48 g) 3 days	2	3.6 / 56	69-73 / 0.2	$C_{14}H_{34}OSi_3$ 302.680	55.55/55.56	11.32/11.36	HF
vinyldimethyl-)methane (5.0 g)	*n*-Pr_3SiH (52 g) 2 days	3	6.4 / 69	100-105 / 0.1	$C_{18}H_{42}Si_3$ 342.788	63.06/63.03	12.35/12.25	HF
vinyldimethyl-)methane (5.0 g)	Et_3SiH (63 g) 3 days	4	4.0 / 62	79-85 / 0.1	$C_{15}H_{36}Si_3$ 300.707	59.91/59.93	12.07/12.07	HF
Divinyltetramethyl- azane (2.4 g)	Et_3SiH (30 g) 4 days	5	1.7 / 43	73 / 0.12	$C_{14}H_{35}NSi_3$ 301.695	55.74/55.90	11.69/11.75	SWK II/
Divinylpentamethyl- azane (2.4 g)	*n*-Pr_3SiH (50 g) 3 days	6	4.5 / 78	140 / 0.02	$C_{18}H_{43}NSi_3$ 357.803	60.42/60.60	12.11/12.14	SWK II/
Divinylpentamethyl- azane (2.4 g)	Et_3SiH (73 g) 6 days	7	8.3 / 84	76 / 0.02	$C_{15}H_{37}NSi_3$ 315.722	57.06/57.36	11.81/11.92	SWK II/
vinyldimethylsilyl)tri hylsilylamine (2.27 g)	*n*-Pr_3SiH (31 g) 2 days	8	1.6 / 32	121-124 / 0.02	$C_{20}H_{49}NSi_4$	57.75/57.99	11.87/11.90	SWK II/

reaction time; includes 1 day of heating reaction mixtures at reflux upon completion of the addition of the peroxide/vinylsilane mi
lsilane/peroxide mixture was added over a period of 1 day; following this, the reaction mixture was heated to reflux for 6 h.
yses of isomer mixtures.
riments performed by Dr. Holger Friedrich, postdoctoral research associate, MIT, 1992-3.

the ^{29}Si NMR spectra of the products **1 - 8** with each other and with those of appropriate model compounds established that all products except for **8** consisted of a mixture of one six-membered and two five-membered ring isomers (Table 2). The cyclic trisilylamine **8** contained only five-membered ring isomers. The six-membered ring isomer predominated in the product mixtures derived from the 1,3-divinyldisiloxane and the bis(vinylsilyl)methane. On the other hand, the five-membered ring isomers were the major components in the product mixtures derived from the 1,3-divinyldisilazanes and bis(vinyldimethylsilyl)trimethylsilylamine (Table 3).

Upon close comparison of the ^{29}Si NMR chemical shifts of the ring-substituted cyclic products **1 - 8** with the chemical shifts of the corresponding unsubstituted cyclic model compounds (Table 2), several trends emerged. First of all, the chemical shifts of the Et_3Si and Pr_3Si substituents remained relatively constant throughout the series of compounds **1 - 8** (ranging from 2.0 to 3.5 ppm for Pr_3Si and 6.5 to 8.6 ppm for Et_3Si), with those of the five-membered ring isomers consistently shifted 0.4 to 1.5 ppm upfield from those of the corresponding six-membered ring isomers. The chemical shifts for the endocyclic Si atoms in the five-membered ring isomers **1b - 7b**, **8** fell within ± 1.7 ppm of those of the corresponding unsubstituted model compounds. In six-membered cyclics **1a - 7a** the chemical shifts of the endocyclic Si atoms not adjacent to the (trialkylsilyl)methyl substituent corresponded well to those of the respective unsubstituted cyclic model compounds (differences ranging from 0.1 to 0.6 ppm); the chemical shifts of the endocyclic Si atoms adjacent to the (trialkylsilyl)methyl substituent were all shifted downfield by 1.4 to 3.7 ppm. This observation is consistent with the established trend that ^{29}Si NMR resonances shift downfield with increasing β substitution.[16]

Table 2. ^{29}Si NMR Chemical Shifts of Products and Model Compounds

						
X =	δ (ppm)	δ (ppm)	R =	δ (ppm)	R =	δ (ppm)
O	12.6[a]	24.3[a]	*n*-Pr (**1a**)	I 14.0 II 12.2 III 3.4	*n*-Pr (**1b**)	I,II 24.0 *(d)*, 25.5 *(d)* III 1.9
			Et (**2a**)	I 14.5 II 12.7 III 8.5	Et (**2b**)	I,II 25.8, 26.0, 24.5 *(d)* III 7.1, 8.1
CH_2	- 0.2[b]	14.0[b]	*n*-Pr (**3a**)	I 3.3 II -0.3 III 2.7	*n*-Pr (**3b**)	I,II 12.4, 13.8, 14.1, 14.3 III 2.1
			Et (**4a**)	I 3.5 II 0.4 III 8.6	Et (**4b**)	I,II 13.1, 14.5, 14.8, 15.0 III 7.3, 8.2
NH	2.8[a]	13.1[a]	Et (**5a**)	I 5.1 II 2.2 III 7.8	Et (**5b**)	I,II 11.6, 13.6 III 6.4, 7.4
NMe	4.7[a]	13.6[a]	*n*-Pr (**6a**)	I 7.8 II 4.4 III 3.5	*n*-Pr (**6b**)	I,II 12.9, 13.3, 15.1 III 2.0, 3.0
			Et (**7a**)	I 7.8 II 4.4 III 8.0	Et (**7b**)	I,II 12.9, 13.3, 15.1 III 6.5, 7.5
$NSiMe_3$	*endo* 1.1	*endo* 15.3	-		*n*-Pr **8**	I,II 14.6, 14.9, 16.1, 16.2 III 2.1, 3.3
	exo 1.7	*exo* 0.4				*exo* -0.9, 1.2

[a]See reference 15

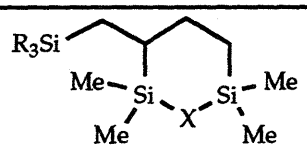
[b]See reference 14

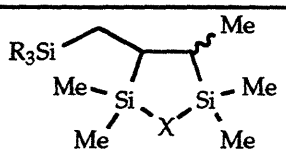
(d) two overlapping signals

endo endocyclic silicon atom

exo exocyclic silicon atom

Table 3. Products of the Hydrosilylation-Cyclization Reactions.





X =	R =			ratio **a** : **b**
O	Pr	**1a**	**1b**	4.7 : 1[x]
O	Et	**2a**	**2b**	2.0 : 1[x]
CH_2	Pr	**3a**	**3b**	2.4 : 1[y]
CH_2	Et	**4a**	**4b**	1.8 : 1[y]
NH	Et	**5a**	**5b**	0.9 : 1[y]
NMe	Pr	**6a**	**6b**	0.4 : 1[y]
NMe	Et	**7a**	**7b**	0.3 : 1[y]
$NSiMe_3$	Pr	-	**8**	n/a

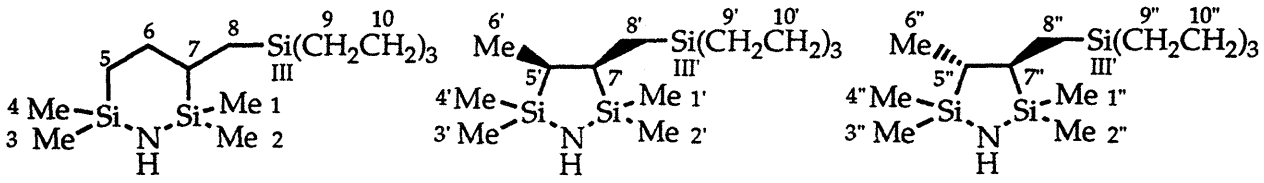
[x] Determined by ^{29}Si NMR

[y] Determined by GC

By preparative GC it was possible in some cases (products **1** - **4**) to obtain samples enriched in the five- or six-membered ring isomer, but complete separation could not be effected with the available gas chromatograph. However, ^{13}C DEPT sequences enabled the assignment of nearly all ^{13}C NMR resonances in the product mixtures, corroborating the results of GC/MS and ^{29}Si NMR measurements. A sample ^{13}C NMR spectrum for product **5** along with its DEPT subspectra for CH_3, CH_2 and CH resonances is shown in Figure 1. ^{13}C and ^{29}Si NMR data are compiled for products **1** - **8** in Table 4.

For five-membered ring products, *cis* and *trans* isomers are possible and in all cases were formed. This was confirmed by the ^{13}C NMR spectra: two signals were observed for each ^{13}C resonance assigned to five-membered

rings except for those due to the peripheral carbons of the trialkylsilyl substituent. Many of these resonances could be assigned based on the known trend that carbon resonances of *trans* 1,2-disubstituted cyclopentanes are shifted up to 5 ppm downfield relative to the *cis* isomers.[32] Two sets of signals could also be observed in most cases for each five-membered ring silicon atom resonance. The *cis* and *trans* isomers were not formed in equal amounts, the ratio being approximately 1.5 : 1 to 2 : 1 depending upon the diene; the predominating isomer could not be identified on the basis of the available spectroscopic information.



5a *cis* **5b** *trans* **5b**

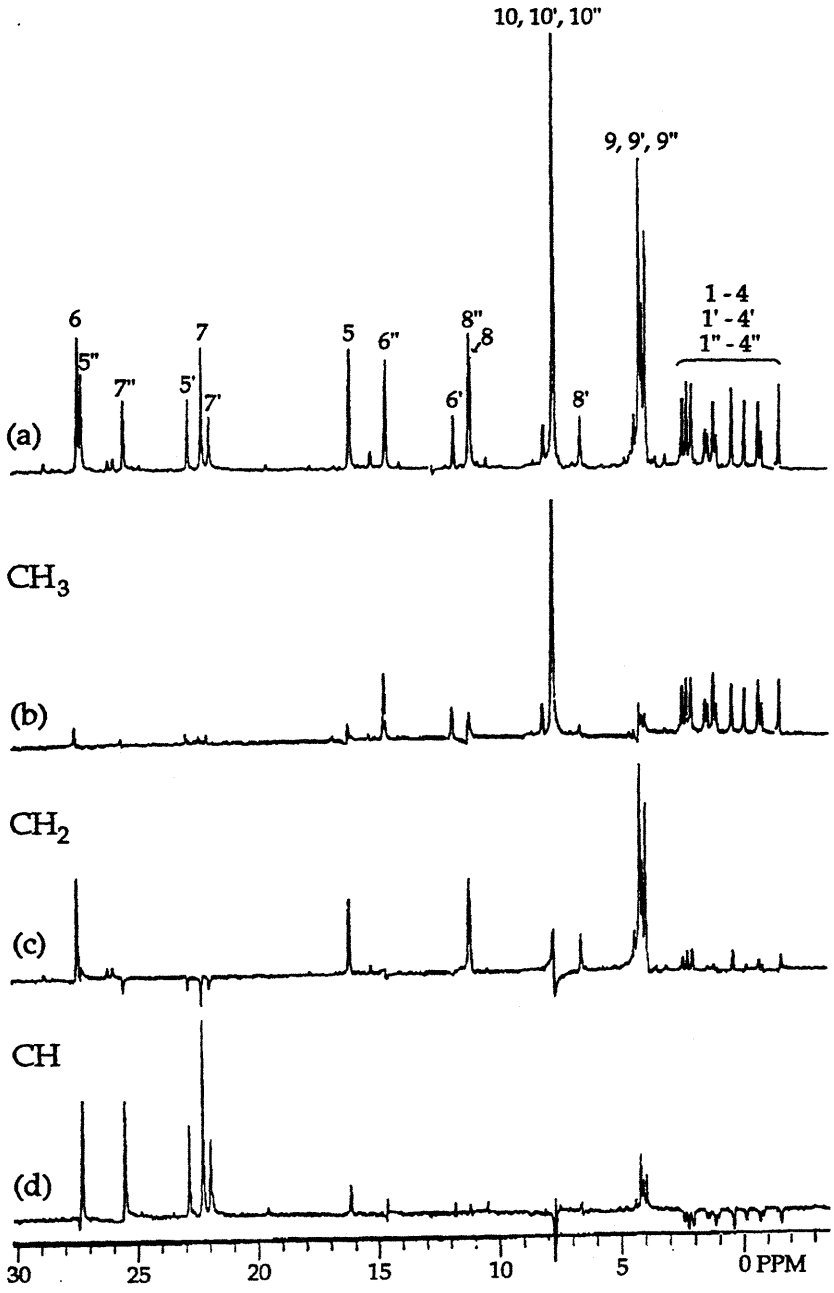


Figure 1. (a) ^{13}C NMR Spectrum and ^{13}C DEPT NMR (b) CH_3, (c) CH_2 and (d) CH Subspectra for Product **5**.

Table 4. NMR Data of the Hydrosilylation-Cyclization Products **1** - **8**.

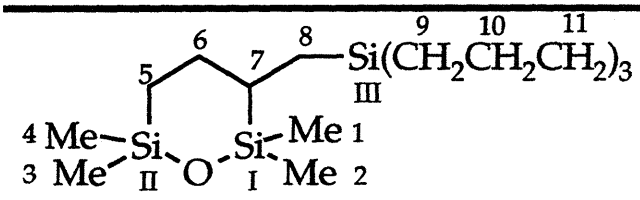
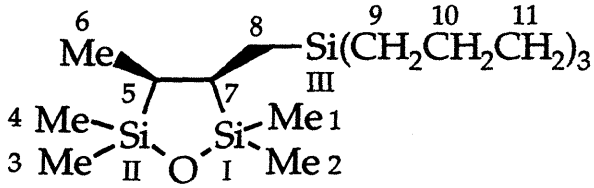
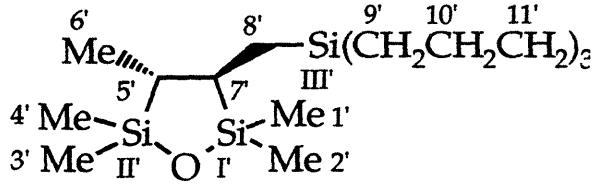
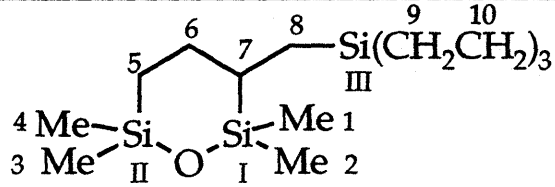
Structure	Chemical shifts in ppm (assignments)
 **1a**	**2,2,6,6-tetramethyl-3-(tripropylsilylmethyl)-2,6-disila-1-oxa-cyclohexane:** *^{13}C:* -3.51, -0.65, 0.29, 1.37 (1 - 4); 11.94 (8); 16.15 (9); 16.70 (5); 17.71 (10); 18.85 (11); 23.09 (7); 27.15 (6). *^{29}Si:* 3.4 (III); 12.2 (II); 14.0 (I).
 *cis* **1b**  *trans* **1b**	***cis/trans* 2,2,4,5,5-pentamethyl-3-(tripropylsilylmethyl)-2,5-disila-1-oxa-cyclopentane:** *^{13}C:* -2.42, -1.90, -1.84, -0.33, -0.05, 0.02, 0.33, 0.80 (1 - 4, 1' - 4'); 7.47 (8); 11.50 (6); 12.29 (8'); 14.09 (6'); 15.89 (9); 15.98 (9'); 17.71 (10, 10'); 18.85 (11, 11'); 22.55 (7); 23.58 (5); 26.82 (7'); 28.34 (5'). *^{29}Si:* 1.9 (III, III'); 24.0 d, 25.5 d (I, II, I', II').
 **2a**	**2,2,6,6-tetramethyl-3-(triethylsilylmethyl)-2,6-disila-1-oxa-cyclohexane:** *^{13}C:* -3.78, -0.85, 0.06, 1.15 (1 - 4); 3.96 (9); 7.46 (10); 10.63 (8); 16.57 (5); 22.86 (7); 27.09 (6) *^{29}Si:* 8.5 (III); 12.7 (II); 14.5 (I).

Table 4. (continued).

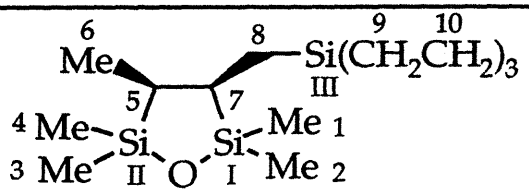
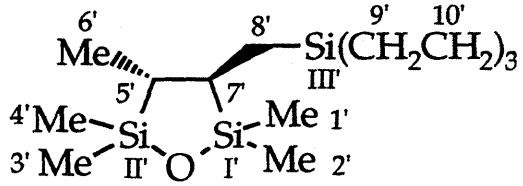
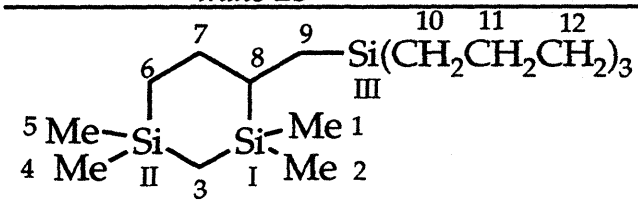
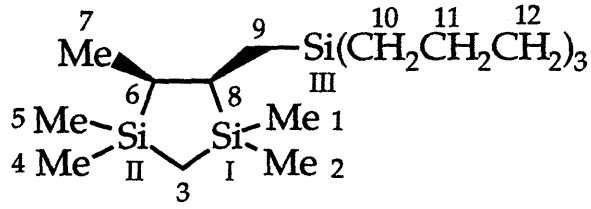
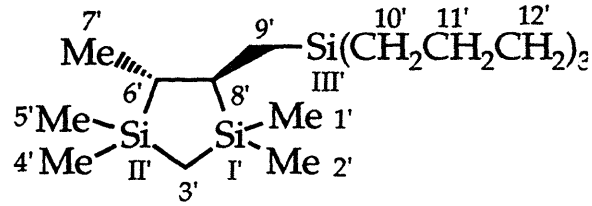
 *cis* **2b**  *trans* **2b**	***cis/trans* 2,2,4,5,5-pentamethyl-3-(triethylsilylmethyl)-2,5-disila-1-oxa-cyclopentane:** *^{13}C:* -2.67, -2.21, -2.07, -0.62, -0.31, d, 0.20, 1.01 (1 - 4, 1' - 4'); 3.69 (9); 3.78 (9'); 6.22 (8); 7.46 (10, 10'); 10.92 (8'); 11.33 (6); 13.90 (6'); 22.48 (7); 23.39 (5); 26.69 (7'); 28.27 (5'). *^{29}Si:* 7.1, 8.1 (III, III'); 24.5 d, 25.8, 26.0 (I, II, I', II').
 **3a**	**2,2,6,6-tetramethyl-3-(tripropylsilylmethyl)-2,6-disila-cyclohexane:** *^{13}C:* -4.38, -0.97, -0.28, 1.09 (1, 2, 4, 5); 1.00 (3); 12.15 (9); 16.17 (10); 16.44 (6); 17.70 (11); 18.88 (12); 22.43 (8); 27.98 (7). *^{29}Si:* -0.3 (II); 2.7 (III); 3.3 (I).
 *cis* **3b**  *trans* **3b**	***cis/trans* 2,2,4,5,5-pentamethyl-3-(tripropylsilylmethyl)-2,5-disila-cyclopentane:** *^{13}C:* -3.69, -2.33 (3, 3'); -3.48, -2.61, -2.13, -1.25, -0.71 (d), -0.14, 0.79 (1, 2, 4, 5, 1', 2', 4', 5'); 7.95 (9); 11.62 (7); 12.06 (9'); 14.66 (7'); 15.99 (10); 16.07 (10'); 17.70 (11, 11'); 18.88 (12, 12'); 23.64 (8); 24.70 (6); 25.92 (8'); 28.55 (6'). *^{29}Si:* 2.1 (III, III'); 12.4, 13.8, 14.1, 14.3 (I, II, I', II').

Table 4. (continued).

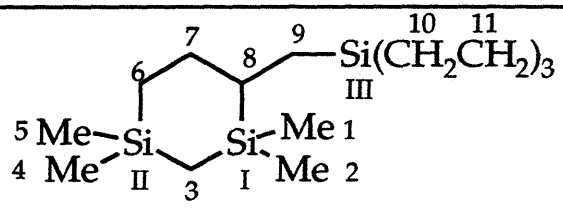
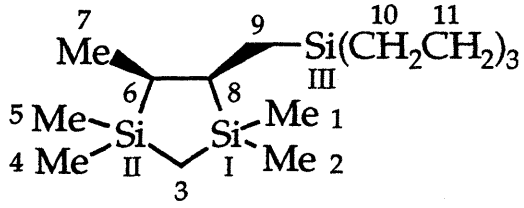
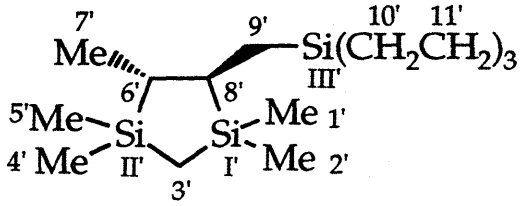
 **4a**	**2,2,6,6-tetramethyl-3-(triethylsilylmethyl)-2,6-disila-cyclohexane:** *^{13}C:* -4.34, -0.92, -0.20, 1.13 (1, 2, 4, 5); 1.06 (3); 4.16 (10); 7.71 (11); 11.05 (9); 16.49 (6); 22.36 (8); 28.01 (7). *^{29}Si:* 0.4 (II); 3.5 (I); 8.6 (III).
 *cis* **4b**  *trans* **4b**	***cis/trans* 2,2,4,5,5-pentamethyl-3-(triethylsilylmethyl)-2,5-disila-cyclopentane:** *^{13}C:* -3.61, -2.28 (3); -3.44, -2.57, -2.08, -1.15, -0.68, -0.63, -0.06, 0.82 (1, 2, 4, 5, 1', 2', 4', 5'); 3.98 (10); 4.06 (10'); 6.97 (9); 7.71 (11, 11'); 10.94 (9'); 11.70 (7); 14.67 (7'); 23.73 (8); 24.61 (6); 25.89 (8'); 28.59 (6'). *^{29}Si:* 7.3, 8.2 (III, III'); 13.1, 14.5, 14.8, 15.0 (I, II, I', II').

Table 4. (continued).

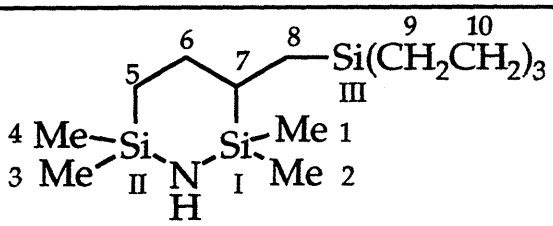
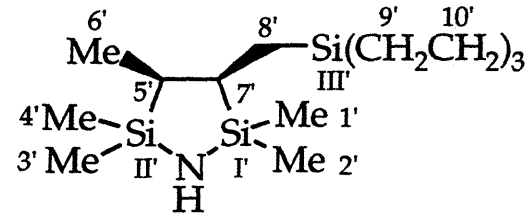
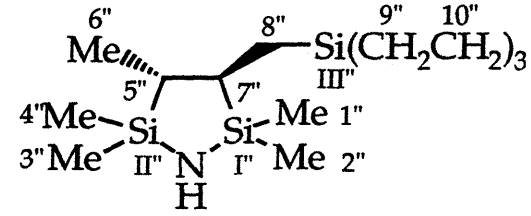
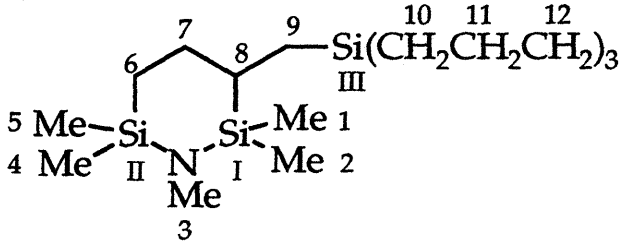
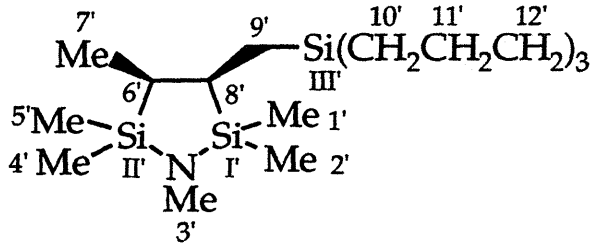
 **5a**	**2,2,6,6-tetramethyl-3-(triethylsilylmethyl)-2,6-disila-1-aza-cyclohexane** and ***cis/trans* 2,2,4,5,5-pentamethyl-3-(triethylsilylmethyl)-2,5-disila-1-aza-cyclopentane:** *^{13}C:* - 1.57, -0.70, -0.12, 0.44, 1.16, 1.50, 2.07, 2.28, 2.43 (1 - 4, 1' - 4', 1" - 4"); 3.97 (9'); 4.08 (9"); 4.19 (9); 6.60 (8'); 7.70 (10, 10', 10"); 11.13 (8); 11.20 (8"); 11.83 (6'); 14.64 (6"); 16.18 (5); 21.97 (7'); 22.30 (7); 22.86 (5'); 25.56 (7"); 27.28 (5"); 27.45 (6). *^{29}Si:* 2.2 (II); 5.1 (I); 6.4, 7.4 (III', III"); 7.8 (III); 11.6, 13.6 (I',II', I", II").
 *cis* **5b**	
 *trans* **5b**	

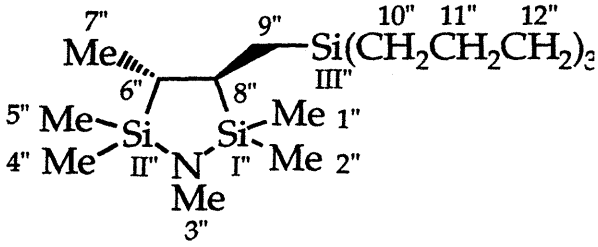
Table 4. (continued).



6a



cis **6b**



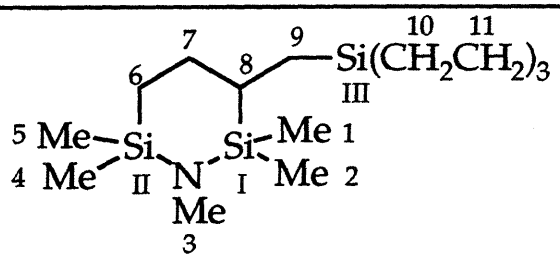
trans **6b**

1,2,2,6,6-pentamethyl-3-(tripropylsilylmethyl)-2,6-disila-1-aza-cyclohexane and *cis/trans* 1,2,2,4,5,5-hexamethyl-3-(tripropylsilylmethyl)-2,5-disila-1-aza-cyclopentane:

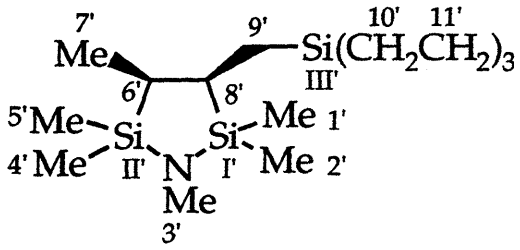
^{13}C: - 5.66, -3.72, -3.28, -1.89, -1.70, -1.65, -1.09, -0.89, -0.74 (1, 2, 4, 5, 1', 2', 4', 5', 1", 2", 4", 5"); 7.73 (9'); 11.74 (7'); 12.38 (9); 12.58 (9"); 14.76 (7"); 15.49 (6); 15.96 (10'); 16.08 (10"); 16.18 (10); 17.67 (11, 11', 11"); 18.79 (12, 12', 12"); 21.31 (8'); 22.32 (6'); 22.83 (8); 25.08 (8"); 26.62 (6"); 26.83 (7); 27.16, 27.24 (3', 3"); 29.06 (3).

^{29}Si: 2.0, 3.0 (III', III"); 3.5 (III); 4.4 (II); 7.8 (I); 12.9, 13.3, 15.1 (I', II', I", II").

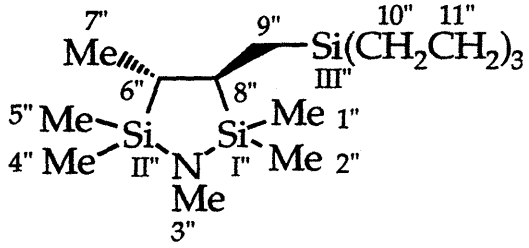
Table 4. (continued).



7a



cis **7b**



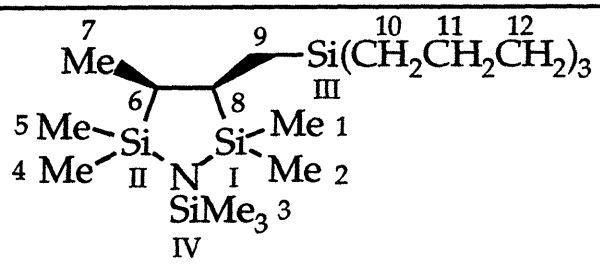
trans **7b**

1,2,2,6,6-pentamethyl-3-(triethylsilylmethyl)-2,6-disila-1-aza-cyclohexane and *cis/trans* 1,2,2,4,5,5-hexamethyl-3-(triethylsilylmethyl)-2,5-disila-1-aza-cyclopentane:

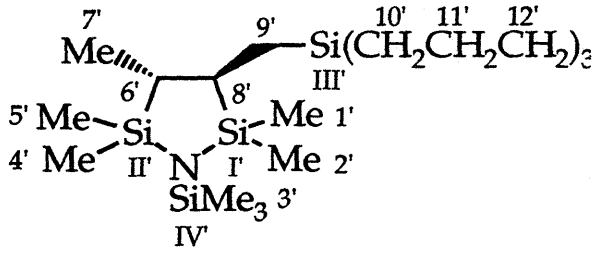
^{13}C: -5.66, -3.69, -3.25, -1.86, -1.70, -1.59, -1.05, -0.74 (1, 2, 4, 5, 1', 2', 4', 5', 1", 2", 4", 5"); 3.90 (10'); 4.04 (10"); 4.14 (10); 6.70 (9'); 7.63 (11, 11', 11:); 11.23 (9); 11.35 (9"); 11.82 (7'); 14.73 (7"); 16.17 (6); 21.35 (8'); 22.22 (6'); 22.74 (8); 25.01 (8"); 26.64 (6"); 26.85 (7); 27.18, 27.25 (3', 3"); 29.07 (3).

^{29}Si: 4.4 (II); 6.5, 7.5 (III', III"); 7.8 (I); 8.0 (III); 12.9, 13.3, 15.1 (I',II', I", II").

Table 4. (continued).



cis **8**



trans **8**

***cis/trans* 2,2,4,5,5-pentamethyl-1-(trimethylsilyl)-3-(tripropylsilylmethyl)-2,5-disila-1-aza-cyclopentane:**

^{13}C: - 0.54, -0.14, 0.38, 1.19, 1.84, 2.16, 2.32, 3.15 (1, 2, 4, 5, 1', 2', 4', 5'); 3.63, 3.71 (3, 3'); 7.01 (9); 11.38 (7); 12.20 (9'); 14.59 (7'); 16.10 (10); 16.17 (10'); 17.77 (11, 11'); 18.91 (12, 12'); 21.77 (8); 23.33 (6); 25.60 (8'); 27.62 (6').

^{29}Si: -0.9, 1.2 (IV, IV'); 2.1, 3.3 (III, III'); 14.6, 14.9, 16.1, 16.2 (I,II, I', II').

Mass spectroscopic data, obtained by GC/MS measurements, are given in Table 5. The mass spectra of the two five-membered ring isomers of each cyclization product are identical, but different from the mass spectrum of the respective six-membered ring isomer. As is commonly observed for alkylsilanes and -siloxanes, fragment ions corresponding to $[M - CH_3]^+$ and $[Me_3Si]^+$ could be detected in most cases.[33] Also observed were peaks due to loss of the R group, $[M - R]^+$ and the R_3Si group, $[M - R_3Si]^+$ (R = Et, *n*-Pr). Another fragment ion, useful in identification of the compound in question, was $[Me_2SiXSiMe_2H]^+$ (X = O, CH_2, NH, NCH_3); in the case of compound **8**, the $[Me_2SiXSiMe_2H]^+$ fragment ion was not observed. The base peak in the mass spectra of all five-membered ring isomers was $[M - R_3Si]^+$; this was not the case, however, for the six-membered ring products. The peak

$[Me_2SiXSiMe_2H]^+$ was of high relative intensity in the mass spectra of all six-membered ring compounds, and for **1a**, **3a**, **5a**, **6a** and **7a** it was the base peak.

In the *n*-$Pr_3SiH/CH_2=CH(CH_3)_2SiOSi(CH_3)_2CH=CH_2$ and the *n*-$Pr_3SiH/CH_2=CH(CH_3)_2SiN(CH_3)Si(CH_3)_2CH=CH_2$ reactions, additional isomeric products were present in low yield: two in the case of the former, one in the case of the latter (comprising 19% and 14% of total isolated product, respectively, as determined by GC). An unambiguous assignment of structure was, however, not possible. Examination of Scheme 2 shows that less likely addition of the $R_3Si\cdot$ radical to the α-carbon atom of the vinyl group would lead to formation of two six-membered ring isomers (*cis* and *trans*) (addition of the intermediate radical to the α-carbon atom of the other vinyl group) and one seven-membered ring isomer (addition to the terminal carbon atom of the other vinyl group).

Table 5. Mass Spectral Data of the Hydrosilylation-Cyclization Products.

2,2,6,6-Tetramethyl-3-(tripropylsilylmethyl)-2,6-disila-1-oxa-cyclohexane (**1a**) and *cis/trans* 2,2,4,5,5-pentamethyl-3-(tripropylsilylmethyl)-2,5-disila-1-oxa-cyclopentane (**1b**)

mass of fragment	fragment	relative intensities (%) in **1a**	relative intensities (%) in **1b**
344	M^+	5	1
329	$(M\text{-}Me)^+$	2	1
301	$(M\text{-}Pr)^+$	20	17
259	$(M\text{-}Pr\text{-}CH_2CHCH_3)^+$	10	2
187	$(M\text{-}SiPr_3)^+$	32	100
186	$(M\text{-}SiPr_3\text{-}H)^+$	100	13
157	$(Pr_3Si)^+$	71	20
133	$(Me_2SiOSiMe_2H)^+$	85	21
115	$(Et_3Si)^+$	100	18
73	$(Me_3Si)^+$	77	22

2,2,6,6-Tetramethyl-3-(triethylsilylmethyl)-2,6-disila-1-oxa-cyclohexane (**2a**) and *cis/trans* 2,2,4,5,5-pentamethyl-3-(triethylsilylmethyl)-2,5-disila-1-oxa-cyclopentane (**2b**)

mass of fragment	fragment	relative intensities (%) in **2a**	relative intensities (%) in **2b**
302	M^+	11	1
287	$(M\text{-}Me)^+$	4	1
273	$(M\text{-}Et)^+$	32	5
187	$(M\text{-}SiEt_3)^+$	39	100
186	$(M\text{-}SiEt_3\text{-}H)^+$	87	12
133	$(Me_2SiOSiMe_2H)^+$	100	33
115	$(Et_3Si)^+$	41	7
73	$(Me_3Si)^+$	35	14

Table 5. (continued).

2,2,6,6-tetramethyl-3-(tripropylsilylmethyl)-2,6-disila-cyclohexane (**3a**) and *cis/trans* 2,2,4,5,5-pentamethyl-3-(tripropylsilylmethyl)-2,5-disila-cyclopentane (**3b**)			
mass of fragment	fragment	relative intensities (%) in **3a**	relative intensities (%) in **3b**
342	M^+	15	3
289	$(M\text{-}Pr)^+$	6	0
257	$(M\text{-}Pr\text{-}CH_2CHCH_3)^+$	5	0
185	$(M\text{-}SiPr_3)^+$	33	100
184	$(M\text{-}SiPr_3\text{-}H)^+$	97	7
157	$(Pr_3Si)^+$	43	16
131	$(Me_2SiCH_2SiMe_2H)^+$	98	20
115	$(Et_3Si)^+$	75	41
73	$(Me_3Si)^+$	100	44
2,2,6,6-tetramethyl-3-(triethylsilylmethyl)-2,6-disila-cyclohexane (**4a**) and *cis/trans* 2,2,4,5,5-pentamethyl-3-(tripropylsilylmethyl)-2,5-disila-cyclopentane (**4b**)			
mass of fragment	fragment	relative intensities (%) in **4a**	relative intensities (%) in **4b**
300	M^+	10	0.8
271	$(M\text{-}Et)^+$	3	0.5
185	$(M\text{-}SiEt_3)^+$	19	100
184	$(M\text{-}SiEt_3\text{-}H)^+$	39	15
131	$(Me_2SiCH_2SiMe_2H)^+$	100	22
115	$(Et_3Si)^+$	27	20
73	$(Me_3Si)^+$	33	30

Table 5. (continued).

2,2,6,6-tetramethyl-3-(triethylsilylmethyl)-2,6-disila-1-aza-cyclohexane (**5a**) and *cis/trans* 2,2,4,5,5-pentamethyl-3-(triethylsilylmethyl)-2,5-disila-1-aza-cyclopentane (**5b**)			
mass of fragment	fragment	relative intensities (%) in **5a**	relative intensities (%) in **5b**
301	M^+	6	2
286	$(M\text{-}Me)^+$	6	1
272	$(M\text{-}Et)^+$	6	4
186	$(M\text{-}SiEt_3)^+$	16	100
132	$(Me_2SiN(H)SiMe_2H)^+$	100	29
116	$(Et_3SiH)^+$	7	29
73	$(Me_3Si)^+$	8	11
1,2,2,6,6-pentamethyl-3-(tripropylsilylmethyl)-2,6-disila-1-aza-cyclohexane (**6a**) and *cis/trans* 1,2,2,4,5,5-hexamethyl-3-(tripropylsilylmethyl)-2,5-disila-1-aza-cyclopentane (**6b**)			
mass of fragment	fragment	relative intensities (%) in **6a**	relative intensities (%) in **6b**
357	M^+	15	5
342	$(M\text{-}Me)^+$	18	1
200	$(M\text{-}SiPr_3)^+$	46	100
157	$(Pr_3Si)^+$	10	3
146	$(Me_2SiN(Me)SiMe_2H)^+$	100	9
115	$(Et_3Si)^+$	18	7
73	$(Me_3Si)^+$	29	14

Table 5. (continued)

1,2,2,6,6-pentamethyl-3-(triethylsilylmethyl)-2,6-disila-1-aza-cyclohexane (**7a**) and *cis/trans* 1,2,2,4,5,5-hexamethyl-3-(triethylsilylmethyl)-2,5-disila-1-aza-cyclopentane (**7b**)

mass of fragment	fragment	relative intensities (%) in **7a**	relative intensities (%) in **7b**
315	M^+	15	9
300	$(M\text{-}Me)^+$	16	3
286	$(M\text{-}Et)^+$	4	2
200	$(M\text{-}SiEt_3)^+$	33	100
146	$(Me_2SiN(H)SiMe_2H)^+$	100	15
115	$(Et_3Si)^+$	9	5
73	$(Me_3Si)^+$	17	14

cis/trans 2,2,4,5,5-pentamethyl-1-(trimethylsilyl)-3-(tripropyl-silylmethyl)-2,5-disila-1-aza-cyclopentane(**8**)

mass of fragment	fragment	relative intensities (%) in **8**
372	$(M\text{-}Pr)^+$	1
258	$(M\text{-}SiPr_3)^+$	100
157	$(Pr_3Si)^+$	5
73	$(Me_3Si)^+$	22

DISCUSSION

Regioselectivity

These investigations have shown that radical-initiated hydrosilylation of bis(vinyldimethylsilyl) compounds forms Si-C and C-C bonds, yielding cyclic products. The addition of the trialkylsilyl radical occurs preponderantly to the terminal carbon atom of one of the diene vinyl groups, forming an α-silyl radical intermediate (Scheme 3). The regioselectivities of the cyclization steps vary strongly with the linking group X of the diene $CH_2=CH(CH_3)_2SiXSi(CH_3)_2CH=CH_2$. When X = O or CH_2, endo cyclization is favored. With nitrogen linking groups (X = NR; R = H, CH_3, $Si(CH_3)_3$) exo cyclization predominates, the exo/endo ratio increasing with the steric bulk of the substituent R. When R = $Si(CH_3)_3$, the reaction gives only five-membered ring products of exo cyclization. Regioselectivities were also found to vary with the choice of trialkylsilane; use of tri-*n*-propylsilane (vs. Et_3SiH) favored the formation of six-membered rings (as well as other regioisomers in the cases of **1** and **6**). Since these reactions are expected to be under kinetic control (i.e., the cyclization is not expected to be reversible);[28] the observed variations in product distributions with choice of trialkylsilane most likely reflect the increased accessibility of higher-energy reaction pathways at the higher reaction temperature of the *n*-Pr_3SiH reactions (171 °C, vs. 107 °C for Et_3SiH reactions).

The results of the cyclization of $CH_2=CH(CH_3)_2SiCH_2Si(CH_3)_2CH=CH_2$ (endo/exo = 1.8 when reacted with Et_3SiH) may be compared to those for the cyclization of the structurally similar 2-sila-5-hexen-1-yl radical (endo/exo = 2.2) illustrated in Scheme 2.[27-29] Both radicals cyclize primarily in an endo fashion, an apparent violation of the Baldwin-Beckwith rules. The endo selectivity for the cyclization of the 2-sila-5-hexen-1-yl radical was attributed to

an increase in the strain energy of the exo transition state resulting from the longer Si-C bond lengths of the molecule (ca. 25% longer than a C-C bond), a view supported by MM2 force-field calculations.[23] A similar reasoning explains the regioselectivity of the hydrosilylation-cyclization of $CH_2=CH(CH_3)_2SiCH_2Si(CH_3)_2CH=CH_2$.

When the diene linker group is changed from X = CH_2 to X = O, endo cyclization is still preferred (endo/exo = 2.0 when reacted with Et_3SiH), despite the fact that Si-O bond lengths are typically shorter than Si-C bond lengths (Si-O bond lengths are typically 1.63 Å; Si-C bond lengths average 1.91 Å).[34] The explanation for the endo selectivity here may lie in the Si-O-Si bond angles which typically range from 142° to 148° but are known to expand to 180° with bulky or electron-withdrawing silicon substituents.[34] This preference for a large bond angle may counteract the effects of shorter Si-O bond lengths in determining the ease of intramolecular attack of the carbon-centered radical on the α carbon of the adjacent vinyl group. In addition, the disiloxane linkage is known to be very conformationally flexible, which may play a role in the observed cyclization regioselectivities.[35]

The preference for exo cyclization found in dienes with nitrogen linker groups (X = NR; R = H, CH_3, $Si(CH_3)_3$) may be attributed to the combination of shorter Si-N (vs. Si-C) bonds (typically 1.72 - 1.73 Å)[34] and greater conformational rigidity imposed by the typically planar[34] $Si_2NC(H)$ or Si_3N moieties. The increase in exo selectivity with increasing steric bulk of diene nitrogen substituent R may reflect relief of unfavorable steric interactions between R and the adjacent SiMe groups in the ground state which are partially relieved in the transition state for exo cyclization. Such steric effects have been invoked to explain the remarkable exo selectivity found in cyclizations of *gem*-dimethyl-substituted all-carbon 5-hexenyl radicals.[23]

Radical Hydrosilylation-Cyclization Reactions as Models for Radical Cyclopolymerization of Bis(vinyldimethylsilyl) Compounds

The cyclopolymerization of α,ω-dienes occurs by a series of alternating intramolecular cyclization and intermolecular propagation steps.[9] The hydrosilylation-cyclization reactions (Scheme 3) of α,ω-dienes in the present study should provide accurate models of the addition of the radical terminus of the growing polymer chain to the first C=C bond of the diene as well as the cyclization of the resulting radical intermediate.

Spectroscopic analyses of the cyclopolymers generated from the reaction of bis(vinyldimethylsilyl) compounds CH_2=CH$(CH_3)_2$SiXSi$(CH_3)_2$CH=CH_2 (X = O, CH_2, NH, NCH_3) with catalytic amounts of peroxide initiators provided evidence for five-, six- and possibly seven-membered cyclic, as well as acyclic, structures in the polymer backbones.[14,15] The results of the present study confirm that radical cyclizations of these monomers indeed give both five- and six-membered ring products. They also lend support to the assumption that during the cyclopolymerization propagating radicals add preponderantly to the terminal carbon of the first vinyl group of the diene. Finally, these reactions provide evidence for the incorporation of other cyclic isomers into the cyclopolymer backbones at elevated reaction temperatures.

In the case of the X = O monomer, the presence of two additional isomers in the *n*-Pr_3SiH/CH_2=CH$(CH_3)_2$SiXSi$(CH_3)_2$CH=CH_2 product mixture (reaction temp. of 171 °C) suggests the presence of other cyclic isomers in the backbone of the cyclopolymer (prepared at 180 - 210 °C). A similar prediction may be drawn for the X = NCH_3 monomer. By the same token, the absence of any additional isomers in the hydrosilylation-cyclization product mixtures for

the X = CH_2 monomer (at 107 or 171 °C) argues against the presence of such isomers in the cyclopolymer. For the X = NH monomer, the reaction temperature of the cyclopolymerization (215 °C) was sufficiently greater than that of the hydrosilylation-cyclization reaction (107 °C) that no definitive statement can be made regarding the presence of additional isomers in the polymer backbone.

CONCLUSIONS

Radical-initiated additions of trialkylsilanes to α,ω-dienes containing Si-X-Si (X = O, CH_2, NH, NCH_3, $NSi(CH_3)_3$) linking groups formed cyclic products through tandem hydrosilylation-cyclization reactions. Both five- and six-membered rings were obtained from these reactions; the regioselectivity of cyclization strongly depended on the nature of the linking group X. Selectivities for exo cyclization to form five-membered rings increased in the series X = O < CH_2 < NH < NCH_3 < $NSi(CH_3)_3$. These reactions modeled radical-initiated cyclopolymerizations of monomers of this type and provided additional insight into the stereoelectronic behavior of dienes linked by Si-X-Si structures.

EXPERIMENTAL SECTION

General comments

All reactions, unless otherwise noted, were performed under an argon atmosphere using standard Schlenk techniques. Glassware was oven dried overnight, assembled while hot and dried *in vacuo* before refilling with Ar. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from United Chemical Technologies and distilled from magnesium turnings before use. 1,3-Divinyltetramethyldisiloxane, 1,3-divinyltetramethyldisilazane and 2,2,5,5-tetramethyl-2,5-disila-1-aza-cyclopentane were purchased from United Chemical Technologies and used as received. Triethyl- and tri-*n*-propylsilane were purchased from Aldrich Chemical Co. and distilled from lithium aluminum hydride before use. Di-*tert*-butyl peroxide was purchased from Aldrich. *n*-Butyllithium was purchased from Aldrich and its concentration determined by the Gilman double titration method.[36] Literature procedures were used in the preparation of bis(dimethylvinylsilyl)methane[14,37] and 2,2,6,6-tetramethyl-2,6-disila-1-azacyclohexane.[38]

Proton NMR spectra were obtained on a Varian XL-300 NMR spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from tetramethylsilane. ^{13}C NMR spectra, proton-decoupled and DEPT sequences, were obtained using a Varian XL-300 NMR spectrometer operating at 75.4 MHz using $CDCl_3/CHCl_3$ as a reference at 77.0 ppm downfield from tetramethylsilane. ^{29}Si NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 59.59 MHz in $CDCl_3$ using tetramethylsilane (0.0 ppm) as the external standard. $Cr(acac)_3$ was used as relaxation agent; this allowed quantitative evaluation of peak areas. Gas chromatography (GC) was performed on an HP 5890 A gas chromatograph (10% SE-30 silicone gum on

Chromosorb; thermal conductivity detector). 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). Melting points of solid compounds were measured in unsealed capillaries in a Büchi oil-filled melting point apparatus with a mechanical stirrer. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Synthesis of Bis(vinyldimethylsilyl) Compounds

Preparation of 1,3-divinylpentamethyldisilazane[39] *(SWK II/51)*

Vinyldimethylchlorosilane (100 ml, 88.4 g, 0.733 mol), triethylamine (204 ml, 148 g, 1.46 mol) and pentane (300 ml) were introduced via cannula into a 1 L three-necked, round-bottomed flask equipped with two dry ice/acetone condensers, a magnetic stir bar and a rubber septum. The reaction flask was then cooled in an ice bath. Methylamine (22 mL, ca. 15 g, ca. 0.50 mol) was condensed in an evacuated 100 mL flask cooled to -78°C; this flask was allowed to warm to room temperature, and the evaporated methylamine directed through a cannula into one of the dry ice/acetone condensers of the reaction vessel. White solids formed immediately, and the reaction mixture was stirred vigorously throughout the course of the methylamine addition (1.25 h). When the addition was complete, the reaction mixture was refluxed 2 h. After cooling to room temperature, the entire contents of the reaction vessel were filtered through a Schlenk frit into a 2 L flask. The salts were washed with 1 L of pentane. Pentane and triethylamine were removed by distillation at ambient pressure under Ar. The remaining liquid was transferred to a smaller flask and distilled at reduced pressure through a 10"

Vigreux column. Yield: 39.6 g (54 %), b.p. 78 °C/15 mm Hg (lit.[39] 110 °C/83 mm Hg).

^{1}H NMR ($CDCl_3$): δ 0.17 (s, 12 H, $Si(C\underline{H}_3)_2CH=CH_2$), 2.49 (s, 3H, NCH_3), 5.69 (dd, J_{cis} = 4.1 Hz, J_{gem} = 20.1 Hz; 2 H; $SiCH=C\underline{H}_2$ (*trans* to Si)), 5.93 (dd, J_{cis} = 4.1 Hz, J_{trans} = 14.6 Hz; 2 H; $SiC\underline{H}=CH_2$), 6.16 (dd, J_{trans} = 14.6 Hz, J_{gem} = 20.1 Hz; 2 H; $SiCH=C\underline{H}_2$ (*cis* to Si)).

^{13}C NMR ($CDCl_3$): δ -0.44 (q, J = 119 Hz, $Si(\underline{C}H_3)_2CH=CH_2$); 31.31 (q, J = 135 Hz, NCH_3); 131.17 (td, ^1J = 154 Hz, ^2J = 8 Hz; $SiCH=\underline{C}H_2$); 140.38 (d, J = 132 Hz, $Si\underline{C}H=CH_2$).

^{29}Si NMR ($CDCl_3$): δ -2.32.

Preparation of Bis(dimethylvinylsilyl)trimethylsilylamine[40] *(SWK IV/55)*

In a 300 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar, divinyltetramethyldisilazane (20.0 mL, 16.4 g, 88.3 mmol) was dissolved in 150 mL of THF. After cooling to -78 °C, 18.0 mL of *n*-BuLi solution (2.50 M in hexanes, 45.0 mmol) was added via syringe over 45 min. After stirring for 2 h at -78 °C, the reaction mixture was warmed slowly to room temperature over a period of 3 h. Trimethylchlorosilane (11.4 mL, 9.76 g, 89.8 mmol) was added via syringe, and the reaction mixture was stirred 10 h at room temperature. After removal of THF at reduced pressure, 150 mL of hexane was added via cannula, and the resulting slurry filtered through a Schlenk frit. After removal of hexane at reduced pressure, the resulting semi-crytalline solid was subjected to Kugelrohr distillation (0.01 mm Hg, 55 °C), yielding a clear, waxy solid. Yield: 19.32 g (85%), m.p. 63-65 °C. Anal. Calcd for $C_{11}H_{27}NSi_3$ (MW = 257.598 g/mol): C, 51.29; H, 10.56%. Found: C, 51.48; H, 10.54%.

^{1}H NMR ($CDCl_3$): δ 0.17 (s, 9 H, $Si(CH_3)_3$), 0.22 (s, 12 H, $Si(C\underline{H}_3)_2CH=CH_2$), 5.63 (dd, J_{cis} = 3.8 Hz, J_{gem} = 20.3 Hz; 2 H; $SiCH=C\underline{H}_2$ (*trans* to Si)), 5.86 (dd, J_{cis} = 3.8 Hz, J_{trans} = 14.7 Hz; 2 H; $SiC\underline{H}=CH_2$), 6.24 (dd, J_{trans} = 14.7 Hz, J_{gem} = 20.2 Hz; 2 H; $SiCH=C\underline{H}_2$ (*cis* to Si)).

^{13}C NMR ($CDCl_3$): δ 3.91 (q, J = 119 Hz, $Si(\underline{C}H_3)_2CH=CH_2$), 5.55 (q, J = 120 Hz, $Si(CH_3)_3$), 130.33 (td, ^1J = 154 Hz, ^2J = 5 Hz; $SiCH=\underline{C}H_2$), 143.44 (d, J = 136 Hz, $Si\underline{C}H=CH_2$).

^{29}Si NMR ($CDCl_3$): δ -6.43 (2 Si, $SiMe_2CH=CH_2$), 3.39 (1 Si, $SiMe_3$).

Hydrosilylation-Cyclization Reactions

Following a description of the general procedure, three specific examples are given. Experimental details for the other reactions carried out are given in Table 1. Product boiling points and combustion analyses are given in Table 1. ^{13}C NMR data are given in Table 4. ^{29}Si NMR data are given in Tables 2 and 4. Low resolution MS data (obtained via GC/MS) are given in Table 5.

General Procedure

The trialkylsilane (20 equiv.; 12 equiv. for the reactions of $CH_2=CH(CH_3)_2SiCH_2Si(CH_3)_2CH=CH_2$ and $CH_2=CH(CH_3)_2SiOSi(CH_3)_2CH=CH_2$ with *n*-Pr_3SiH) was added via cannula to a 200 mL round-bottomed, three-necked flask equipped with a magnetic stir bar, a pressure-equalizing addition funnel, a reflux condenser topped with a vacuum line adapter, a glass stopper and a rubber septum. The bis(vinyldimethylsilyl) compound (1 molar equiv.) was mixed with di-*tert*-butyl peroxide (0.2 molar equiv.) in the dropping funnel. The trialkylsilane

was heated to a gentle reflux, and the bis(vinyldimethylsilyl) compound/peroxide mixture added very slowly, one drop at a time, over a period of one to several days. Upon completion of the addition, the reaction mixture was refluxed for several hours to one day. Unreacted trialkylsilane was distilled from the reaction mixture. The product was isolated by distillation at reduced pressure.

*Reaction of Tri-*n*-propylsilane with 1,3-Divinyltetramethyldisiloxane (HF)*

Following the above procedure, 1,3-divinyldisiloxane (3.87 g, 20.8 mmol) mixed with di-*tert*-butyl peroxide (0.63 g, 4.2 mmol) was added over a period of one day to refluxing (171 °C) tri-n-propylsilane (37 g, 240 mmol). After completion of the addition, the reaction mixture was refluxed an additional 6 h. Unreacted tri-*n*-propylsilane was removed from the reaction mixture by distillation, leaving a residue which was distilled at reduced pressure to give 4.40 g (61%) of a clear, colorless liquid **1**. A viscous oil (2.3 g) remained as distillation residue.

Reaction of Triethylsilane with 1,3-Divinylpentamethyldisilazane (SWK II/55)

Following the general procedure, a mixture of 1,3-divinylpentamethyldisilazane (6.29 g, 31.5 mmol) and di-*tert*-butyl peroxide (0.9 g, 6 mmol) was added over a period of five days to refluxing (107 °C) triethylsilane (73.24 g, 630 mmol). After completion of the addition, the reaction mixture was refluxed for an additional day. Triethylsilane was removed by distillation (75 mm Hg, 46 °C) leaving behind a yellow, slightly viscous liquid. Distillation of the latter gave 8.32 g (84%).of a clear, colorless liquid **7**. A yellow, viscous oil (1.62 g) remained as residue.

*Reaction of Tri-*n*-propylsilane with Bis(vinyldimethylsilyl)(trimethylsilylamine) (SWK II/56)*

The amine (2.27 g, 8.8 mmol) and 0.26 g of di-*tert*-butyl peroxide (1.8 mmol) were dissolved in 5 mL *n*-Pr_3SiH and added over the course of one day to refluxing (171 °C) tri-*n*-propylsilane (total amount used: 31.0 g, 196 mmol). After an additional period of reflux of 18 h, tri-*n*-propylsilane was removed by distillation (2 mm Hg, 32 °C) leaving a slightly yellow oil. Distillation of the latter gave 1.55 g (32%) of product **8** as a clear, colorless liquid. The distillation residue was a yellow, viscous oil (1.19 g).

Synthesis of Model Compounds

Preparation of 1-Trimethylsilyl-2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane (SWK III/8)

In a 100 mL Schlenk flask, 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane (0.846 g, 5.30 mmol) was dissolved in 40 mL of THF. The mixture was cooled to -78 °C, and 2.30 mL of *n*-BuLi solution (2.50 M in hexanes, 5.75 mmol) was added via syringe. After stirring for 2 h at -78 °C, the reaction mixture was quenched with 0.80 mL (0.68 g, 6.3 mmol) of Me_3SiCl added via syringe, and allowed to warm to room temperature while it was stirred overnight. The reaction mixture was further stirred at 50 °C for one day. THF was removed at reduced pressure and hexane (20 mL) was added. The resulting mixture was filtered through Celite, rinsing with three 20 mL portions of hexane. Hexane was removed at reduced pressure, and the remaining oil purified by Kugelrohr distillation (0.06 mm Hg, 25-60 °C), yielding clear, colorless crystals. Yield: 0.81 g (66%); m.p. 38-40 °C. Anal. Calcd

for $C_9H_{25}NSi_3$ (MW = 231.561 g/mol): C, 46.68; H, 10.88%. Found: C, 46.73; H, 10.87%.

^{1}H NMR ($CDCl_3$): δ 0.09 (s, 9H, $Si(C\underline{H}_3)_3$), 0.10 (s, 12H, $Si(C\underline{H}_3)_2CH_2CH_2Si$), 0.65 (s, 4H, $SiC\underline{H}_2CH_2Si$).

^{13}C NMR ($CDCl_3$): δ 2.68 (q, J = 117 Hz, $Si(\underline{C}H_3)_2CH_2CH_2Si$), 3.71 (q, J=116 Hz, $Si(\underline{C}H_3)_3$), 10.01 (tm, ^1J = 121 Hz, $^2J \sim 2$ Hz, $Si\underline{C}H_2CH_2Si$).

^{29}Si NMR ($CDCl_3$): δ 0.39 (s, 1 Si, $\underline{Si}(CH_3)_3$), 15.34 (s, 2 Si, $\underline{Si}CH_2CH_2Si$).

MS(EI): *m/z* = 231 {M^+, 2}, 216 {$(M\text{-}Me)^+$, 100}, 188 {8}, 130 {$(Me_2Si{=}N\text{-}SiMe_2)^+$, 12}, 100 {24}, 73 {$SiMe_3^+$, 16}.

Preparation of 1-Trimethylsilyl-2,2,6,6-tetramethyl-2,6-disila-1-azacyclohexane (SWK III/32)

In a 100 mL Schlenk flask, 2,2,6,6-tetramethyl-2,6-1-azadisilacyclohexane (1.71 g, 9.87 mmol) was dissolved in 50 mL of THF. The mixture was cooled to -78 °C, and 6.20 mL of *n*-BuLi solution (1.60 M in hexanes, 9.92 mmol) was added via syringe. After stiring 2 h at -78 °C, the reaction mixture was quenched with 1.30 mL (1.11 g, 10.2 mmol) of Me_3SiCl added via syringe, and allowed to warm to room temperature while stirring overnight. THF was removed at reduced pressure and pentane (10 mL) added. The resulting mixture was filtered through a glass frit, rinsing with 25 mL pentane. Pentane was removed at reduced pressure, and the remaining oil purified by Kugelrohr distillation (0.04 mm Hg, 35-40 °C), yielding clear, colorless crystals. Yield: 0.615 g (25%); m.p. 42-42.5 °C. Anal. Calcd for $C_{10}H_{27}NSi_3$ (MW = 245.588 g/mol): C, 48.91; H, 11.08%. Found: C, 49.04; H, 11.10%.

^{1}H NMR ($CDCl_3$): δ 0.12 (s, 12H, $Si(C\underline{H}_3)_2CH_2CH_2CH_2Si$), 0.15 (s, 9H, $Si(C\underline{H}_3)_3$), 0.58 (t, 4H, J = 6.5 Hz, $Si(CH_3)_2C\underline{H}_2CH_2$), 1.75 (m, $Si(CH_3)_2CH_2C\underline{H}_2$).

^{13}C NMR ($CDCl_3$): δ 3.44 (q, J = 118 Hz, $Si(\underline{C}H_3)_3$), 4.46 (q, J = 118 Hz, $Si(\underline{C}H_3)_2CH_2CH_2CH_2Si$), 17.35 (tp, ^1J = 128 Hz, ^2J ~ 6 Hz, $Si(CH_3)_2CH_2\underline{C}H_2$), 20.06 (tm, ^1J = 117 Hz, ^2J ~ 6 Hz, $Si(CH_3)_2\underline{C}H_2CH_2$).

^{29}Si NMR ($CDCl_3$): δ 1.06 (s, 2 Si, $\underline{Si}CH_2CH_2CH_2Si$), 1.73 (s, 1 Si, $\underline{Si}(CH_3)_3$).

MS(EI): *m/z* = 245 {M+, 3}, 230 {$(M\text{-}CH3)^+$, 100}, 202 {$(M\text{-}Pr)^+$, 100}, 130 {$(Me_2Si{=}N\text{-}SiMe_2)^+$, 27}, 100 {21}, 73 {$SiMe_3^+$, 13}.

REFERENCES

1. Regitz, M.; Giese, B. "C-Radikale," In *Houben-Weyl Methoden der Organischen Chemie;* 4th ed.; Georg Thieme Verlag: Stuttgart, 1989; Vol. E19a
2. Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237-86.
3. Hanessian, S.; Léger, R. *J. Am. Chem. Soc.* **1992**, *114*, 3115-7.
4. Ballestri, M.; Chatgilialoglu, C.; Guerra, M.; Guerrini, A.; Lucarini, M.; Seconi, G. *J. Chem. Soc. Perkin Trans. 2* **1993**, 421-5.
5. Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron* **1993**, *49*, 2793-804.
6. Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron* **1993**, *49*, 7193-214.
7. Nishiyama, K.; Oba, M.; Oshimi, M.; Sugawara, T.; Ueno, R. *Tetrahedron Lett.* **1993**, *34*, 3745-8.
8. Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188-94.
9. Butler, G. B. *Cyclopolymerization and Cyclocopolymerization;* Marcel Dekker: New York, 1992, p 557.

10. Billingham, N. C.; Jenkins, A. D.; Kronfli, E. B.; Walton, D. R. M. *J. Polym. Sci., Polym. Chem.* **1977**, *15*, 675-81.

11. Butler, G. B.; Stackman, R. W. *J. Macromol. Sci.-Chem.* **1969**, *A3*, 821-34.

12. Solovskaya, N. A.; Zakharov, S. K.; Asinovskaya, D. N.; Lukyashina, V. A.; Andreev, D. N. *Acta Polym.* **1992**, *43*, 180-2.

13. Saigo, K.; Tateishi, K.; Adachi, H. *J. Polym. Sci., Part A, Polym. Chem.* **1988**, *26*, 2085-97.

14. Robison, J. L. *Synthesis and Reactivity of Silicon Containing Linear and Cyclic Monomers and Polymers;* Ph.D. Dissertation, Massachusetts Institute of Technology: Cambridge, MA, 1992.

15. Seyferth, D.; Robison, J. *Macromolecules* **1993**, *26*, 407-18.

16. Williams, E. A.; Cargioli, J. D. "Silicon-29 NMR Spectroscopy," In *Annual Reports on NMR Spectroscopy;* Webb, G. A., Ed.; Academic Press: New York, 1979; Vol. 9, pp 221-318.

17. Kraus, G. A.; Liras, S. *Tetrahedron Lett.* **1990**, *31*, 5265-68.

18. Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2348-55.

19. Hanessian, S.; Ninkovic, S. *J. Org. Chem.* **1996**, *61*, 5418-24.

20. Baldwin, J. E. *J. Chem. Soc. Chem. Comm.* **1976**, 734-6.

21. Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc. Chem. Comm.* **1980**, 482-3.

22. Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, *26*, 373-6.

23. Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925-41.

24. Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959-74.

25. Chatgilialoglu, C.; Woynar, H.; Ingold, K. U.; Davies, A. G. *J. Chem. Soc. Perkin Trans. 2* **1983**, 555-61.

26. Barton, T. J.; Revis, A. *J. Am. Chem. Soc.* **1984**, *106*, 3802-5.

27. Wilt, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 5251-3.

28. Wilt, J. W. *Tetrahedron* **1985**, *41*, 3979-4000.

29. Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281-7.

30. Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon: Oxford, 1992.

31. El-Durini, N.; Jackson, R. A. *J. Organomet. Chem.* **1982**, *232*, 117-21.

32. Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy: High-Resolution Methods and Applications in Organic Chemistry and Biochemistry*; 3rd ed.; VCH: New York, 1987, p 515.

33. Schwarz, H. "Positive and Negative Ion Chemistry of Silicon-Containing Molecules in the Gas Phase," In *The Chemistry of Organic Silicon Compounds*; Patai, S. and Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 2, pp 445-510.

34. Lukevics, E.; Pudova, O.; Sturkovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis-Horwood: Chichester, 1989.

35. Voronkov, M. G.; Mileshkevich, V. P.; Yuzlelevskii, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978, pp 9-47.

36. Gilman, H.; Klein, R. A.; Winkler, J. S. *J. Org. Chem.* **1961**, *26*, 2474.

37. Greber, G.; Degler, G. *Makromol. Chem.* **1962**, *52*, 184.

38. Andrianov, K. A.; Kotrelev, K. V.; Kononov, A. M.; Prudnik, I. M. *Dokl. Akad. Nauk SSR (Chemistry)* **1974**, *216*, 1041-4.

39. Elliott, R. L.; Breed, L. W. *J. Chem. Engr. Data* **1966**, *11*, 604-5.

40. Flatt, D. V.: U.S. Patent 3,453,233, 1969; C.A. **71**: 71748b (1969).

CHAPTER TWO

Anionic Cyclopolymerization of 1,3-Divinylpentamethyldisilazane and Bis(vinyldimethylsilyl)(trimethylsilyl)amine

INTRODUCTION

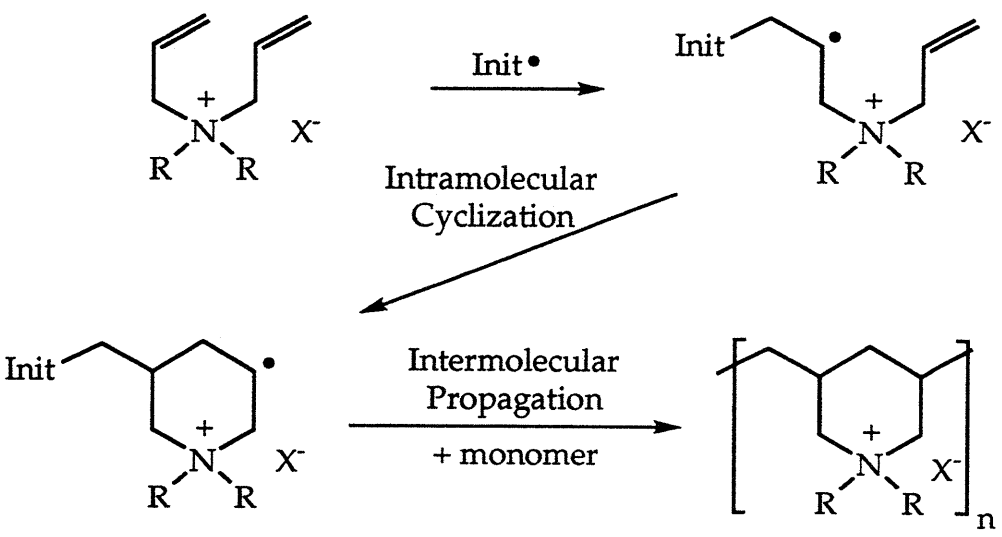
Synthesis plays a central role in driving the advancement of polymer science and technology.[1,2] While production methods for commodity polymers continue to develop at an evolutionary pace, the synthesis of new, advanced polymeric materials targeted for specific technological applications possesses virtually unlimited growth potential. Emerging niche markets, particularly in the biomedical, defense and electronics industries, require the production of small quantities of specially tailored polymers with high unit costs. Some examples include polymeric drug delivery systems, biocompatible polymers, electrically conducting polymers for batteries and capacitors, high-resolution photoresists for deep submicron VLSI technology, high-performance elastomers for manufacturing, and liquid crystalline polymers for advanced fibers and optical applications.

Synthetic control over polymer chain architecture has led to significant advances in polymer science in the past, the most important example being the development of the Ziegler and Phillips processes for making high-density polyethylene (HDPE) in the late 1950's.[2] By virtue of its essentially unbranched backbone, HDPE is five times stronger, an order of magnitude stiffer, and melts at a temperature ~30 °C higher than low-density polyethylene (LDPE), which is highly branched. Another notable success story is the development of Kevlar by chemists at DuPont in the late 1960's.[3] Kevlar derives its great strength (spun fibers of Kevlar are seven times stronger than steel) from the inherent stiffness of its polymer backbone and strong chain-chain interactions.

The creation of polymers with unique backbone topologies continues to be a fertile area of research, holding the promise of tailoring polymer physical and chemical properties through changes in chemical composition.

Cyclopolymers are one such class of uniquely shaped polymers.[4] The backbones of cyclopolymers are constructed of saturated rings linked together by short (generally one- or two-carbon) linear segments; such a structure would be expected to exhibit chain rigidity intermediate to that of conventional flexible polymers (like polyethylene) and rigid-rod polymers (like Kevlar). Indeed, cyclopolymers retain many of the same desirable physical properties of traditional flexible polymers, but with increased chain stiffness and thermal stability like rigid polymers.

From a chemical perspective, cyclopolymers excite interest stemming from the unexpected chemistry that leads to their formation. From very early on in the history of polymer synthesis, chemists believed that polymerization of unconjugated α,ω-dienes would lead only to cross-linked, insoluble materials. However, in the early 1950's, studies by Butler and coworkers showed that radical polymerization of diallyl quaternary ammonium salts gave soluble polymers with no residual allyl groups. To account for this surprising observation, they proposed a mechanism involving alternating cyclization and chain propagation steps, giving a polymer consisting of rings linked together by short linear segments (Scheme 1).[5]



Scheme 1. Cyclopolymerization of Diallyl Quaternary Ammonium Salts.

Since that time, the cyclopolymerization of many symmetric and unsymmetric difunctional monomers has been studied.[4] Various polymerizable functional groups (e.g. alkynes, nitriles, epoxides and aldehydes) have been tested, linked together with groups of varying composition and length. Not all difunctional monomers cyclize completely during polymerization, giving rise to varying degrees of residual unsaturation and/or cross-linking in the resulting polymer. Additional issues of regio- and stereoselectivity arise in the cyclization steps. Most 1,6-diene monomers follow the Baldwin-Beckwith rules for cyclization[6,7] and give five-membered rings in the polymer backbone; however, exceptions have been reported. In addition to all these considerations are the usual factors common to all polymerizations, such as rates of initiation, propagation, chain-transfer and termination reactions, which effect the final molecular weight distribution, and hence the physical properties, of the final

product. Good levels of control of all these various factors will enable well-defined polymers with desirable physical properties to be produced.

All of the different modes of initiation–cationic, anionic, coordination and radical–have been used for forming cyclopolymers. Historically, however, radical initiatiors have been preferred for cyclopolymerizations due to their relative ease of use and their ability to polymerize a wide variety of functional groups.[4] Even though anionic and coordination initiators generally are able to give greater control over chain length and molecular weight distribution, their use in cyclopolymerization has not been fully exploited. Two recent examples highlight the potential of coordination initiators in cyclopolymerization. Soluble metallocene-based Ziegler-Natta coordination initiators cyclopolymerize 1,6-hexadiene derivatives with high degrees of control over tacticity; when chiral catalysts are used, the resulting polymers are chiral.[8-13] Metathesis cyclopolymerization of 1,6-diynes, catalyzed by well-defined Mo alkylidene catalysts, proceeds in a living manner, giving cyclopolymers of controlled microstructure.[14,15]

Anionically initiated cyclopolymerizations have only recently begun to attract attention. Historically, their development has been slow, presumably due to a lack of suitable difunctional monomers which are activated toward nucleophilic addition. Carbon-heteroatom multiple bonds and strained rings are known to polymerize anionically. Early work involved the anionic cyclopolymerization of di- and triisocyanates.[16,17] More recently, the anionic cyclopolymerization of diepoxides has been shown to give highly regular carbohydrate polymers.[18,19] The anionic cyclopolymerization of dienes requires the presence of electron-withdrawing groups α to the C=C bonds in the monomer. Early successes with anionic cyclopolymerizations of diene monomers were based on linked styrenes (2,6-diphenyl-1,6-heptadiene[20]) or

acrylates (diacrylylmethane[21]). Recent work by Kodaira and coworkers has demonstrated the effectiveness of anionic initiators in the cyclopolymerizations of diacrylamides and N-allylacrylamides[22-24]. Extension of the scope of anionic cyclopolymerization of dienes beyond this point will require the utilization of new activating groups on the diene C=C bonds.

Organosilicon chemistry has made significant contributions to polymer science, in particular to the field of cyclopolymerization.[25] Silicon-containing dienes, particularly diallylsilanes, were some of the earliest monomers to be tested for their cyclopolymerization behavior.[26-30] Studies on diallylsilanes have continued over the years,[31-34] while other researchers have investigated the cyclopolymerizations of silicon-containing diacetylenes[35-37] and bis(vinylsilyl) monomers.[38-43]

While diallylsilanes and bis(silylacetylene) compounds are not expected to be suitable monomers for anionic cyclopolymerization, bis(vinylsilyl) compounds show promise in this regard. Organosilicon substituents are known to behave as electron-withdrawing groups through the so-called "α-effect" whereby the presence of a silicon atom stabilizes an adjacent carbanion through subtle hyperconjugative interactions.[44] This activates adjacent C=C bonds towards nucleophilic addition. The anionic polymerization of vinylsilanes CH_2=CHSiR_3 (R = alkyl or aryl) has been extensively investigated by several groups since the early 1960's.[38,41,42,45-62]

Silicon-activated diene monomers suitable for cyclopolymerization may be obtained by linking two vinylsilyl moieties. Divinyldimethylsilane $(CH_2=CH)_2SiMe_2$, the simplest such monomer which could be envisioned, undergoes anionic cyclopolymerization poorly, leaving a large percentage of unreacted vinyl groups (30%) in the polymer.[38] This low degree of cyclization is probably due to the proximity of the vinyl groups in the monomer which

hinders their reacting in an intramolecular fashion. Joining two vinyldimethylsilyl moieties with some spacer group X, giving a monomer like that shown in Figure 1, can conceivably lead to a greater propensity towards cyclization by reducing the strain in the transition state. The linking group X must be chosen such that the Si-X-Si moiety is not reactive with the alkyllithium initiators or propagating chain ends. In addition, the conformational behavior of the Si-X-Si linkage will most likely affect the course of the cyclization reaction, thereby changing the degree of cyclization and/or the ring-size distribution in the resulting polymer.

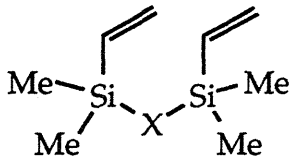


Figure 1. Linked Bis(vinylsilyl) Monomer for Cyclopolymerization.

The radical-initiated cyclopolymerization of several linked bis(vinyldimethylsilyl) compounds (X = O, CH_2, NH, NCH_3 in Figure 1) was recently studied in these laboratories.[39,40] These monomers gave soluble, low molecular weight polymers with low (3 - 5%) degrees of residual unsaturation, broad molecular weight distributions and somewhat irregular microstructures. Anionic initiation would be expected to give better control over both the molecular weight and the microstructure of the resulting polymers. However, of all the monomers employed in the above study, only those with X = CH_2 and NCH_3 linker groups possess Si-X-Si moieties expected to be stable to nucleophilic attack by alkyllithiums.[63,64] The anionic polymerization of the X = NCH_3 monomer was briefly studied by Stober,

Michael and Speier in the late 1960's.[41,42] They reported obtaining a soluble polymer with low residual unsaturation, and postulated a structure for the polymer consisting of six-membered disilazane rings linked together by methylene units. However, given the incomplete characterization of the polymer (only osmometry, combustion analysis and infrared spectroscopy data are reported), the validity of the proposed structure is unclear, warranting further investigation. More recently, bis(vinyldimethylsilyl)methane (Figure 1, X = CH_2) has been cyclopolymerized using anionic initiators to give soluble polymers reported to consist entirely of six-membered ring repeat units.[43]

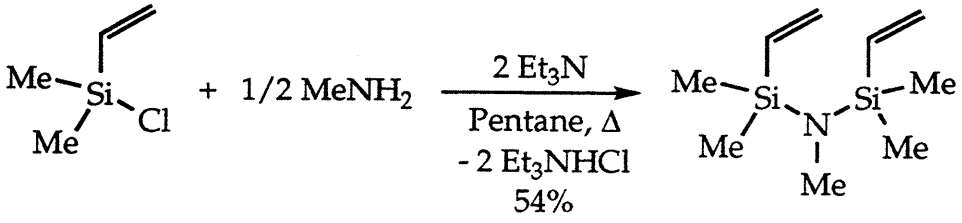
Clearly, silicon-activated dienes are potentially useful monomers for anionic cyclopolymerization. Thus, the anionic polymerization behavior of the linked bis(vinylsilyl) compound 1,3-divinylpentamethyldisilazane (Figure 1, X = NCH_3) was reexamined. In addition, the related bis(vinyldimethylsilyl)(trimethylsilyl)amine (Figure 1, X = $NSi(CH_3)_3$) was tested as a monomer for anionic cyclopolymerization; the incorporation of a sterically demanding substituent ($SiMe_3$) on the nitrogen was expected to favor the cyclization reaction over linear propagation and possibly change the regiochemistry of cyclization. This compound had appeared only once previously in the literature, as a cross-linking agent for silicones.[65]

These studies demonstrated that linked vinylsilanes can be anionically cyclopolymerized to give polymers with well-defined structures. The size of the nitrogen substituent in the linking group exerted a strong effect on the reactivity of the monomer, leading to marked changes in polymer structure.

RESULTS AND DISCUSSION

Synthesis of Monomers

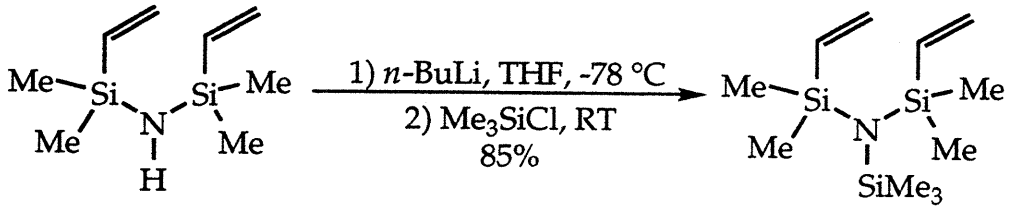
The formation of disiloxane hydrolysis products often complicates the synthesis of disilazanes and trisilylamines. Silazanes themselves are known to be slightly moisture-sensitive; this sensitivity decreases with increasing substituent size but is greatly enhanced by the presence of acids.[63,64] Since these siloxane by-products readily quench alkyllithium polymerization initiators as well as propagating polymer chain ends, they must be completely removed if the polymerizations are to be successful. 1,3-Divinylpentamethyldisilazane, hereafter referred to as the **NMe** monomer, can be prepared on a large scale (typically 40 g for purposes of these studies) by the reaction of commercially available vinyldimethylchlorosilane with methylamine (eq. 1). Obtaining this monomer, which is highly sensitive to traces of acid, free of 1,3-divinyldisiloxane requires multiple distillations.



(1)

Bis(vinyldimethylsilyl)(trimethylsilyl)amine, hereafter referred to as the **NTMS** monomer, is prepared by deprotonation/silylation of commercially available divinyltetramethyldisilazane (eq. 2). Obtaining this monomer free from siloxanes is not difficult, since the starting disilazane is available in highly pure form, and the alkaline reaction conditions are not conducive to siloxane formation. This monomer is a solid and is easily purified by sublimation. It is stable to exposure to atmospheric moisture over

long periods of time (although it was stored under nitrogen for the purposes of these studies).

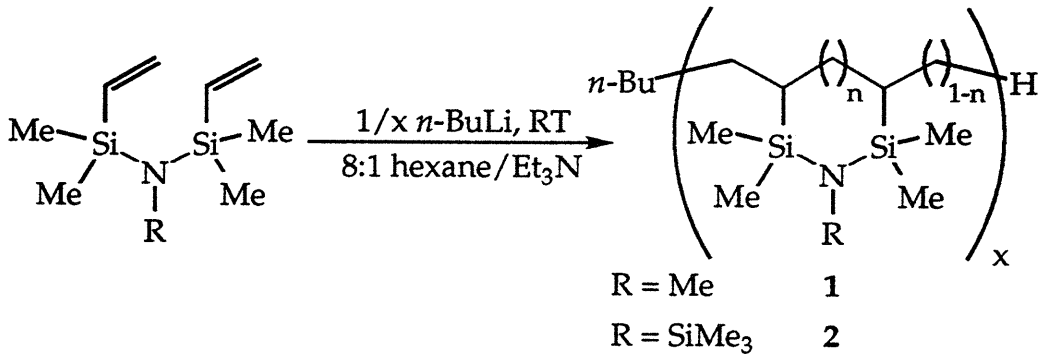


(2)

Preparation and Analysis of Cyclopolymers

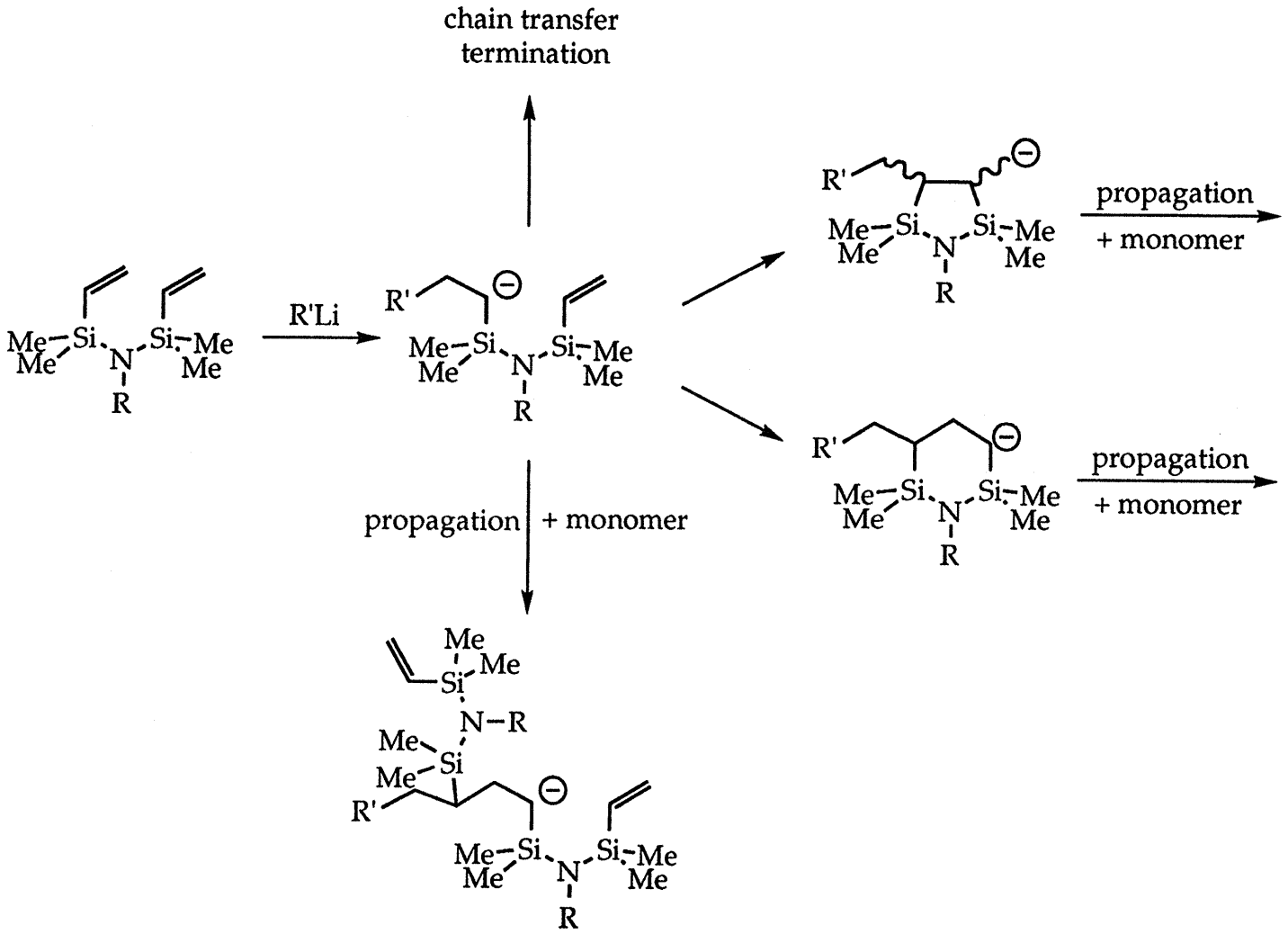
Synthesis

Stober, Michael and Speier reported the **NMe** monomer formed only insoluble, cross-linked polymers when polymerized with *n*-BuLi in hydrocarbon solvent; when triethylamine cosolvent was added, however, soluble polymers were obtained.[42] In light of this, polymerizations of the **NMe** and **NTMS** monomers were carried out in an 8 : 1 mixture of hexane and triethylamine using *n*-BuLi as initiator (eq. 3). The high sensitivity of these reactions to moisture and air required all solvents to be vacuum-transferred from *n*-BuLi directly into the reaction vessel. Reactions were carried out under an argon atmosphere at a concentration of approximately 1.1 M at ambient temperature for 3 -5 days. After completion of the reaction, solvents and unreacted monomer were removed *in vacuo* to give the products in good yields as white solids which were purified by precipitation from toluene/methanol. The resulting white powders were very soluble in common organic solvents such as hexane and ethers.



(3)

Several reaction pathways are available in the anionic cyclopolymerization of the **NMe** and **NTMS** monomers. As shown in Scheme 2, the reaction of monomer with alkyllithium initiator or growing polymer chain end (R'Li) likely occurs at the terminal position of the vinyl group, yielding a stabilized carbanionic intermediate.[44] The intramolecular reaction of this intermediate with the second vinylsilyl moiety in either an endo or exo fashion leads to the formation of six- and five-membered ring repeat units, respectively, which can then go on and further propagate the chain. Two other pathways for the acyclic intermediate are also feasible, termination/chain transfer or intermolecular reaction with a second monomer unit. Lithium hydride elimination from the active chain end is one possible termination reaction that has been observed in reactions of vinylsilanes with stoichiometric[66] and catalytic[49,52,55,58,60,61] quantities of alkyllithiums. Reaction of the active chain end with the Si-N bond of either a molecule of monomer or a repeat unit of another polymer molecule would also terminate chain propagation; this reaction, however, has not been observed in other anionic polymerizations of silylamines.[42] Chain transfer, via LiH-elimination or direct metallation of a second polymer chain by the growing chain end, can also be envisioned.[49] Intermolecular reaction of the uncyclized intermediate in Scheme 2 with a second monomer unit would



Scheme 2. Possible Reaction Pathways in the Anionic Cyclopolymerization of Silicon-Containing Dienes.

incorporate a SiNSi linkage into the polymer backbone and leave a dangling vinyl group capable of forming cross-links with other growing polymer chains. The presence of either termination and/or linear propagation pathways should lead to broadened molecular weight distributions in the final product.

Results of the polymerizations of the **NMe** and **NTMS** monomers carried out with different monomer/initiator ratios are compiled in Table 1. The polymerization of the **NMe** monomer to **1a** and **1b** was observed to terminate prior to complete conversion of monomer, with consumption of monomer decreasing with lower amounts of initiator used. Exhaustive distillation of the monomer and its vacuum-transfer from dibutylmagnesium directly into the reaction vessel did not result in any improvement in yield, nor did increasing the reaction time beyond three days. In contrast, the **NTMS** monomer quantitatively polymerized at a variety of monomer/initiator ratios over three days to give polymers **2a - d** in high isolated yields.

Analysis of polymers **1** and **2** by gel-permeation chromatography (GPC) revealed relatively narrow, monomodal distributions (Table 1). Molecular weight distributions of polymer **1** were somewhat more diffuse than those of **2** and broadened with increasing monomer/initiator ratio (from 1.51 for **1a** to 2.03 for **1b**). Molecular weights of **1** increased only slightly upon decreasing the amount of initiator, due to lower monomer conversion as a result of termination reactions. The monomodal distribution and absence of higher MW fractions in the GPC trace of **1** argue against the presence of cross-linking reactions in the polymerization of the **NMe** monomer.

The polydispersities of polymers **2a - d** ranged from 1.08 to 1.20, with no dependence on the monomer/initiator ratio. Molecular weights increased

Table 1. Polymerizations of the **NMe** and **NTMS** Monomers in Hexane/Triethylamine Solvent Mixtures

Monomer	*n*-BuLi (mol %)	Polymer	Yield	M_n[a]	M_w[a]	M_w/M_n[a]	Notebook Reference
NMe	10	**1a**	87[b]	4570[b]	6870[b]	1.51[b]	SWK II/64, III/11, VI/38a, VI/38b
NMe	5	**1b**	53[c]	5060[c]	10100[c]	2.03[c]	SWK II/67, III/1
NTMS	10	**2a**	92	6330	6940	1.10	SWK II/71
NTMS	5	**2b**	96[d]	9440[d]	10800[d]	1.14[d]	SWK II/75, IV/61, VI/51a
NTMS	4	**2c**	97[c]	10600[c]	11400[c]	1.08[c]	SWK V/6, VI/2a
NTMS	2.2	**2d**	99	15000	17900	1.20	SWK VI/15

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

monotonically with increasing monomer/initiator ratios, suggesting rates of cyclization and propagation for the **NTMS** monomer much greater than the rates of termination and cross-linking.

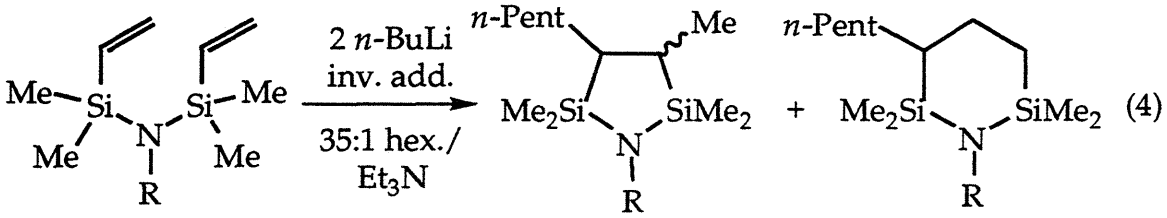
Model Anionic Cyclization Studies

Effects arising from the great size and inherent disorder of polymer chains often complicate the precise characterization of their microstructures by spectroscopic and other instrumental techniques.[67] For this reason, small molecules, which are simple to isolate and characterize, are often used to model the chemical and spectroscopic properties of structures found in the polymer of interest. For cyclopolymers, model cyclization reactions provide insight into the nature of cyclic units in the polymer backbone; this can be difficult to determine based only on spectroscopic measurements on the polymer.[4] Saigo, et. al. recently employed a model radical cyclization reaction to aid in the determination of the structure of a poly(diallylsilane).[34] Radical cyclizations of bis(vinyldimethylsilyl) compounds, described in Chapter 1, provided useful information about the radical cyclopolymerization of these monomers.[40]

In the present study, a method was sought to test the reactivity of the **NMe** and **NTMS** monomers with alkyllithium reagents under conditions which would give easily isolable and characterizable monomolecular products. These reactions would directly model the initiation, cyclization and propagation steps of the cyclopolymerization process, and would thus assist in the determination of the types of ring structures incorporated into the cyclopolymer backbones and in the identification of possible termination and cross-linking reactions. Although anionic cyclizations of substituted alkenyllithiums have been studied for some time, the methods used to

generate the carbanionic intermediate (usually lithium-halogen exchange or transmetallation) do not involve the reaction of an α,ω-diene with an alkyllithium.[68-71] Therefore, a new methodology was devised for the model anionic cyclizations of the **NMe** and **NTMS** monomers.

Stoichiometric reactions of the **NMe** and **NTMS** monomers with *n*-BuLi were carried out under high-dilution conditions. Solutions of the two monomers were slowly added dropwise to dilute solutions of *n*-BuLi (2 molar equivalents) in 35:1 hexane/triethylamine solvent mixtures (eq. 4). These conditions were chosen to enhance the yield of monomolecular products by keeping the concentrations of unreacted monomer and *n*-BuLi/monomer adducts low relative to that of unreacted *n*-BuLi.



(4)

Despite these precautions, significant amounts of oligomerization occurred in the reactions of both of the monomers with excess *n*-BuLi. The desired monomolecular products **3** and **4** were obtained in low yields (14% and 11%, respectively) as colorless oils after separation from the nonvolatile oligomeric side-products by vacuum distillation. These oils gave the correct elemental analyses for monomolecular adducts of the monomers with one equivalent of *n*-butane, but were shown by GC/MS to consist of mixtures of isomers (three for product **3**, two for product **4**).

The low-resolution mass spectra of the three isomers of product **3** each exhibited a parent ion peak corresponding to the **NMe** monomer + C_4H_{10}; the mass spectra of two of the isomers were nearly identical but distinct from that of the third. The two isomers with similar mass spectra (**3a**) were separated from the third (**3b**) by means of preparative GC, and both fractions were fully characterized by multinuclear (^1H, ^{13}C DEPT and ^{29}Si) NMR spectroscopy. Careful analysis of these spectra and comparison with the mass and NMR spectra of products of the radical hydrosilylation-cyclization reactions of the **NMe** monomer (Chapter 1) identified the two isomers of **3a** as five-membered rings and the single isomer **3b** as a six-membered ring. The ratio of five- to six-membered rings was 1.3 : 1, and the two five-membered ring isomers (*cis* and *trans*) were present in a 1.5 : 1 ratio (the predominating stereoisomer was not identified).

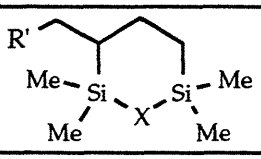
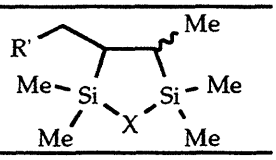
The two isomers of product **4** (present in a 1 : 1 ratio) gave nearly identical low-resolution mass spectra, with parent ions corresponding to the **NTMS** monomer + C_4H_{10}. Careful analysis of their ^1H, ^{13}C DEPT and ^{29}Si NMR spectra and comparison with the spectroscopic data of products of the radical hydrosilylation-cyclization reactions of the **NTMS** monomer (Chapter 1) confirmed these isomers were five-membered rings with *cis* and *trans* orientations of the *n*-pentyl and methyl ring substituents.

For the anionic cyclizations of both the **NMe** and **NTMS** monomers, the observed products were formed from an initial β-addition of *n*-BuLi to one of the monomer's vinyl groups followed by cyclization. No products arising from SiN bond cleavage by *n*-BuLi were observed, and only small amounts (< 5%) of compounds were detected in the GC/MS traces of **3** and **4** which possessed the correct masses for LiH-elimination products. These results suggest very regular microstructures for polymers **1** and **2**. The

backbone of polymer **1** most likely contains a mixture of five- and six-membered rings, and that of polymer **2** is probably constructed only of five-membered rings.

As shown in Table 2, the anionic and radical cyclization reactions of the **NMe** and **NTMS** monomers showed very similar regioselectivities (for radical cyclizations, see Chapter 1). For both types of cyclizations, the **NMe** monomer gives a mixture of five- and six-membered rings, and the **NTMS** monomer forms only five-membered rings (eq. 3). This behavior is similar to that of 5-hexen-1-yl carbanions and radicals, which also show similar regioselectivities of cyclization.[68,70,71]

Table 2. Product Ratios of Model Radical and Anionic Cyclizations.

Monomer (X)	Conditions	R'		
NMe	radical	*n*-Pr_3Si	29%	71%
NMe	radical	Et_3Si	23%	77%
NMe	anionic	*n*-Bu	44%	56%
NTMS	radical	*n*-Pr_3Si	-	100%
NTMS	anionic	*n*-Bu	-	100%

Spectroscopic Analysis of Polymer 1

In order to obtain more detailed information on its microstructure, polymer **1** was characterized by infrared (IR); ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, and its spectra compared to those of cyclic model compounds.

The IR spectrum of **1** provided only general structural information: the presence of $SiCH_3$, NCH_3 and aliphatic groups, and the absence of residual unsaturation. (IR assignments were based on those for the $(CH_3)_3SiN(CH_3)Si(CH_3)_3$ model compound[72,73] and other common organosilicon compounds.[74]) The ^1H NMR spectrum of **1** (Figure 2) was more informative. The absence of residual vinyl resonances (usually found in the 5.5 to 6.5 ppm region) and the presence of broad aliphatic signals (0.4 to 2.0 ppm) indicated that complete polymerization of the vinyl groups had taken place. The sharpness and complexity of the $SiCH_3$ signals (-0.2 to 0.2 ppm) provided evidence that the $SiCH_3$ groups were incorporated into cyclic backbone units (linear units would be expected to exhibit a broader, simpler signal). The spectrum of **1** also contained a broad singlet at 2.39 ppm arising from the NCH_3 group and sharper signals in the aliphatic region (at 0.87 and 1.2 ppm) assignable to the *n*-pentyl terminus of the polymer. The high relative intensity of the *n*-pentyl end-group resonances suggested that **1** had a fairly low degree of polymerization.

Analysis of the ^{13}C NMR spectrum of **1** (Figure 3a) was aided by comparison with the spectra of cyclic model compounds **3a** and **3b**. The $SiCH_3$ region of the spectrum of **1** (-5 to 0 ppm) consisted of five broad sets of resonances and resembled in its complexity, sharpness and range the $SiCH_3$ signals of superimposed spectra of **3a** and **3b**. For the model compounds, inequivalency of the $SiCH_3$ signals arises as a consequence of incorporation of the $Si(CH_3)_2$ groups into an asymmetrically substituted cyclic structure. The same reasoning would explain the appearance of the $SiCH_3$ region of the spectrum of polymer **1**.

The aliphatic region of the ^{13}C NMR spectrum of **1** consists of four sets of broad polymer backbone CH and CH_2 resonances in the region of 25 to 35

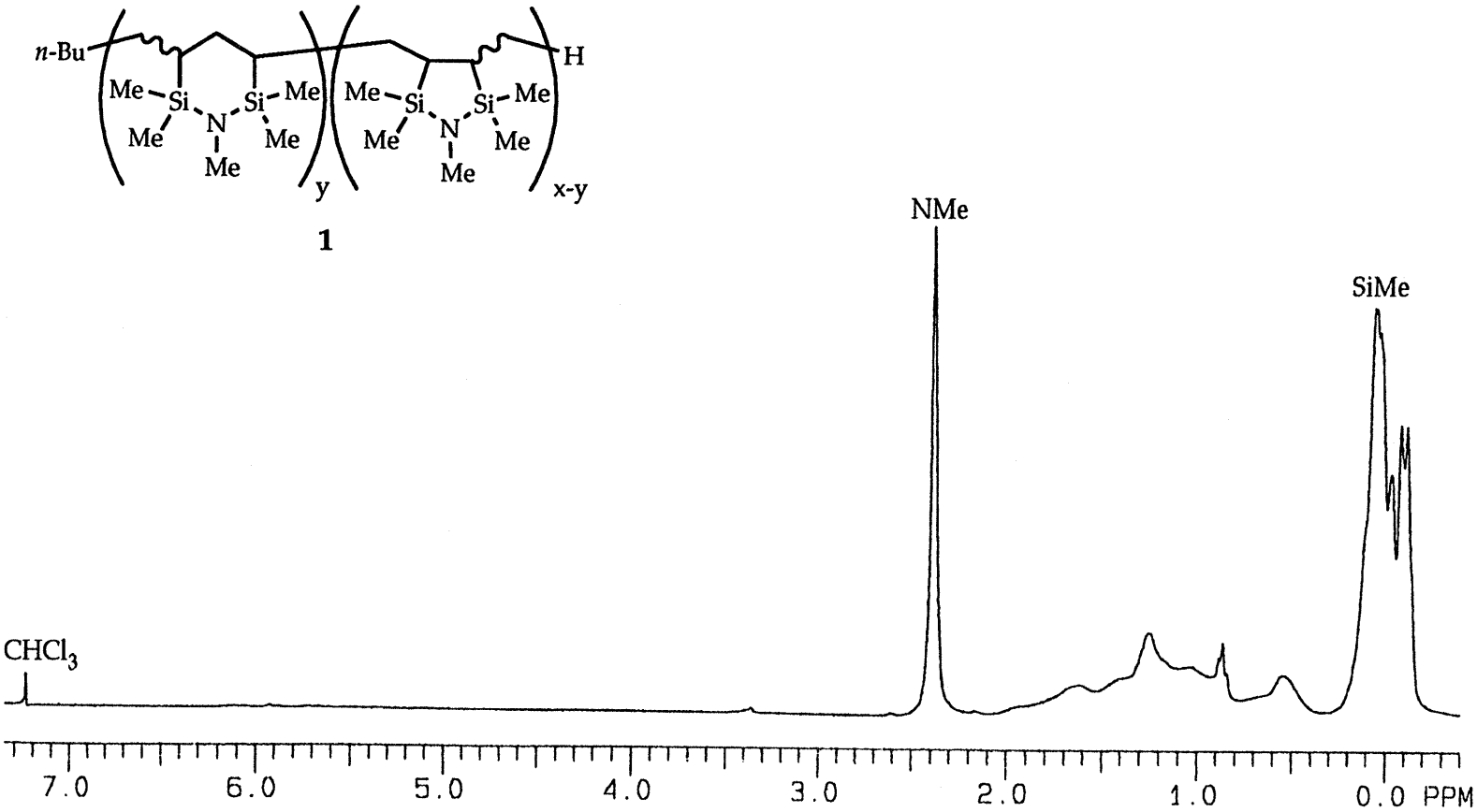


Figure 2. ^{1}H NMR Spectrum of Polymer **1**.

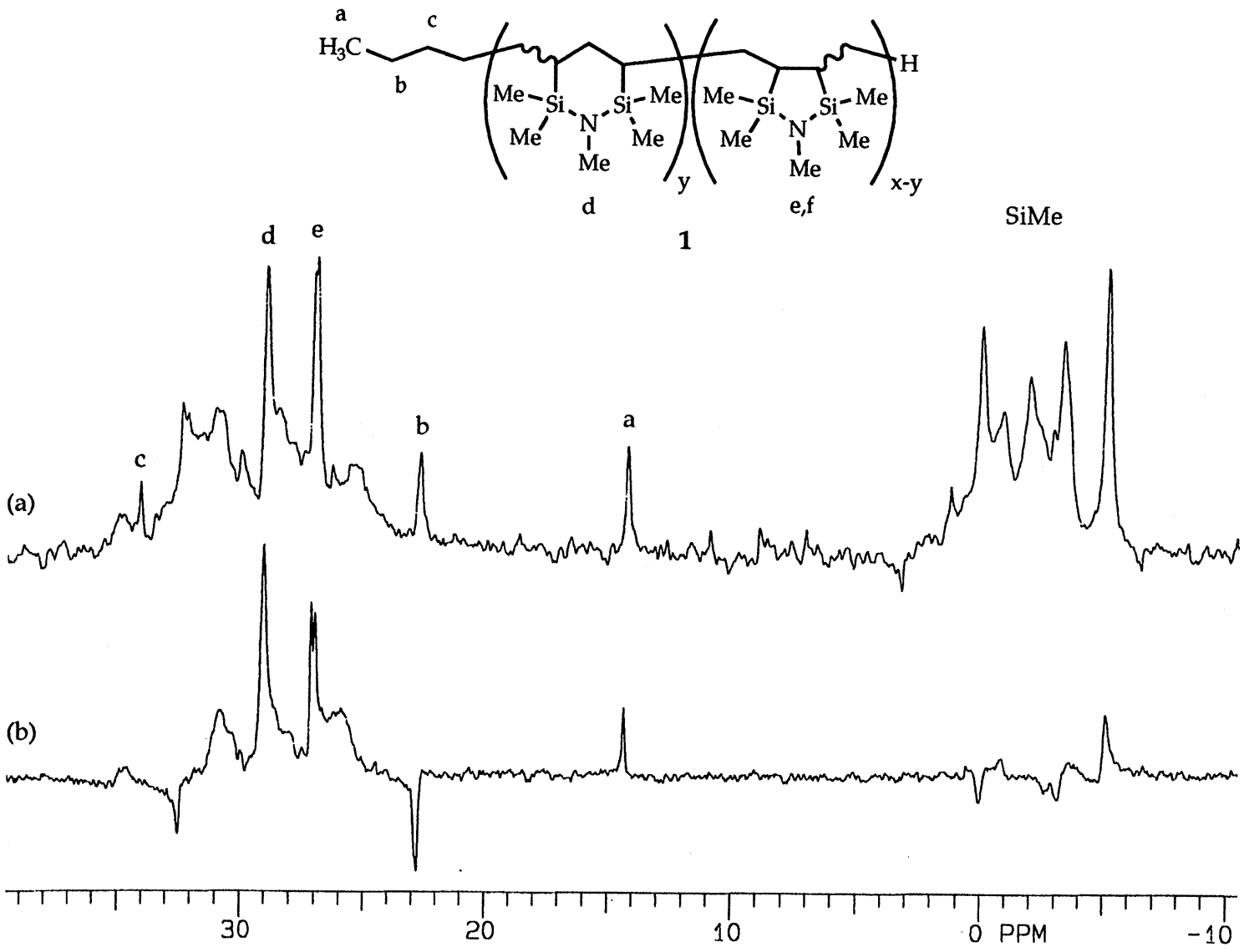


Figure 3. (a) ^{13}C and (b) ^{13}C DEPT (Mult = 1.5; CH, CH_3 up; CH_2 down) NMR Spectra of Polymer **1**

ppm and seven sharp resonances. A ^{13}C DEPT NMR spectrum of **1** (Figure 3b) assigned four of the sharp resonances (14.2, 26.91, 27.02 and 28.97 ppm) to CH_3 groups and the other three (22.6, 22.7 and 32.35 ppm) to CH_2 groups; assignment of the broad aliphatic resonances by this technique proved ambiguous. Four of the sharp aliphatic resonances (14.2, 22.6, 22.7 and 32.35 ppm) corresponded well to the signals for the terminal methyl carbons and the two adjacent methylene carbons of the *n*-pentyl groups in model compounds **3a** and **3b**. The three remaining methyl signals in the spectrum of **1** provided the most revealing information about the its structure. As shown in Figure 4, the chemical shifts of these three methyl signals are nearly identical to those of the NCH_3 resonances of model compounds **3a** and **3b**. Thus, all the evidence in the ^{13}C NMR spectrum of **1** points to a polymer consisting of both five-membered and six-membered cyclic repeat units.

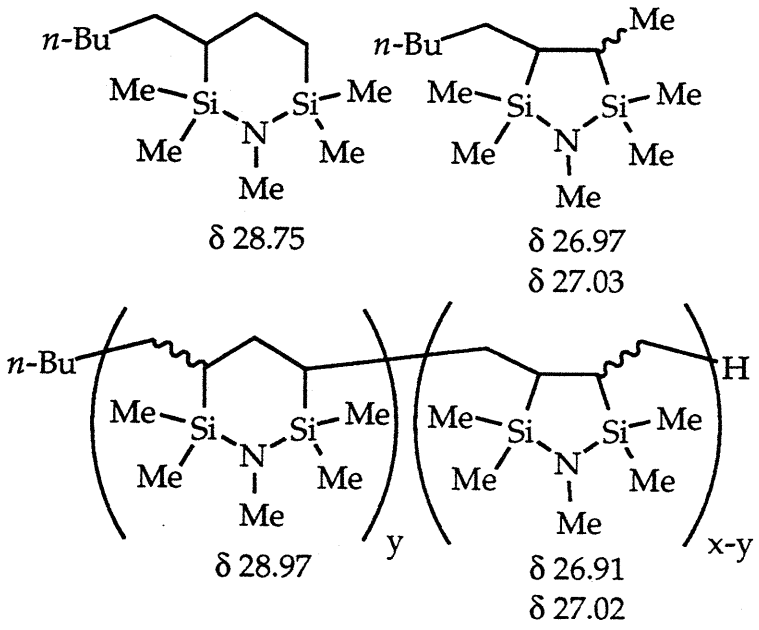


Figure 4. ^{13}C NMR NCH_3 Resonances of Polymer **1** and Model Compounds.

Chemical shifts of ^{29}Si NMR resonances for silicon atoms incorporated into cyclic structures are known to be very sensitive to the size of the ring.[75] Thus ^{29}Si NMR was expected to be a useful tool for the characterization of polymers **1** and **2**. The ^{29}Si NMR spectrum of **1** is presented along with the spectra of model compounds **3a** and **3b** in Figure 5. The spectrum of **1** consists of a broad singlet at 7.4 ppm and two broad overlapping signals at 13.7 and 14.1 ppm; the ratio of the integrated areas of the signals in the 7 and 14 ppm regions is 0.9 : 1. The 7.4 ppm resonance in the spectrum of **1** corresponds to the downfield resonance (6.82 ppm) of six-membered cyclic compound **3b**. The silicon atom associated with this resonance is located adjacent to the alkyl ring substituent in **3b**, and thus experiences a magnetic environment similar to that of the silicon atoms in the proposed structure of polymer **1**.

The chemical shifts of the two resonances near 14 ppm in the spectrum of **1** occur in the same region as those of the two five-membered ring model compounds **3a**. The *cis* and *trans* isomers of **3a** exhibit different chemical shifts for both of their silicon resonances. The fact that there are also two five-membered ring resonances in the spectrum of **1** is best explained by the presence of *cis* and *trans* isomers in the polymer backbone. Taken together, the ^{29}Si NMR results corroborate those of the ^{13}C NMR investigation and the model cyclization reactions in showing that polymer **1** consists of both five- and six-membered ring repeating units.

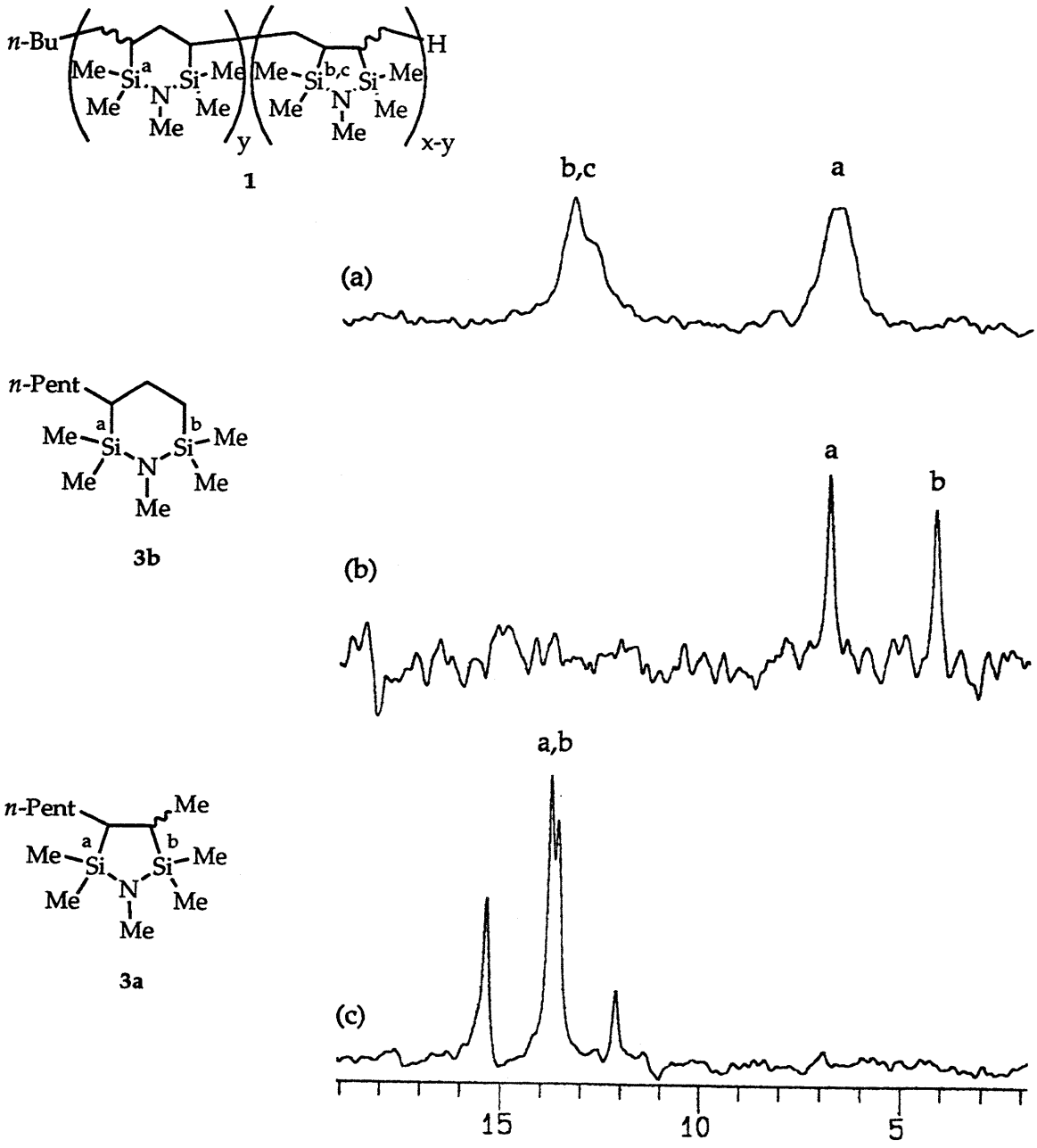


Figure 5. ^{29}Si NMR Spectra of (a) Polymer **1**, (b) Compound **3b** and (c) Compound **3a**.

Spectroscopic Analysis of Polymer 2

The spectroscopic properties of polymer **2**, except for the intensities of endgroup signals, were essentially independent of molecular weight. The IR spectrum of polymer **2** is simpler than that of polymer **1** due to the lack of NCH_3 vibrations. (IR assignments were based on those for the $((CH_3)_3Si)_3N$ model compound[73] and other common organosilicon compounds.[74]) The ^1H NMR spectrum of **2** (Figure 6) was also simpler than that of **1**. The $SiCH_3$ region only extended from 0 to 0.2 ppm (vs. -0.2 to 0.2 ppm for **1**) and contained two $Si(CH_3)_2$ signals (vs. three for **1**) in addition to a sharp, intense singlet at 0.087 ppm assigned to the $NSi(CH_3)_3$ group. The aliphatic region of **2** had an appearance very similar to that of **1**, except that the *n*-pentyl endgroup resonances at 0.87 and 1.24 ppm were less pronounced in the spectrum of **2** (this was true even for **2a** which had a monomer/initiator ratio comparable to that of **1**). Like **1**, polymer **2** had no residual vinyl groups in its ^1H NMR spectrum.

The ^{13}C NMR spectrum of **2** is shown in Figure 7. The $SiCH_3$ region (from 0 to 5 ppm) is shifted 5 ppm downfield from that of **1**. It contains a strong $Si(CH_3)_3$ resonance at 3.75 ppm and four smaller $Si(CH_3)_2$ resonances. There is a good correspondence between the chemical shifts of the $SiCH_3$ resonances of **2** and those of model compound **4**. As was explained for polymer **1**, the existence of multiple, sharp $Si(CH_3)_2$ signals supports the idea of a cyclic repeat unit in the polymer.

The aliphatic region of the ^{13}C NMR spectrum of **2** is considerably simpler than that of **1**. Three relatively sharp resonances at 14.2, 22.6 and 32.3 ppm are assigned to the terminal methyl group and adjacent methylene carbon atoms, respectively, of the *n*-pentyl terminus of the polymer; these signals are of much lower relative intensity in the spectrum of **2** than in the

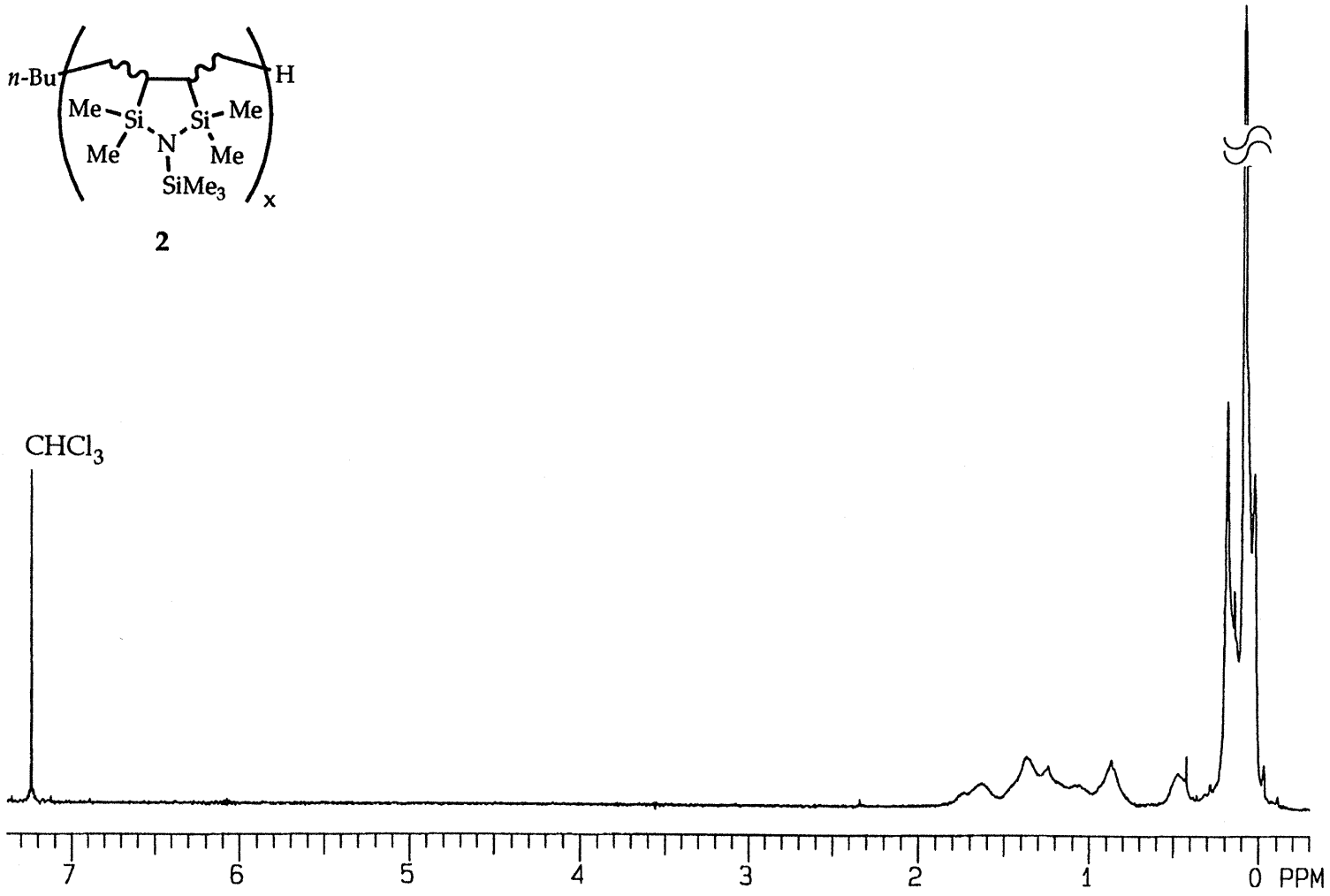


Figure 6. ^{1}H NMR Spectrum of Polymer **2**.

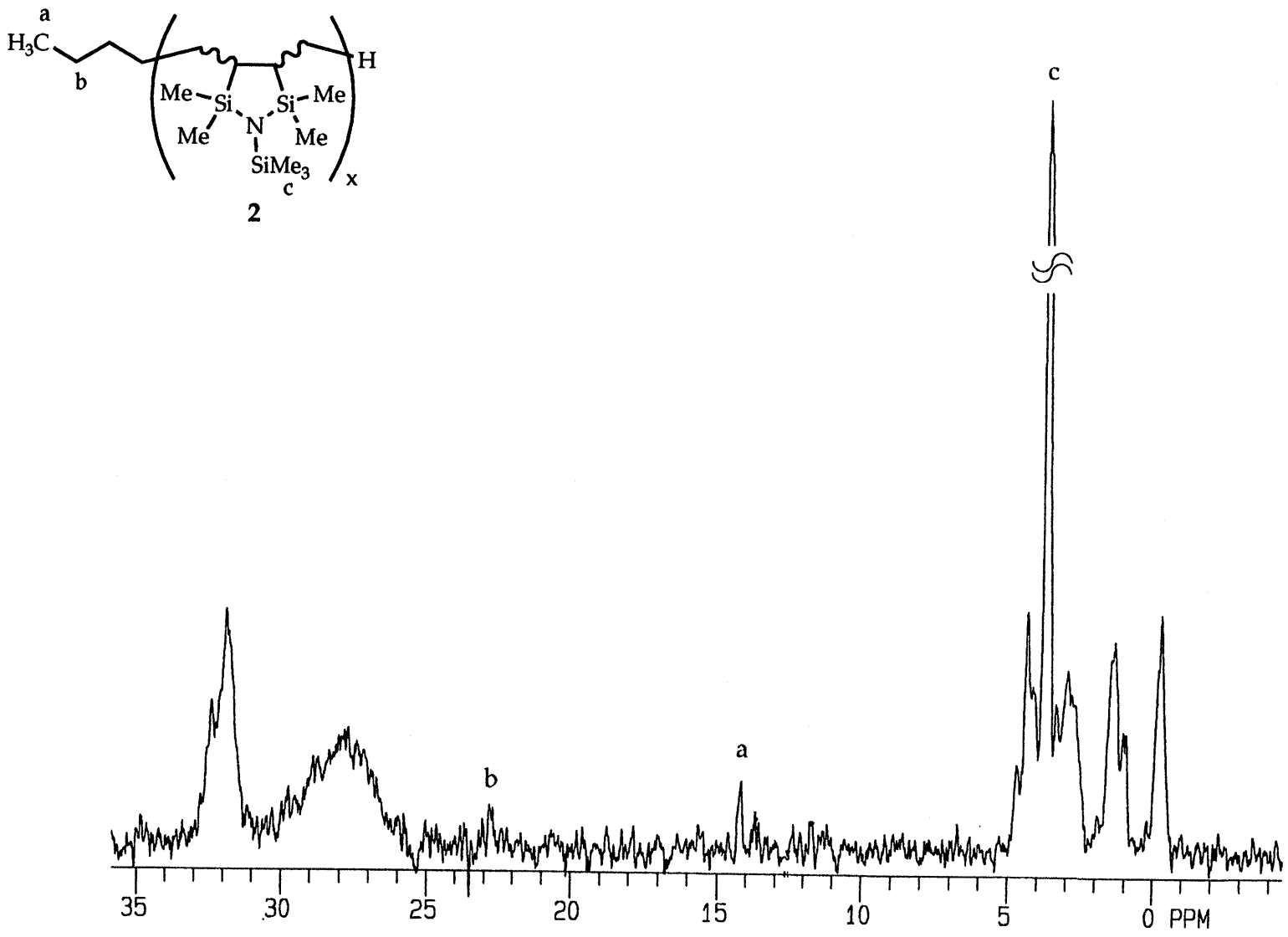


Figure 7. ^{13}C NMR Spectrum of Polymer **2**.

spectrum of **1**. The aliphatic backbone resonances of **2** are much simpler than those of **1**, reflecting the more regular structure of polymer **2**. A very broad ($\Delta\nu_{1/2} \approx 190$ Hz), rounded signal is centered at 28 ppm, and a sharper signal is found at 31.9 ppm. An attempt to assign these aliphatic resonances to either CH or CH_2 groups using a DEPT sequence failed. Instead, it is postulated that each of these signals contains both CH and CH_2 components, and represents either a *cis* or *trans* five-membered ring cyclic repeat unit. This hypothesis gains further support from spectroscopic studies of polymers prepared from the **NTMS** monomer in various co-solvent mixtures (*vide infra*).

The ^{29}Si NMR of polymer **2** (Figure 8a), like that of polymer **1**, exhibits two five-membered ring $Si(CH_3)_2$ resonances near 14 ppm. As these signals are better resolved in the spectrum of **2**, it can be seen that the higher field resonance is broader and less intense than the other, although the two appear roughly equal in area. Two additional sharp resonances of equal intensity (but half the integrated intensity of the signals at 14 ppm) are found near 0 ppm; these are assigned to exocyclic $Si(CH_3)_3$ groups for *cis* and *trans* five-membered ring repeat units. The excellent agreement between the spectra of polymer **2** (Figure 8a) and model compound **4** (Figure 8b) lends strong support to the structural model of polymer **2** consisting of linked five-membered cyclic units.

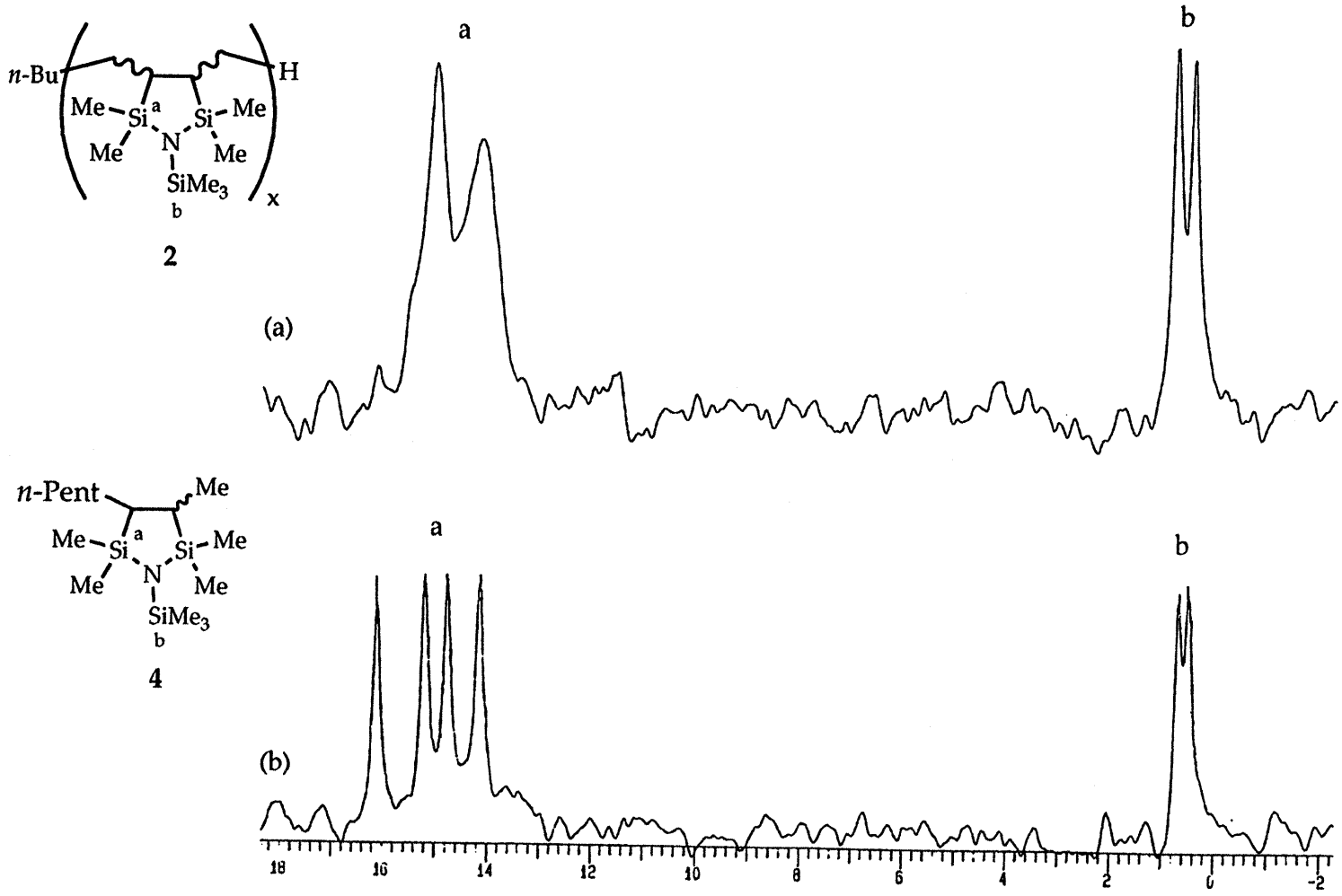


Figure 8. ^{29}Si NMR Spectra of (a) Polymer **2** and (b) Compound **4**.

Comparison of Cyclopolymers of the ***NMe*** *Monomer Prepared by Anionic and Radical Methods*

In a previous study, the **NMe** monomer was cyclopolymerized under radical conditions using 2.5 mol% di-*tert*-butylperoxide initiator.[39,40] A low molecular weight polymer was obtained (M_n = 1190) which contained ~3% unreacted vinyl groups. This polymer was much less regular than **1**, and exhibited very broad signals in its NMR spectra that overall provided little structural information; however, in two cases useful comparisons can be made. The ^{13}C NMR spectrum of the radically formed polymer contained three NCH_3 resonances at 27.04, 28.55 and 28.70 ppm; the first and last resonances correspond to those observed for five- and six-membered rings, respectively, in polymer **1** (see Figure 4). The middle resonance may have arisen from linear units or seven-membered rings. The ^{29}Si NMR spectrum of the radically generated cyclopolymer contained two very broad signals ranging from 0 to 9 and 11 to 18 ppm. The former signal is centered about the six-membered ring signal of polymer **1** (Figure 5a), and the latter about the five-membered ring signal. Thus, it appears that both radical and anionic initiation produce cyclopolymers from the **NMe** monomer that contain five- and six-membered rings, although the anionically generated cyclopolymer possesses a higher molecular weight and a much more regular microstructure.

Co-solvent Dependence in the Polymerization of the ***NTMS*** *Monomer*

Various aspects of the mechanisms of many anionic polymerization reactions, including the rates of initiation and propagation and the regio- and stereoselectivities of anion addition to monomer, have been found to be highly solvent-dependent.[76] The anionic polymerization of the **NMe**

monomer showed a strong dependence on solvent: the reaction in hexane alone gave insoluble, cross-linked gels, but the reaction in hexane with triethylamine co-solvent led to soluble polymers with a high degree of cyclized units.[42] Since the **NTMS** monomer also formed soluble polymers when anionically polymerized in a hexane/triethylamine solvent mixture, it was of interest to see how its polymerization behavior changed in the absence of co-solvent and using THF in place of triethylamine as co-solvent.

The *n*-BuLi-initiated polymerization of the **NTMS** monomer in hexane alone and in an 8 : 1 mixture of hexane and THF gave polymers **2e** and **2f**, respectively, as white solids. While the reaction in hexane was quantitative after three days, the reaction in THF gave only 95% conversion of monomer in the same period of time (Table 3). Analysis by GPC showed narrow monomodal molecular weight distributions. The molecular weights of polymers **2e** and **2f** differed somewhat from that of **2b**, which was polymerized with triethylamine co-solvent using a similar monomer/initiator ratio. These differences in molecular weight may reflect different degrees of unutilized initiator depending on the reaction solvent. Due to their high propensity for aggregation, alkyllithium initiators often are not completely consumed during anionic polymerizations in hydrocarbon media.[76] For example, in the *n*-BuLi-initiated polymerization of isoprene carried out in cyclohexane, fully 40% of the initiator remains unreacted at completion of the polymerization. The addition of small amounts of ether or amine co-solvents breaks up these aggregates and facilitates consumption of initiator. Thus, the variations in molecular weight of polymers **2b**, **2e** and **2f** may indicate that significant amounts of initiator remain in an unreactive, aggregated state during the polymerization of the **NTMS** monomer, and that triethylamine and THF disrupt these aggregates, freeing more initiator to

react with monomer; this disruption is more effective when the reaction is carried out in an 8 : 1 hexane/THF mixture than in an 8 : 1 hexane/triethylamine mixture (perhaps simply due to the greater molar concentration of coordinating solvent molecules in the THF case). The incomplete consumption of monomer observed in the hexane/THF solvent mixture most likely reflects a termination reaction of the growing chain end with a molecule of THF; such reactions are known to occur during anionic polymerizations in this solvent at room temperature.[77]

Table 3. Effect of Solvent on Polymerizations of the **NTMS** Monomer with 5 mol% *n*-BuLi.

Solvent System	Polymer	Yield	M_n[a]	M_w[a]	M_w/M_n[a]	Notebook Reference
hexane/ Et_3N	**2b**	96[b]	9440[b]	10800[b]	1.14[b]	SWK II/75, IV/61, VI/51a
hexane	**2e**	99[c]	11500[c]	12900[c]	1.12[c]	SWK VI/16, VI/37
hexane/ THF	**2f**	97[d]	6260	7740	1.24	SWK VI/19

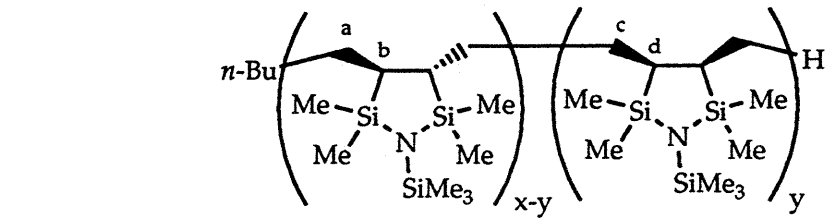
[a] Determined by gel permeation chromatography (GPC) relative to polystyrene standards.
[b] Average of three experiments.
[c] Average of two experiments.
[d] Only 95% of monomer was consumed.

To determine if reaction solvent affected the microstructures of the polymers formed from the **NTMS** monomer, polymers **2e** and **2f** were fully spectroscopically characterized. The IR and ^1H NMR spectra of polymers **2e**

and **2f** were essentially identical to those of **2b**. The ^{13}C NMR spectra of **2b**, **2e** and **2f** also appeared at first glance to be the same. However, closer examination of the aliphatic regions (Figure 9) revealed dramatic changes in the ratio of the intensities of the sharp and broad aliphatic backbone resonances at 31.9 and 28 ppm, respectively. This ratio was nearly twice as large in the spectrum of polymer **2e** as it was in the spectrum of polymer **2b**; for polymer **2f**, this ratio was 40% smaller than it was for polymer **2b**.

The ^{29}Si NMR spectra of polymers **2b**, **2e** and **2f** (Figure 10) exhibited a congruent trend in the intensities of the sharp endocyclic silicon resonance at 14.7 ppm and its corresponding exocyclic $Si(CH_3)_3$ resonance at 0.2 ppm vs. those of the broad endocyclic silicon resonance at 14.0 ppm and its corresponding exocyclic resonance at 0.5 ppm. Polymer **2e**, which exhibited a higher intensity for the sharp aliphatic backbone signal in its ^{13}C NMR spectrum, showed higher intensities for the sharp endocyclic silicon signal and its corresponding $Si(CH_3)_3$ signal in its ^{29}Si NMR spectrum. Conversely, polymer **2f**, which had a lower intensity for the sharp aliphatic backbone signal in its ^{13}C NMR spectrum, displayed lower intensities for this pair of resonances.

These interesting solvent effects in the polymerization of the **NTMS** monomer aid in the interpretation of the ^{13}C and ^{29}Si NMR spectra of polymer **2**. The correlated changes in the intensities of the ^{13}C NMR aliphatic backbone resonances and the ^{29}Si NMR resonances suggest that the stereoselectivity of the cyclization step in the polymerization reaction is solvent dependent. Each set of ^{13}C and ^{29}Si NMR resonances represents one of the two possible (*cis* or *trans*) isomers. By comparing the ^{13}C NMR resonances of the polymer with those of disubstituted five-membered ring model compounds (Figure 11), the two aliphatic backbone resonances, and



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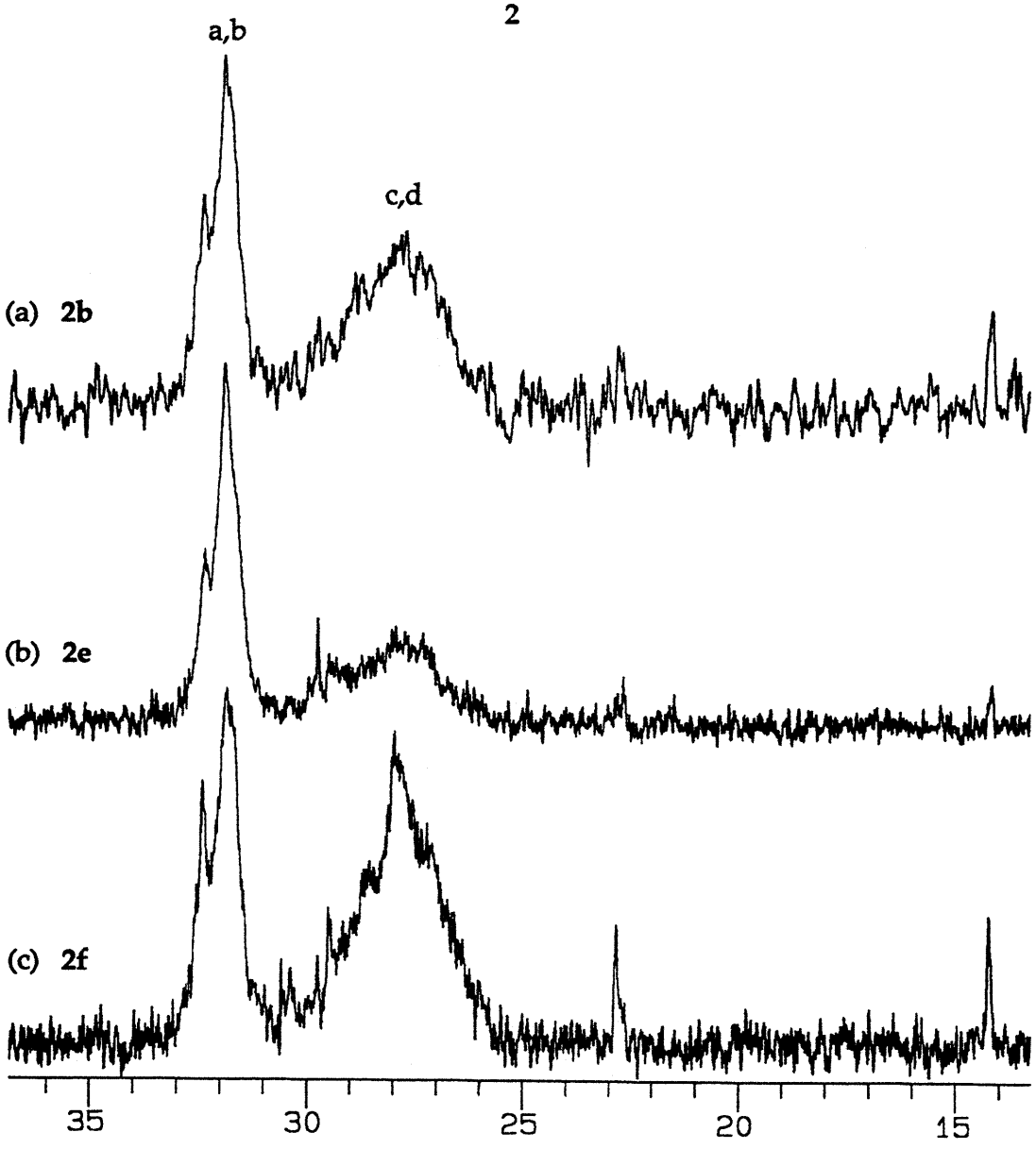
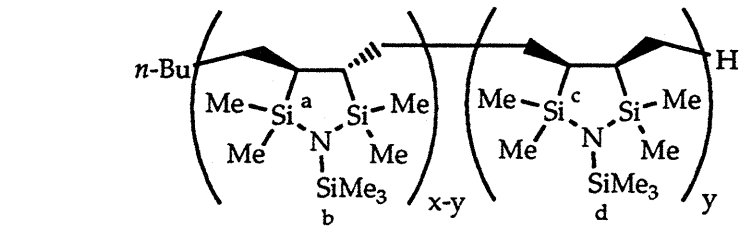


Figure 9. Aliphatic Region of ^{13}C NMR Spectra of Polymers (a) **2b**, (b) **2e** and (c) **2f**.



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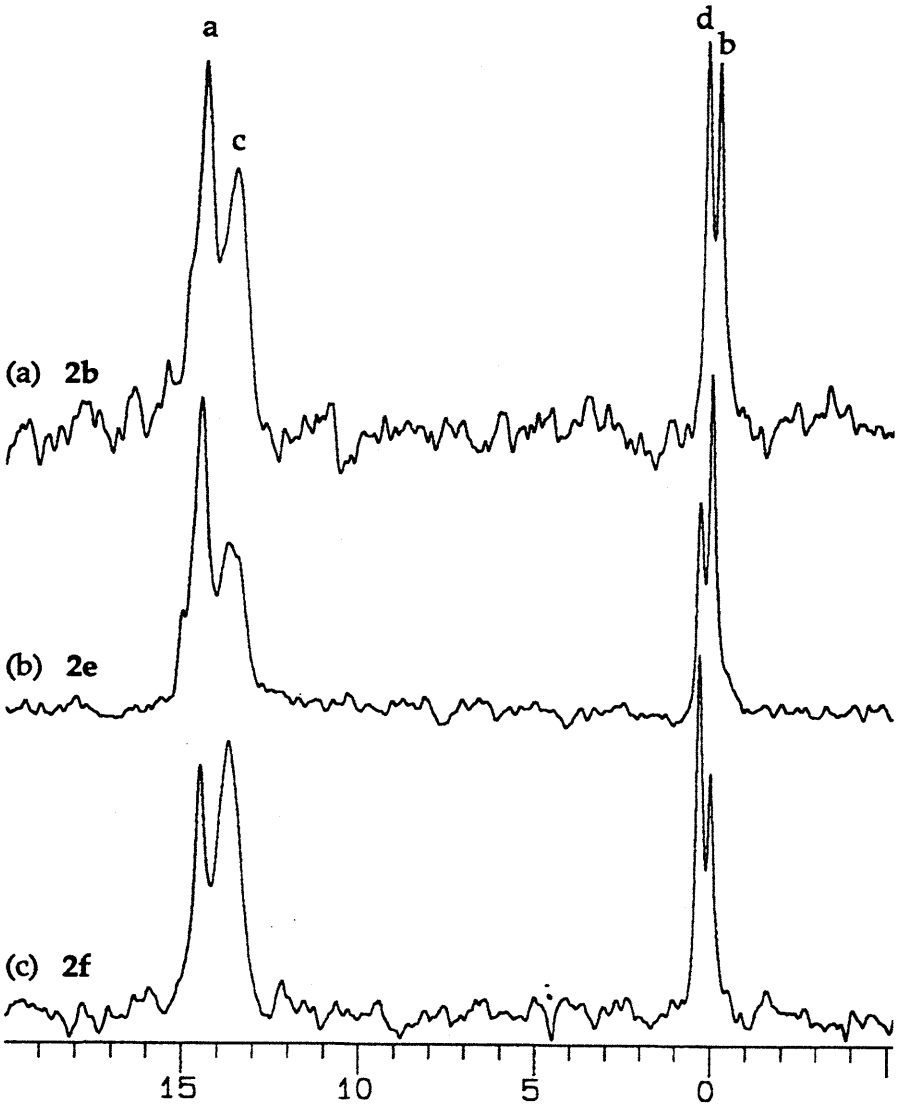


Figure 10. ^{29}Si NMR Spectra of Polymers (a) **2b**, (b) **2e** and (c) **2f**.

hence their corresponding ^{29}Si NMR resonances, can be assigned directly to *cis* or *trans* isomers.

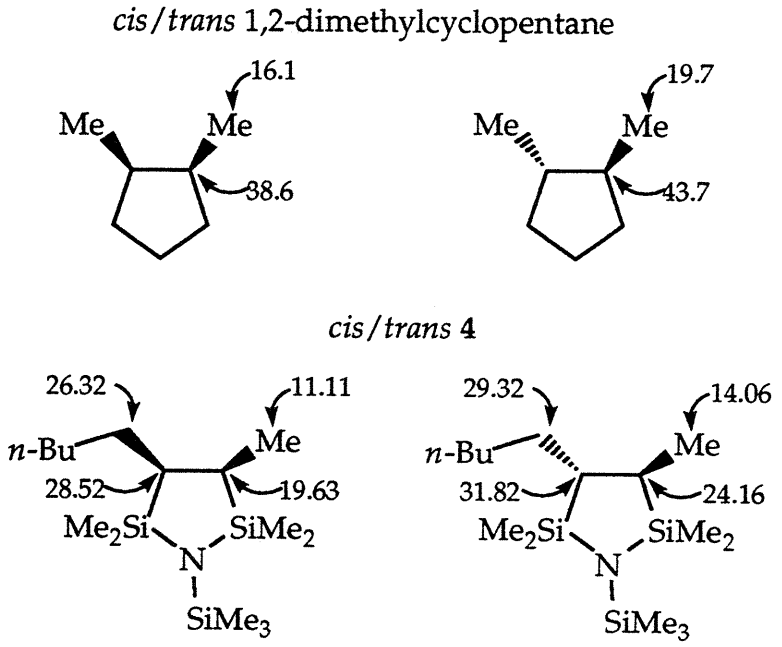


Figure 11. Chemical Shifts of *Cis* and *Trans* Disubstituted Five-Membered Ring Model Compounds. (1,2-Dimethylcyclopentane chemical shifts from reference 78)

For both sets of model compounds in Figure 11, the ^{13}C NMR resonances of the methine carbons and the α-carbons of the exocyclic substituents are shifted 3 - 5 ppm downfield for the *trans* isomer relative to the *cis;* this is also the splitting found between the two aliphatic backbone signals of polymer **2** (3.9 ppm). In addition there is a good agreement between the chemical shifts of the methine carbons of *cis* and *trans* **4** (28.52 and 31.82 ppm, respectively) and the chemical shifts of the two backbone resonances of **2** (28 and 31.9 ppm). Thus, the broad (28 ppm) and sharp (31.9 ppm) aliphatic

resonances are assigned, respectively, to *cis* and *trans* five-membered ring backbone units in polymer **2**.

As was stated previously, the two aliphatic backbone signals are each expected to be comprised of both CH and CH_2 resonances. The α-methylene carbon atoms of the *n*-pentyl substituents of *cis* and *trans* **4** resonate at 26.32 and 29.32 ppm, respectively, approximately 2 ppm upfield from the broad and sharp aliphatic resonances of polymer **2**. This discrepancy can be attributed to differences in shielding caused by incorporation of the α-methylene carbon into the polymer backbone (rather than in an *n*-pentyl chain) where it is γ to a second Si atom in the adjacent monomer unit. Silyl substituents tend to exert stronger deshielding effects on γ-carbons than do all-carbon substituents; for example, the methyl group of the tripropylsilyl substituent (see Chapter 1) resonates approximately 5 ppm downfield from the methyl resonance of pentane and higher linear hydrocarbons.[78].

The preceding arguments closely parallel those used to assign the structure of poly(diallyldimethylammonium) chloride employing ^{13}C NMR spectroscopy.[79] This polymer, like **2**, is proposed to consist entirely of *cis* and *trans* 1,2-disubstituted five-membered rings linked by ethylene units. The methine and α-methylene ring substituent carbon resonances of this polymer are shifted 3.7 - 5 ppm downfield for the *trans* isomers relative to the *cis*, exactly the trend observed for the shifts of the analogous carbon atoms of polymer **2**.

The assignments of the ^{29}Si NMR resonances of polymer **2** can be made based on the previously established correlations to the ^{13}C NMR resonances. Thus, the pair of resonances at 0.5 and 14.0 ppm are assigned to *cis* five-membered ring repeat units, and the pair of resonances at 0.2 and 14.7 ppm are assigned to *trans* ring structures.

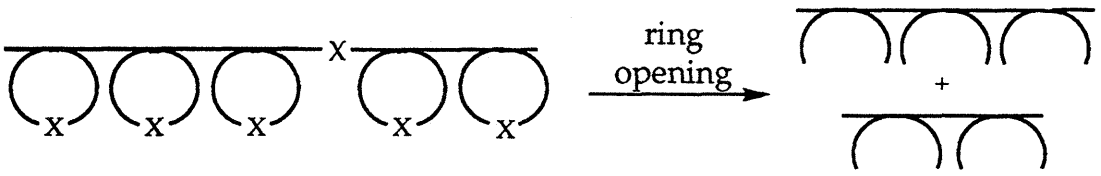
With the spectroscopic data now systematically assigned to *cis* and *trans* repeat units, the stereoselectivity of the cyclization reaction can be discussed in greater detail. When the polymerization is carried out in hexane with no coordinating co-solvent, the cyclization step favors formation of a five-membered ring with a *trans* orientation of the polymer chain and the newly formed exocyclic methylene anion (see Scheme 2). Addition of coordinating co-solvents triethylamine and THF favors formation of the *cis* repeat unit; the *cis* selectivity is greater in the THF case than in the triethylamine case. This changing selectivity is most easily seen in the changing heights of the two exocyclic $SiMe_3$ signals in the ^{29}Si NMR (Figure 10). 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. The difference in *cis* selectivities observed between reactions carried out with THF and triethylamine co-solvents may be a factor of the differing molar concentrations of the two co-solvents or may reflect something more fundamental about the types of complexes they form with organolithium compounds.

Polymer Derivatization Studies

Ring-Opening Reactions of Polymers **1** *and* **2** *with HF(aq)*

Chemical degradation studies historically have played a significant role in establishing the cyclopolymerization mechanism of dienes.[4] By incorporating a functional group into the monomer which can be selectively cleaved subsequent to polymerization, the presence of ring structures in the polymer backbone can be established by comparing the molecular weight distributions of the polymer before and after the cleavage reaction (Scheme 3). Any linear units in the polymer backbone will be cleaved by the ring-opening

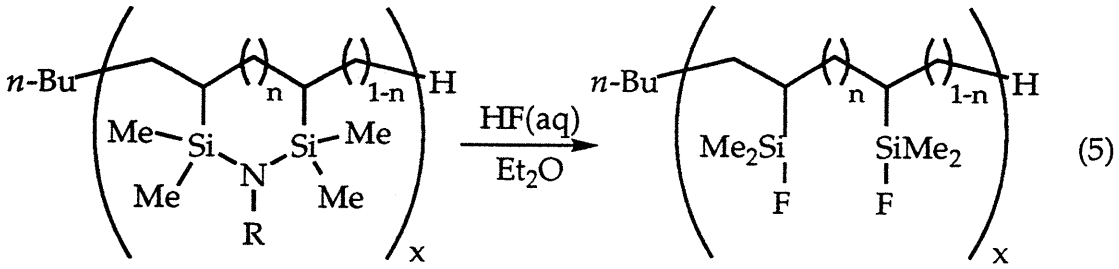
reaction, resulting in dramatic drops in M_w and M_n values and significant broadening of the molecular weight distribution (reflected in an increased M_w/M_n value). However, even in the absence of backbone-cleaving reactions the apparent M_w and M_n values of the cyclopolymer (as measured by GPC) are expected to decrease significantly upon ring-opening due to the drop in hydrodynamic volume accompanying the transformation from cyclic to linear units in the polymer backbone. In this case, the M_w/M_n value should still provide a sensitive measure of the presence of linear fragments in the polymer backbone. Because any linear units would be expected to be randomly distributed throughout the polymer chain, their rupture during the ring opening reaction would drastically broaden the molecular weight distribution. Calculations by Berlin and Yenikolopyan showed that only 2% ruptures per polymer chain were sufficient to transform a monodisperse polymer ($M_w/M_n = 1$) to one with a most probable weight distribution ($M_w/M_n = 2$).[80]



Scheme 3. Backbone Degradation During Ring-Opening of Cyclopolymers.

In the present study, the Si-N-Si linkage in the cyclopolymers is known to be easily cleaved using Brønsted or Lewis acid reagents. Since these reagents are not expected to cleave C-C, C-H or aliphatic Si-C bonds to any appreciable degree, the ring-opening reactions of polymers **1** and **2** should proceed cleanly, facilitating interpretation of the results.[64] Aqueous HF was

chosen as the Brønsted acid reagent for the ring-opening reaction (eq. 5) since it is predicted to convert Si-N bonds quantitatively to moisture-stable Si-F bonds which are amenable to further functionalization with nucleophilic reagents.[64]

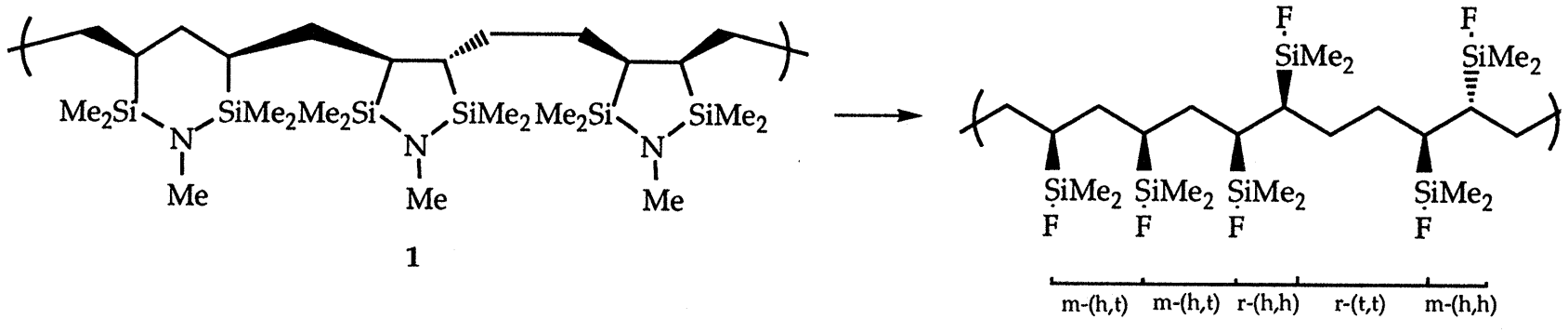


(5)

R = Me; n = 0, 1 **1** **5**

R = $SiMe_3$, n = 0 **2** **6**

When ethereal solutions of the cyclopolymers were added to mixtures of ether and an excess of aqueous HF, an exothermic reaction ensued. After brief stirring, the reaction was neutralized and the products **5** and **6** (arising from **1** and **2**, respectively) were isolated in good yields from the organic layer as analytically pure, clear, colorless viscous oils (Table 4). The poly(vinyldimethylfluorosilane) products of these reactions should contain, depending upon the parent polymer, differing connectivity of monomer units in the backbone (Scheme 4): polymer **5** is expected to consist of a complex mixture of head-to-head (h,h), tail-to-tail (t,t) and head-to-tail (h,t) monomer sequences (arising from the mixture of five- and six-membered rings in the parent polymer), and polymer **6** is expected to consist exclusively of alternating head-to-head (h,h) and tail-to-tail (t,t) sequences. The relative stereochemistry of the dimethylfluorosilyl substituents will be that fixed by the cyclization steps in the cyclopolymerization reactions. This is denoted in Scheme 4 using the Bovey mr stereochemical notation, where m represents



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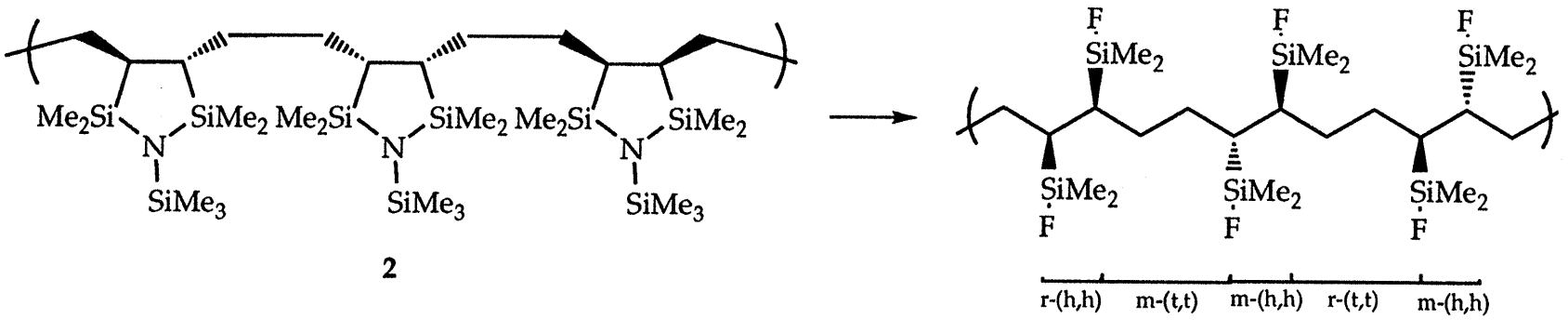

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6

Scheme 4. Relative Stereochemistry of Poly(vinyldimethylfluorosilanes) Prepared by Ring-Opening of Polymers **1** and **2** with HF (aq).

meso relative stereochemistry of two adjacent stereocenters, and r represents a racemic relationship.[67]

Table 4. Results of Ring-Opening Reactions of Polymers **1** and **2** with HF(aq).

Parent Polymer	Product	Yield	M_n[a] (Δ)[b]	M_w[a] (Δ)[b]	M_w/M_n[a] (Δ)[b]	Notebook Reference
1a	**5a**	89[c]	2890[c] (-1680)	5010[c] (-1860)	1.74[c] (+0.23)	SWK VI/47a, VI/47b
2a	**6a**	93	2250 (-4080)	2920 (-4020)	1.30 (+0.20)	SWK IV/39
2b	**6b**	89[c]	6910[c] (-2500)	7850[c] (-2950)	1.16[c] (+0.02)	SWK IV/72, VI/51b
2c	**6c**	89[c]	5770[c] (-4830)	6750[c] (-4650)	1.18[c] (+0.02)	SWK V/70, VI/2b
2d	**6d**	93	8680 (-6320)	9790 (-8110)	1.13 (-0.07)	SWK VI/39
2e	**6e**	82	5920 (-5580)	6630 (-6270)	1.12 (0)	SWK VI/29a
2f	**6f**	83	3780 (-2480)	4690 (-3050)	1.24 (0)	SWK VI/29b

[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.

As shown in Table 4, GPC analysis of these oils showed a drop in both M_n and M_w when compared to the parent polymers, consistent with the expected change in hydrodynamic volume upon conversion from cyclic to

linear repeat units. The high yields of these reactions and the relatively small change in polydispersity indices (M_w/M_n) suggest the absence of any backbone-cleaving reactions (and, hence, linear units) in the original polymers **1** and **2**.

Spectroscopic Analyses of Polymers 5 and 6

Polymers **5** and **6** were completely spectroscopically characterized. The infrared spectra of **5** and **6** were identical, and lacked the N-C, Si-N and NC-H vibrations found in the spectra of **1** and **2**. The ^{1}H NMR spectra of **5a** (Figure 12), **5b**, **6b** (Figure 13), **6e** and **6f** were also very similar to one another and greatly simplified compared to those of parent polymers **1** (Figure 2) and **2** (Figure 6). The spectrum of **5a** lacked the NMe resonance found at 2.39 ppm in the spectrum of **1**, and the spectra of **6b**, **6e** and **6f** lacked the intense $SiMe_3$ resonance found at 0.087 ppm in the spectrum of **2**, indicating complete reaction had occurred in all cases. In the product spectra, a broad $SiCH_3$ resonance replaced the multiple sharp $SiCH_3$ resonances in the parent polymer spectra, consistent with the change from a cyclic to a linear repeat unit upon ring-opening. The appearance of this resonance varied depending upon the microstructure of the parent polymer. The spectrum of **5a** possessed a large peak at 0.204 ppm with a shoulder at 0.227 ppm. The $SiCH_3$ region of the spectra of **6b**, **6e** and **6f** (Figure 14) exhibited three overlapping signals at 0.215, 0.236 and 0.255 ppm. The regular spacing of these three signals suggests they are actually two overlapped doublets ($^3J_{H\text{-}F} \approx 6$ Hz; cf. $^3J_{H\text{-}F} = 7.2$ Hz in Me_3SiF)[81] centered at 0.225 and 0.246 ppm; the former doublet is assigned to racemic head-to-head (r-(h,h)) arrangements of adjacent $SiMe_2F$ groups and the latter to m-(h,h) arrangements. Accordingly, the intensity of the former doublet relative to the latter increased in the order **6f** > **6b** > **6e**.

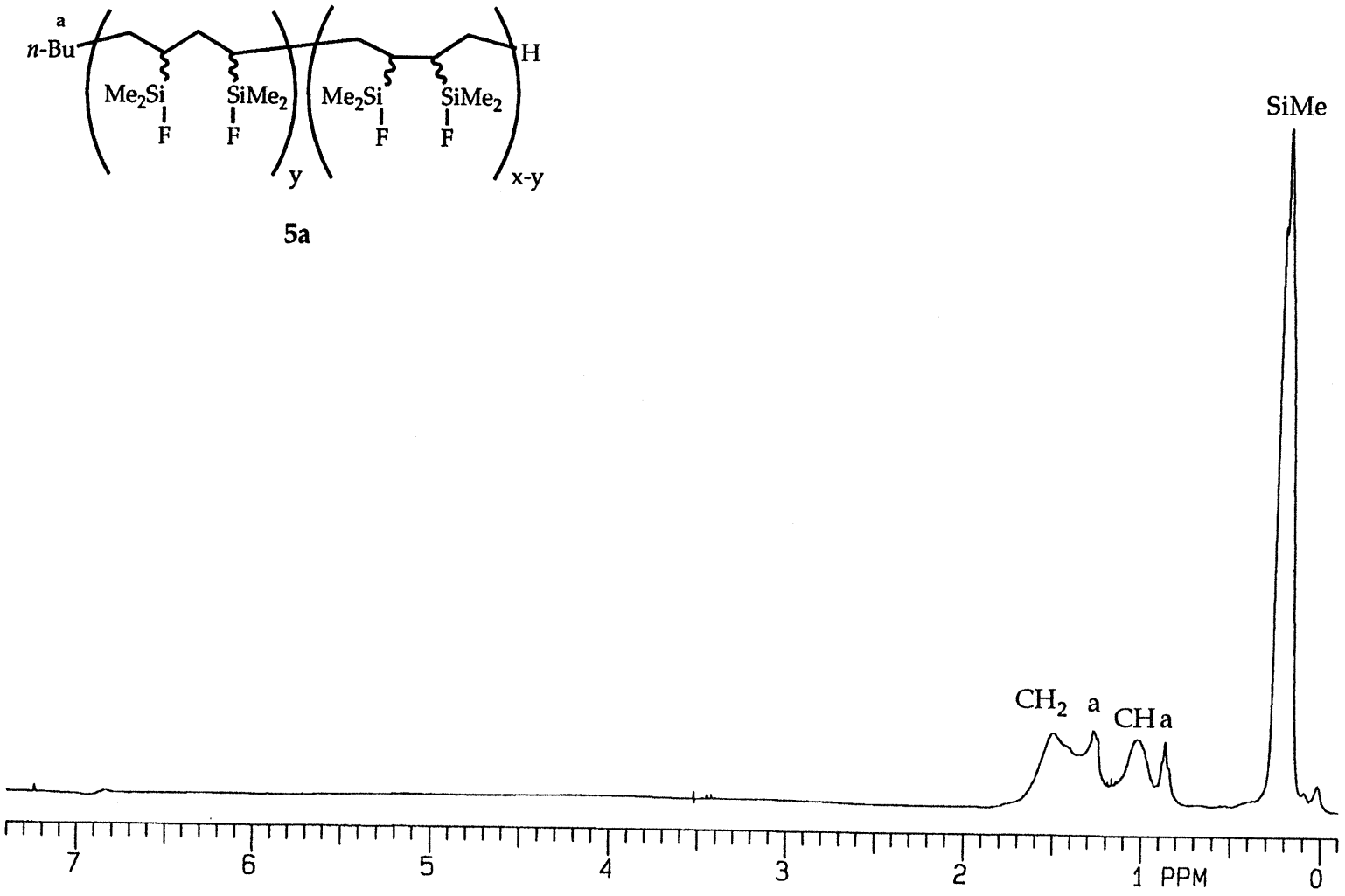


Figure 12. ^{1}H NMR Spectrum of Polymer **5a**.

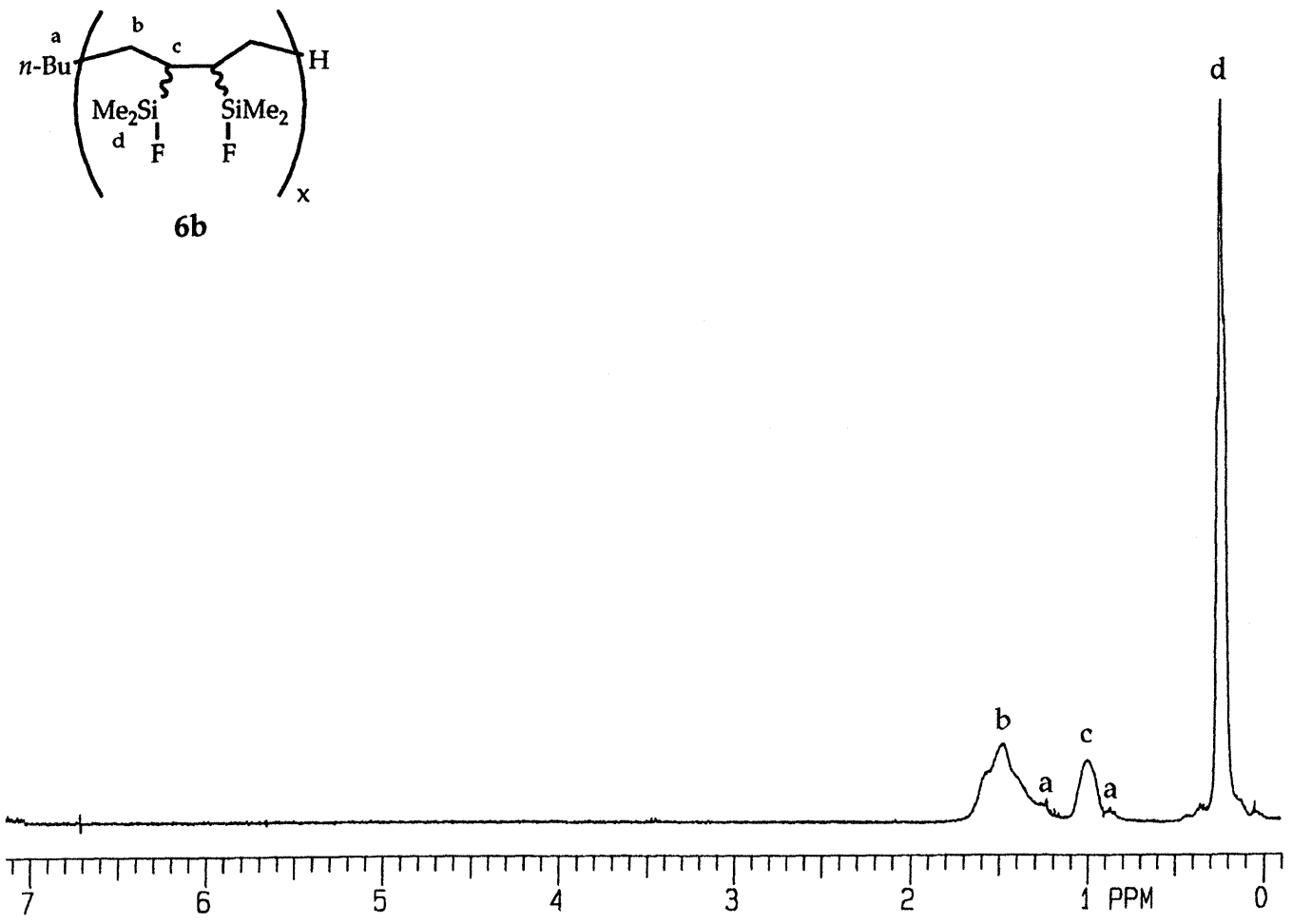
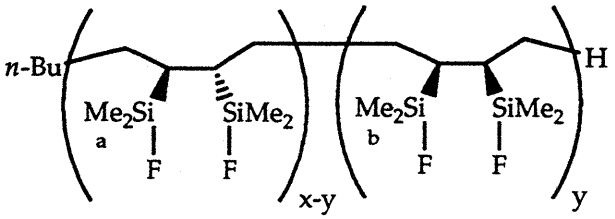


Figure 13. ^{1}H NMR Spectrum of Polymer **6b**.



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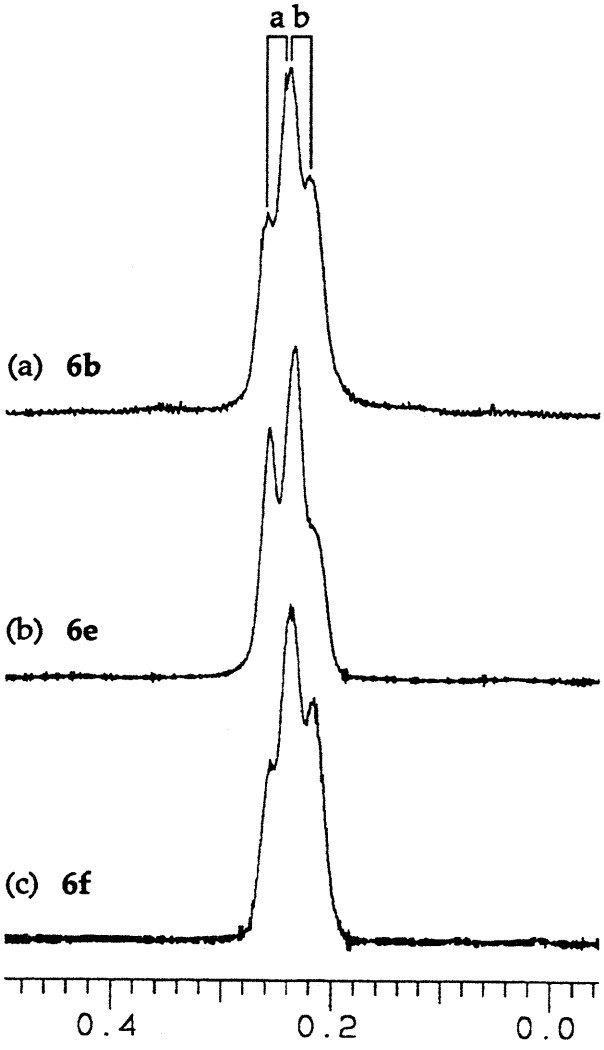


Figure 14. SiMe Signal in the ^{1}H NMR Spectra of Polymers (a) **6b**, (b) **6e** and (c) **6f**.

The aliphatic resonances in the ^1H NMR spectra of **5** and **6** were also considerably simpler than those of **1** and **2**, consisting of two relatively narrow signals arising from the *n*-pentyl endgroup and two broad signals at 1.05 and 1.55 ppm assigned to methine and methylene backbone resonances, respectively. The intensities of the endgroup signals in the spectra of **6b**, **6e** and **6f** were lower than those in the spectrum of **5a**, consistent with the intensities observed in the spectra of the parent polymers.

The ^{13}C NMR spectrum of **5a** (Figure 15a) displayed two broad, well separated $SiCH_3$ signals of roughly equal intensity at -2.64 and -0.93 ppm; the spectra of **6b** (Figure 16a), **6e** and **6f**, on the other hand, contained only one broad signal at -0.85 ppm. Thus, the -2.64 ppm signal in the spectrum of **5a** represents head-to-tail monomer sequences derived from six-membered rings in the parent polymer, and the -0.9 ppm resonance in the spectra of **5a** and **6b** corresponds to head-to-head monomer sequences arising from five-membered rings in the parent polymers.

The aliphatic regions of the ^{13}C NMR spectra of **5a** (Figure 15a) and **6b** (Figure 16a) were considerably simplified compared to the spectra of the parent polymers as a result of the change from a cyclic to a linear repeat unit. The methylene and methine backbone resonances of polymers **5a** and **6b** became clearly resolved in the ^{13}C NMR and distinguishable by DEPT sequences. The aliphatic region of **5a** displayed five sharp *n*-pentyl endgroup resonances and several broad aliphatic backbone resonances. Through the use of a DEPT sequence (Figure 15b), two intense CH backbone resonances at 24.2 and 28.6 ppm, two weaker CH backbone resonances at 26.3 and 27.5 ppm, and one broad CH_2 backbone resonance at 29.8 ppm were identified. The *n*-pentyl endgroup resonances in the ^{13}C NMR spectrum of **6b** were much weaker than those in the spectrum of **5a**, as expected. The aliphatic backbone

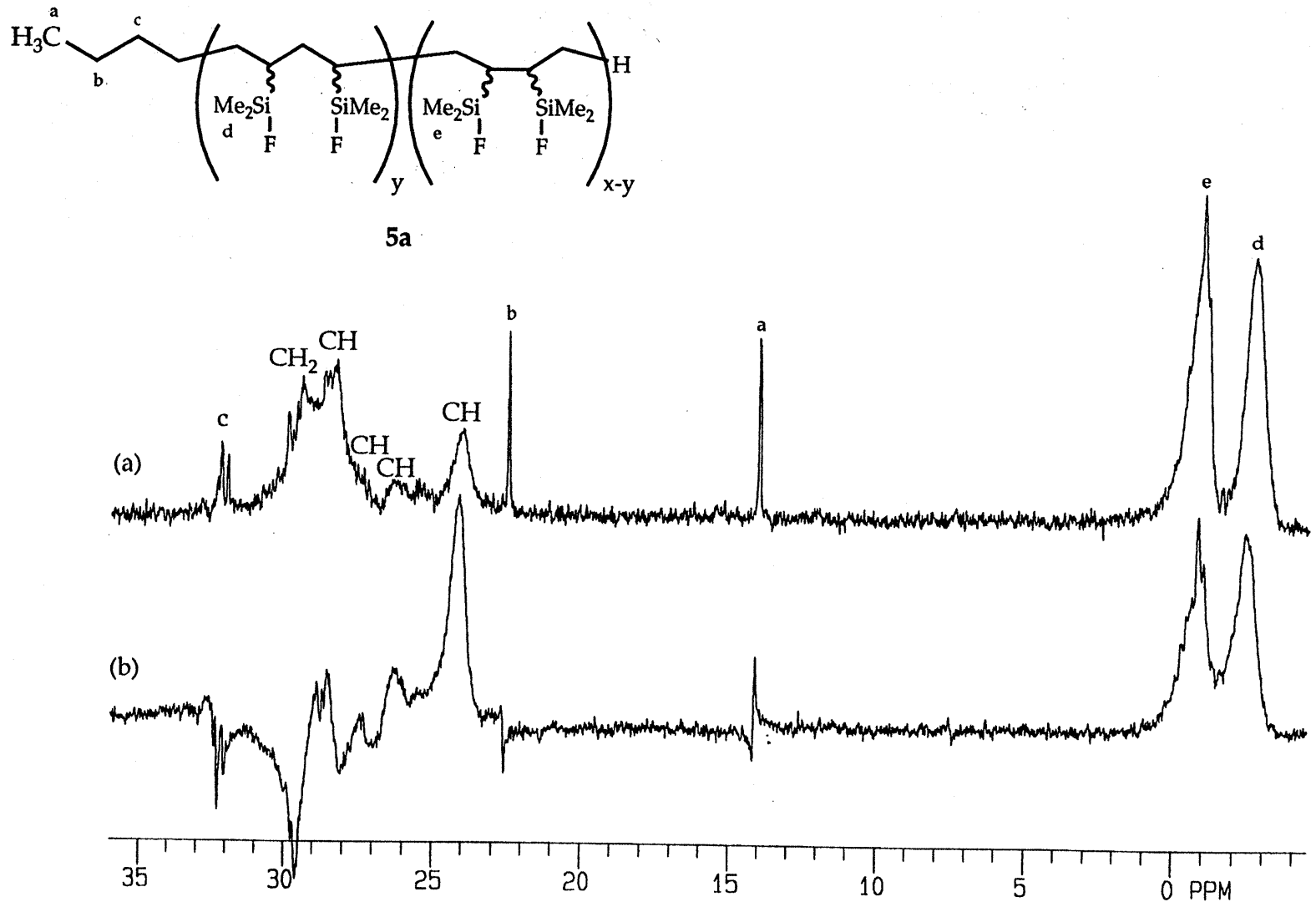


Figure 15. (a) ^{13}C and (b) ^{13}C DEPT (Mult = 1.5; CH, CH_3 up; CH_2 down) NMR Spectra of Polymer **5a**.

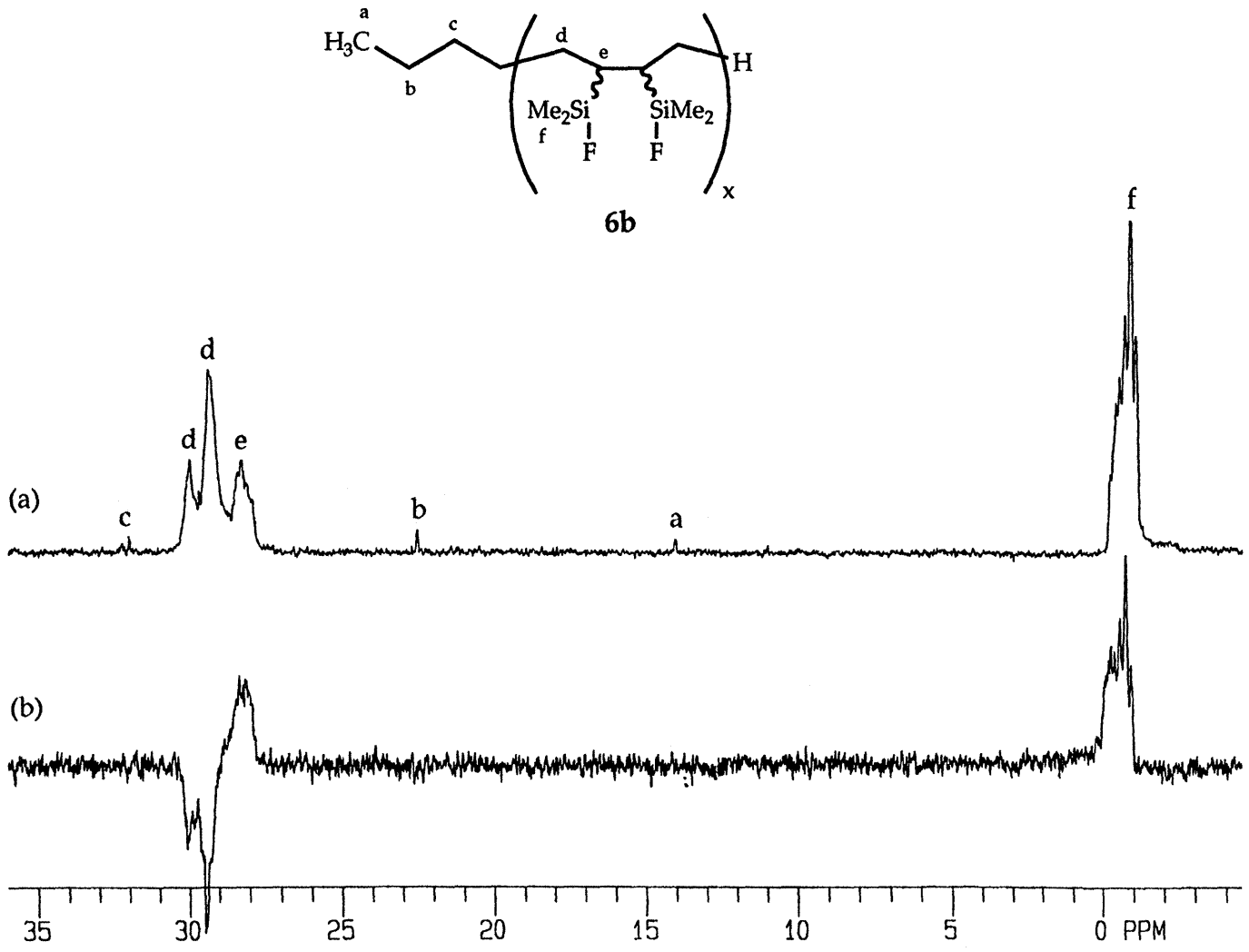
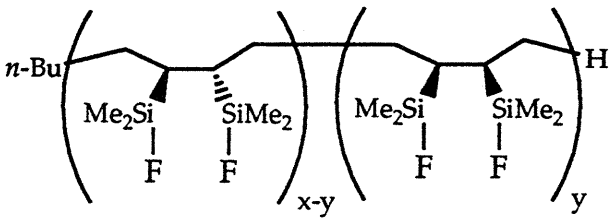


Figure 16. (a) ^{13}C and (b) ^{13}C DEPT (Mult = 1.5; CH, CH_3 up; CH_2 down) NMR Spectra of Polymer **6b**.

resonances were assigned using a DEPT sequence (Figure 16b). The one CH resonance in the spectrum of **6b** (at 28.3 ppm) corresponded well to the downfield member of the pair of intense CH resonances in the spectrum of **5a** (at 28.6 ppm), suggesting that the upfield member of the pair belonged to head-to-tail monomer sequences in the backbone of **5a** (arising from six-membered ring repeat units in **1a**). The methylene resonances of polymer **6** (at 29.4 and 30.0 ppm) occurred at approximately the same chemical shift as the broad methylene resonance of **5a**. The appearance of these methylene resonances differed slightly among the three polymers **6b**, **6e** and **6f** (Figure 17). The 30.0 ppm shoulder nearly disappeared in the spectrum of **6e**, indicating that this peak may be arising from m-(h,h) units in the polymer backbone (which should be present in lower concentration in polymer **6e**).

The ^{19}F spectra of **5a** (Figure 18) and **6** (Figure 19) were more difficult to interpret. Each exhibited signals in the expected region for R_3SiF compounds:[81] three broad, overlapping resonances at -161.4, -159.0 and -157.7 ppm in the spectrum of **5a**, and two broad, overlapping signals at -159.5 and -158.8 ppm along with two sharp, equally intense singlets at -157.6 and -157.2 ppm in the spectrum of **6**. The intensities of the three sets of resonances in the spectra of polymers **6b**, **6e** and **6f** (Figure 19) varied according to the m/r-(h,h) ratios of the dangling $SiMe_2F$ substituents (as fixed by the *cis/trans* ratios in the parent cyclopolymers). The pair of singlets centered at -157.4 ppm were of approximately equal height to one another in all three spectra; however, their height relative to the two broader signals increased with increasing amounts of *cis* five-membered rings in the parent polymer, indicating that they are to be assigned to m-(h,h) sequences in polymer **6**, and that the other two resonances at -159.5 and -158.8 ppm are associated with r-(h,h) sequences. The appearance of two signals at -157.4 ppm instead of one most likely arises



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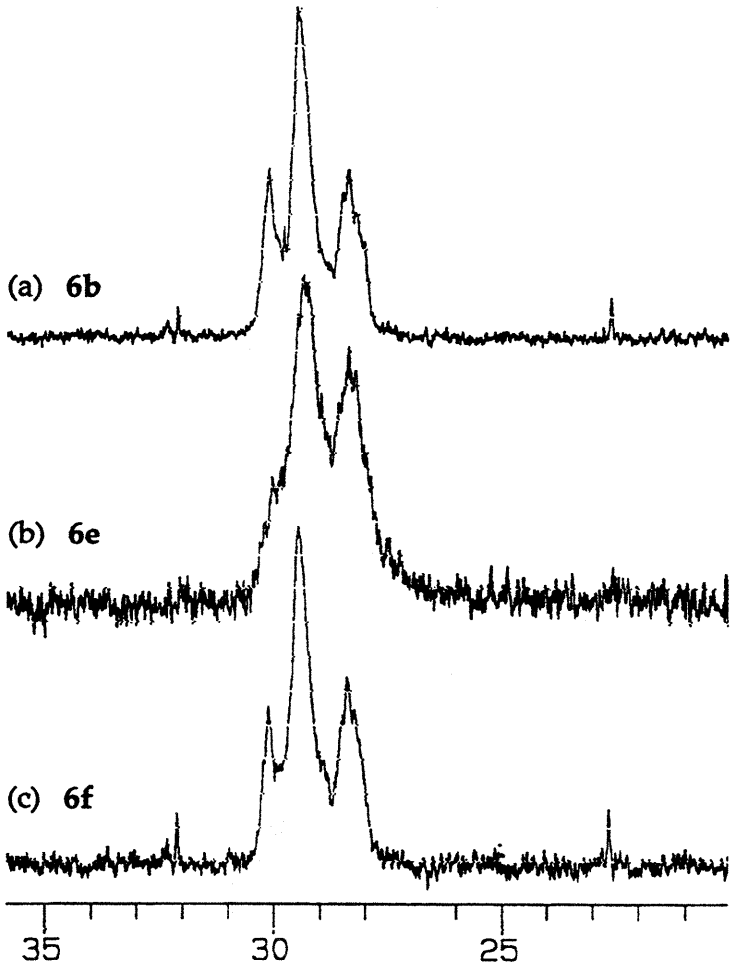
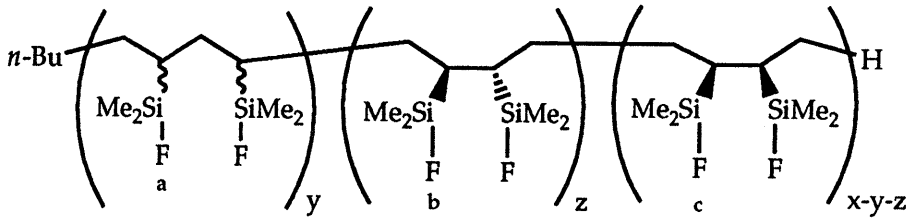


Figure 17. Aliphatic Region of ^{13}C NMR Spectra of Polymers (a) **6b**, (b) **6e** and (c) **6f**.



5a

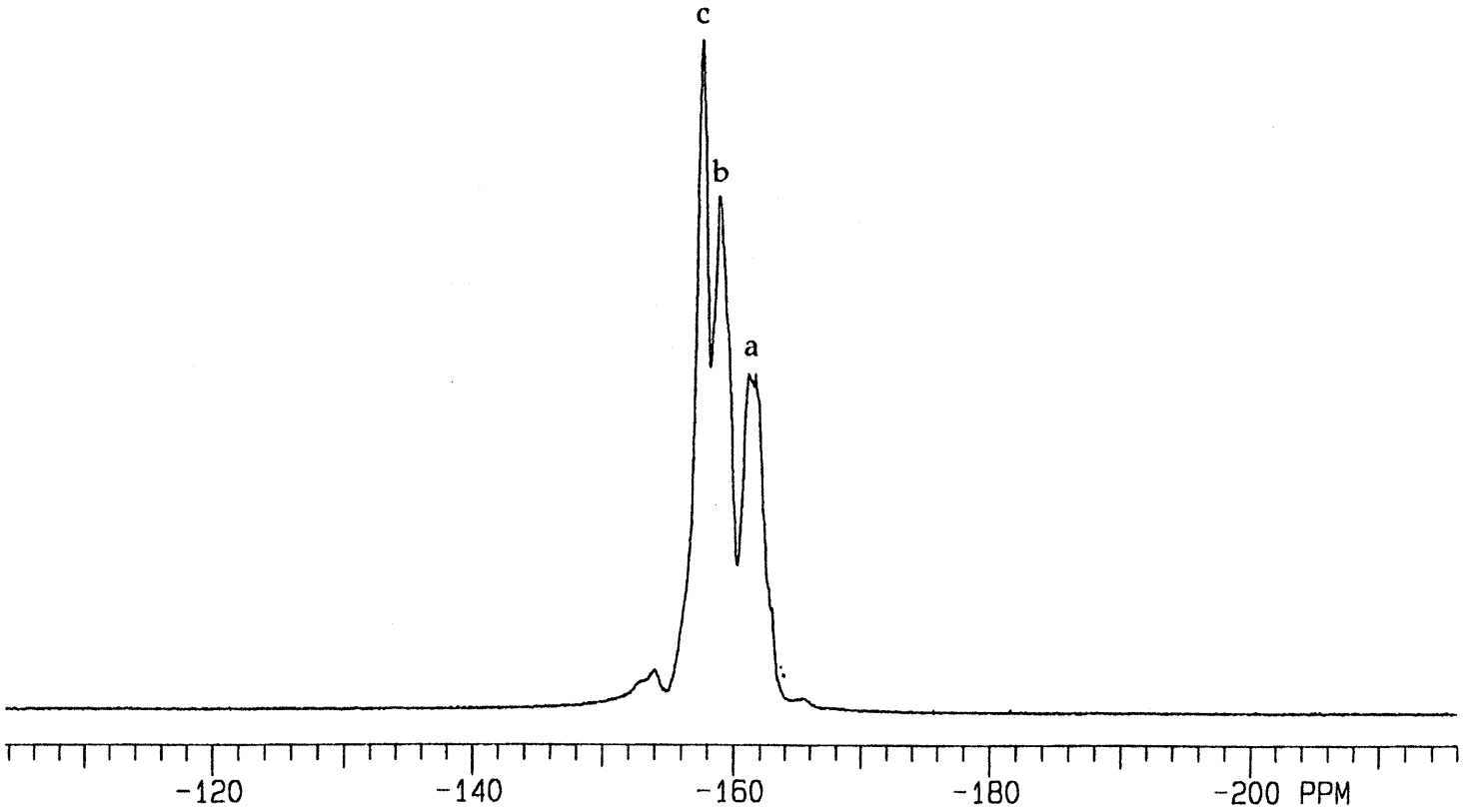
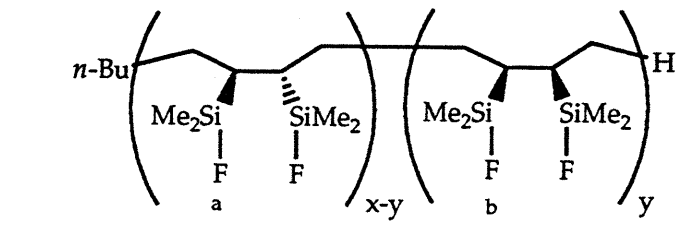


Figure 18. ^{19}F NMR Spectrum of Polymer **5a**.



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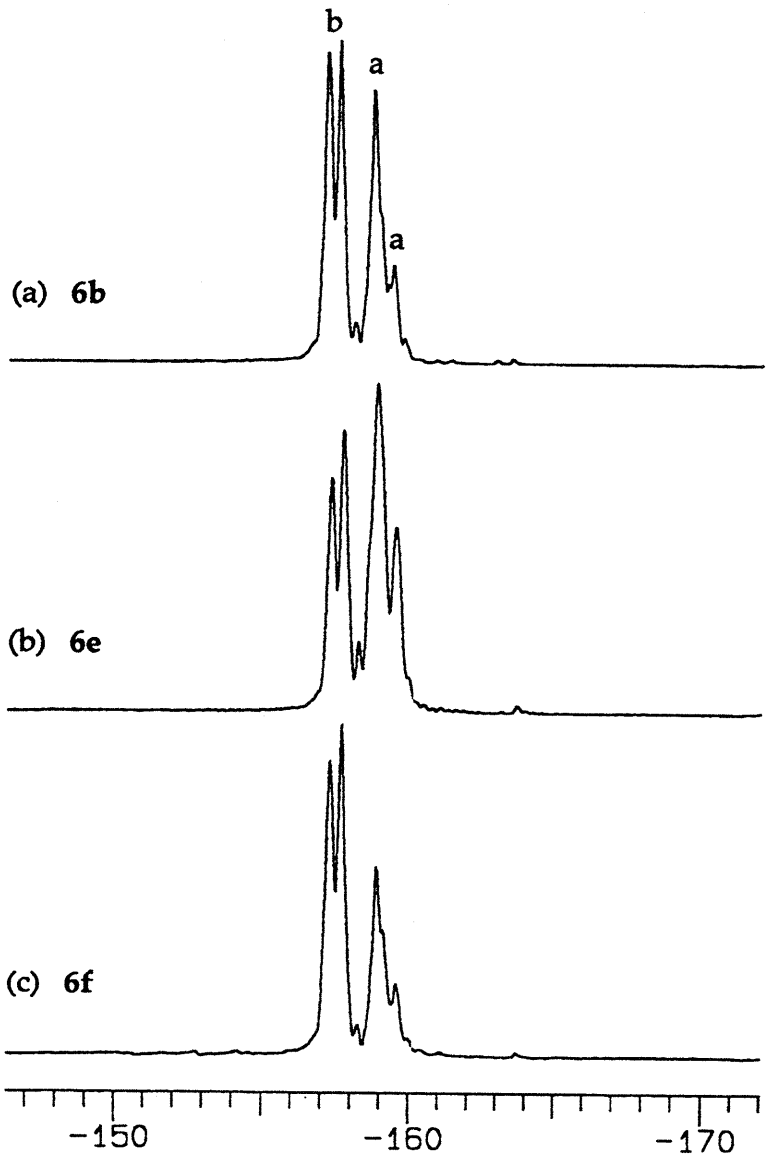


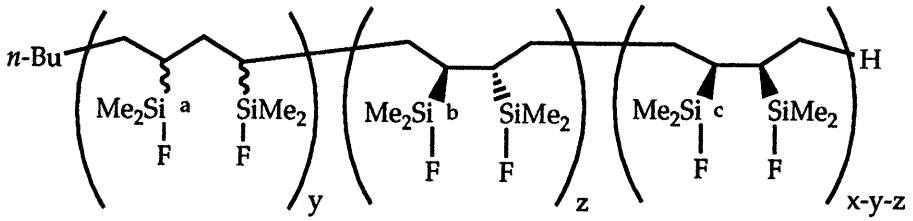
Figure 19. ^{19}F NMR Spectra of Polymers (a) **6b**, (b) **6e** and (c) **6f**.

from the relative stereochemistry of the adjacent monomer unit (attached in a tail-to-tail fashion); that these signals are equally intense indicates a 50/50 mixture of r- and m-(t,t) sequences, which would be expected if the enantioselectivity of the cyclization step was not affected by the absolute configuration of the penultimate monomer unit.

By analogy to the assignments of the ^{19}F NMR resonances of **6**, those at -159.0 and -157.7 ppm in the spectrum of **5a** were assigned, respectively, to r-(h,h) and m-(h,h) sequences. The remaining signal at -161.4 ppm, which had no counterpart in the spectrum of **6**, was assigned to head-to-tail units. The increased broadness of the resonances of **5a** speak to the greater irregularity of the polymer backbone relative to **6** as a consequence of the incorporation of both head-to-head and head-to-tail monomer sequences.

The ^{29}Si NMR spectra of **5a** (Figure 20) and **6** (Figure 21) contained no residual resonances of **1** or **2**. Instead, each displayed a pair of doublets ($J_{Si-F} \approx$ 286 Hz, typical for R_3SiF compounds[75]) at approximately 32 and 34 ppm, in the region normally associated with R_3SiF compounds.[75] The lower-field resonance in the spectra of **6b**, **6e** and **6f** increased in height with the percentage of *trans* units in the parent cyclopolymer. By deduction, then, the lower-field resonance in the spectra of **5a** and **6** is assigned to r-(h,h) sequences, while the higher-field signal is assigned to m-(h,h) sequences for polymer **6** and a mixture of m-(h,h) and r/m-(h,t) sequences for polymer **5a**. The increased broadness and intensity of the higher-field resonance of **5a** relative to that of **6** is consistent with its being a superposition of m-(h,h) and r/m-(h,t) signals.

The results of ring-opening reactions of polymers **1** and **2** with HF(aq) established the cyclic nature of the repeat units in the backbones of these polymers. In addition, spectroscopic analyses of the product polymers **5** and **6**



5a

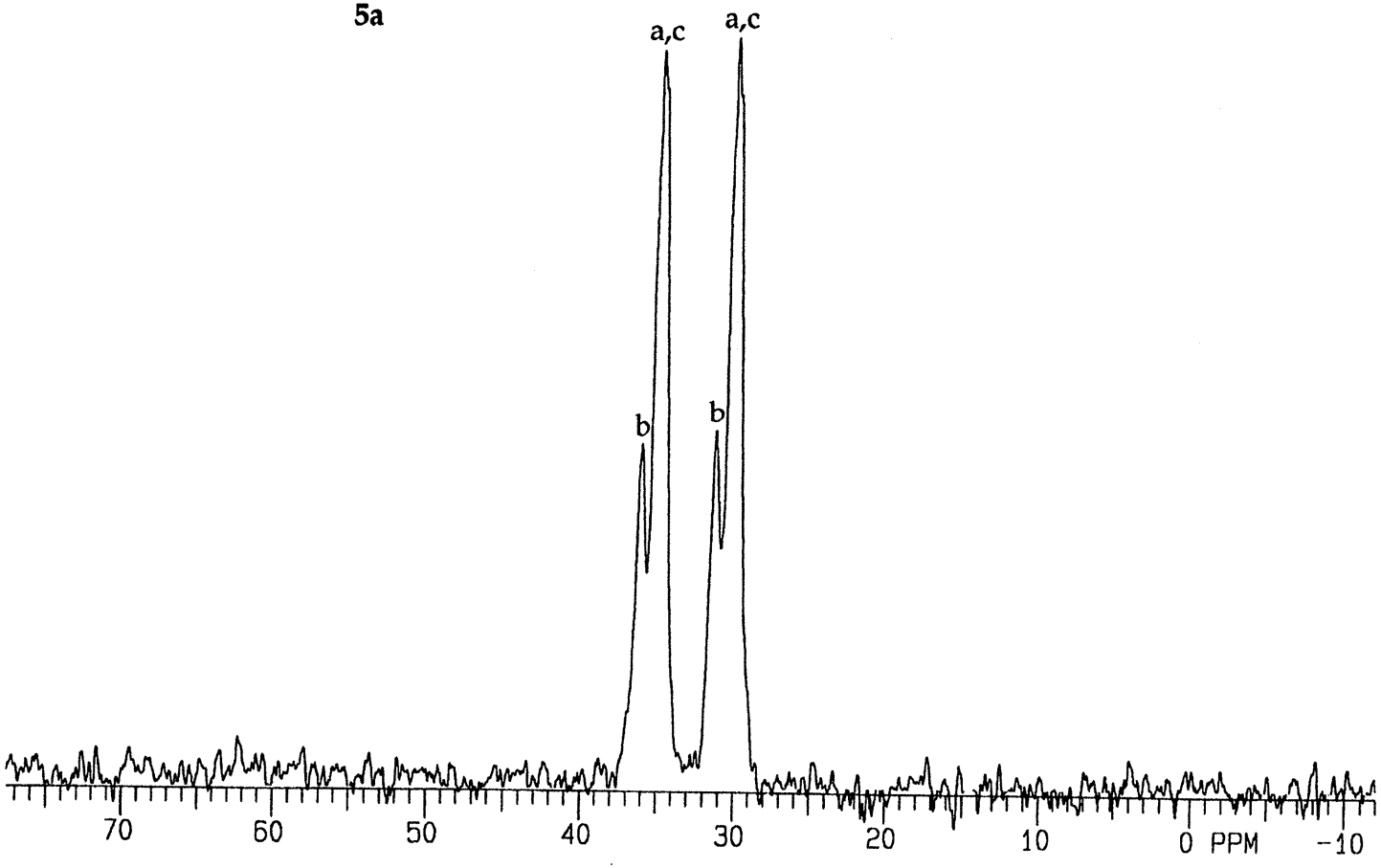
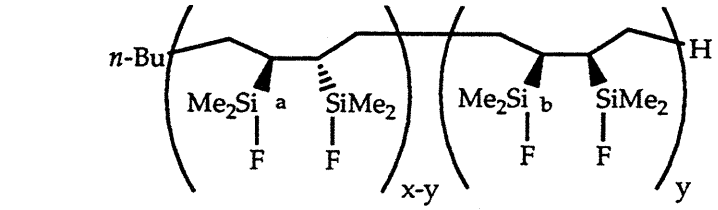


Figure 20. ^{29}Si NMR Spectrum of Polymer **5a**.



6

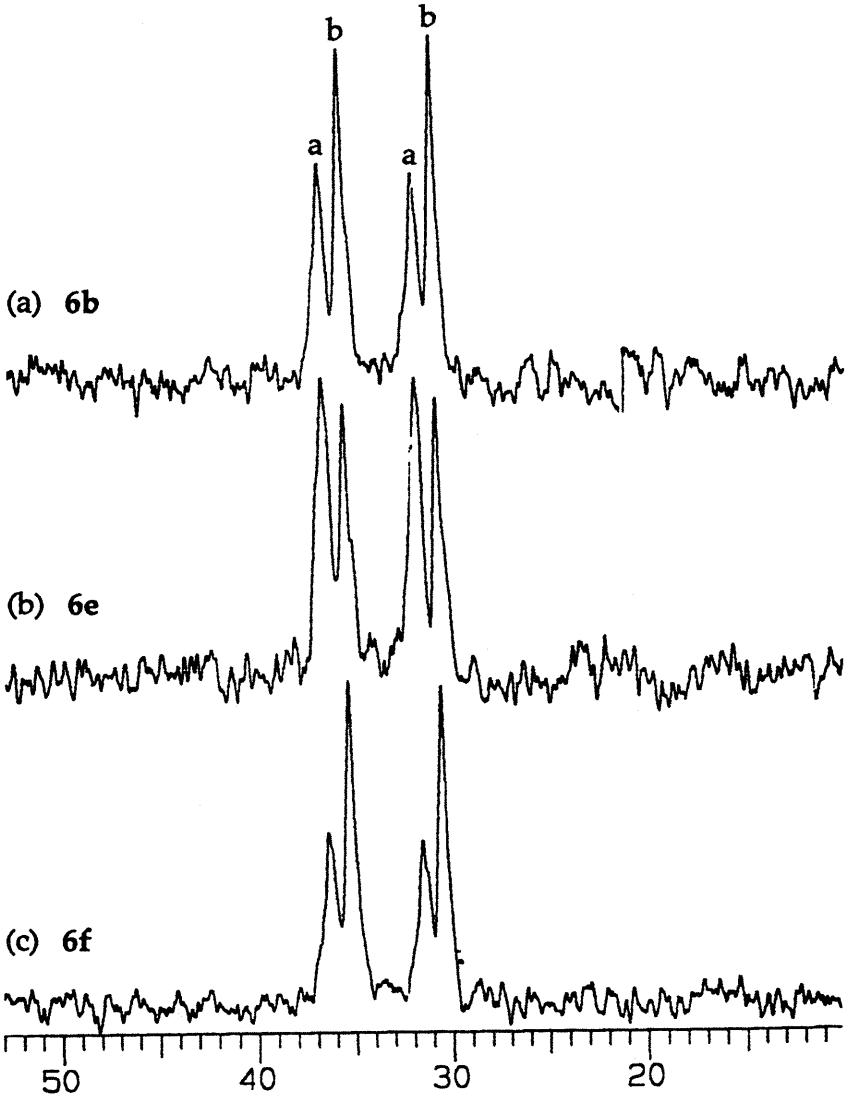


Figure 21. ^{29}Si NMR Spectra of Polymers (a) **6b**, (b) **6e** and (c) **6f**.

gave results entirely consistent with the structural models of the parent cyclopolymers **1** and **2** derived from the results of spectroscopic studies and model reactions.

Derivatization Reactions of Polymer 6 with Nucleophilic Reagents

Organosilicon chemistry has found broad application in the chemical modification of polymers and surfaces. [25] The poly(vinyldimethylfluorosilane) **6** produced by the ring-opening of cyclopolymer **1** contains many reactive Si-F bonds which may be derivatized with nucleophilic reagents to give new, highly functionalized organosilicon polymers. Polymer **6** was chosen for these derivatization studies due to its highly regular microstructure consisting of alternating head-to-head and tail-to-tail sequences of vinyldimethylfluorosilane units. The results of these studies are compiled in Table 5. Similar derivatization studies were reported utilizing a poly(vinyldimethylfluorosilane) polymer prepared from the aqueous hydrofluoric acid ring-opening reaction of a cyclopolymer generated from 1,3-divinyltetramethyldisilazane using radical initiators.[40]

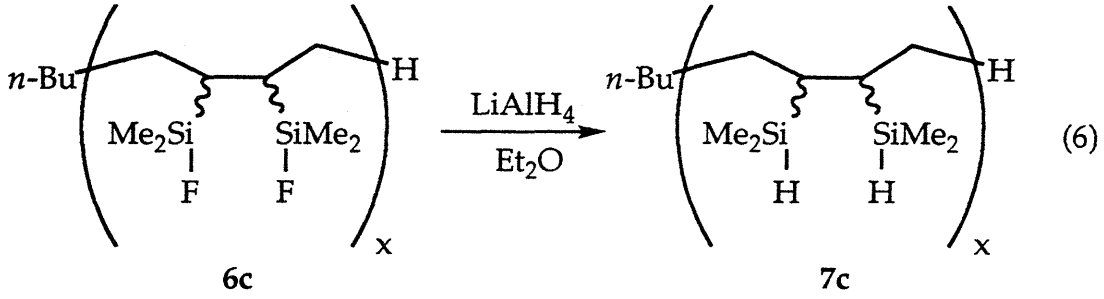
Table 5. Derivatizations of Polymer **6** with Nucleophilic Reagents.

Parent Polymer	Nucleophilic Reagent	Product	Yield	M_n[a] (Δ)[b]	M_w[a] (Δ)[b]	M_w/M_n[a] (Δ)[b]
6c	$LiAlH_4$	**7c**	76	8230 (+3540)	8740 (+3090)	1.06 (-0.15)
6b	MeLi	**8b**	93	8390 (+30)	9160 (+80)	1.09 (0)
6b	CH_2=CHLi	**9b**	88	13300[c] (+7900)	23500[c] (+16900)	1.76[c] (+0.54)
6d	CH_2=CHMgBr	**9d**	64	15800[c] (+7200)	26400[c] (+16600)	1.67[c] (+0.54)
6b	HC≡CMgBr	**10b**	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.

The simplest derivative of **6** that can be envisioned possesses SiH groups in place of fluorosilane moieties. The reduction of **6c** with lithium aluminum hydride in diethyl ether gave polymer **7c** as a clear, colorless oil in good yield after aqueous workup (eq. 6). Polymer **7c** possessed a narrow, monomodal molecular weight distribution like that of **6c**; it was significantly shifted, however, towards higher molecular weights. The fact that **7c**, which has a lower monomer molecular weight than **6c** and the same average chain length, exhibits a higher apparent molecular weight by GPC serves to

underscore the subtlety of the factors which control the hydrodynamic volume of polymers.



6c **7c** (6)

The presence of SiH moieties in polymer **7c** was indicated by the observation of a strong Si-H stretching band at 2104 cm^{-1} in its IR spectrum. The ^{1}H NMR spectrum of **7c** (Figure 22) displayed a slightly broadened SiH resonance at 3.90 ppm with clearly visible ^{29}Si satellites, a narrow $SiCH_3$ signal with weak coupling to the SiH group (^{3}J = 4 Hz) and well-resolved silylmethine and methylene resonances. The ^{13}C NMR spectrum of **7c** (Figure 23a) was also very simple and easy to interpret. The r- and m-(h,h) $SiCH_3$ signals appeared as two sharp singlets at -3.91 and -3.25 ppm. Two clearly resolved sets of broad aliphatic backbone resonances at 28 and 31 ppm were assigned to methine and methylene carbons, respectively, using a DEPT sequence (Figure 23b). The methylene resonance was split into two signals, most likely arising from r- and m-(h,h) sequences. The silylmethine resonance was split into at least four sharper signals, probably reflecting the contributions of r- and m-(t,t) sequences in addition to the r/m-(h,h) effects.

The ^{29}Si NMR spectrum of **7c** (Figure 24) also reflected the effects of both head-to-head and tail-to-tail relative stereochemistry. It consisted of one broad resonance in the expected region for R_3SiH compounds,[75] composed of at least four distinguishable sharper signals. This pattern of multiple

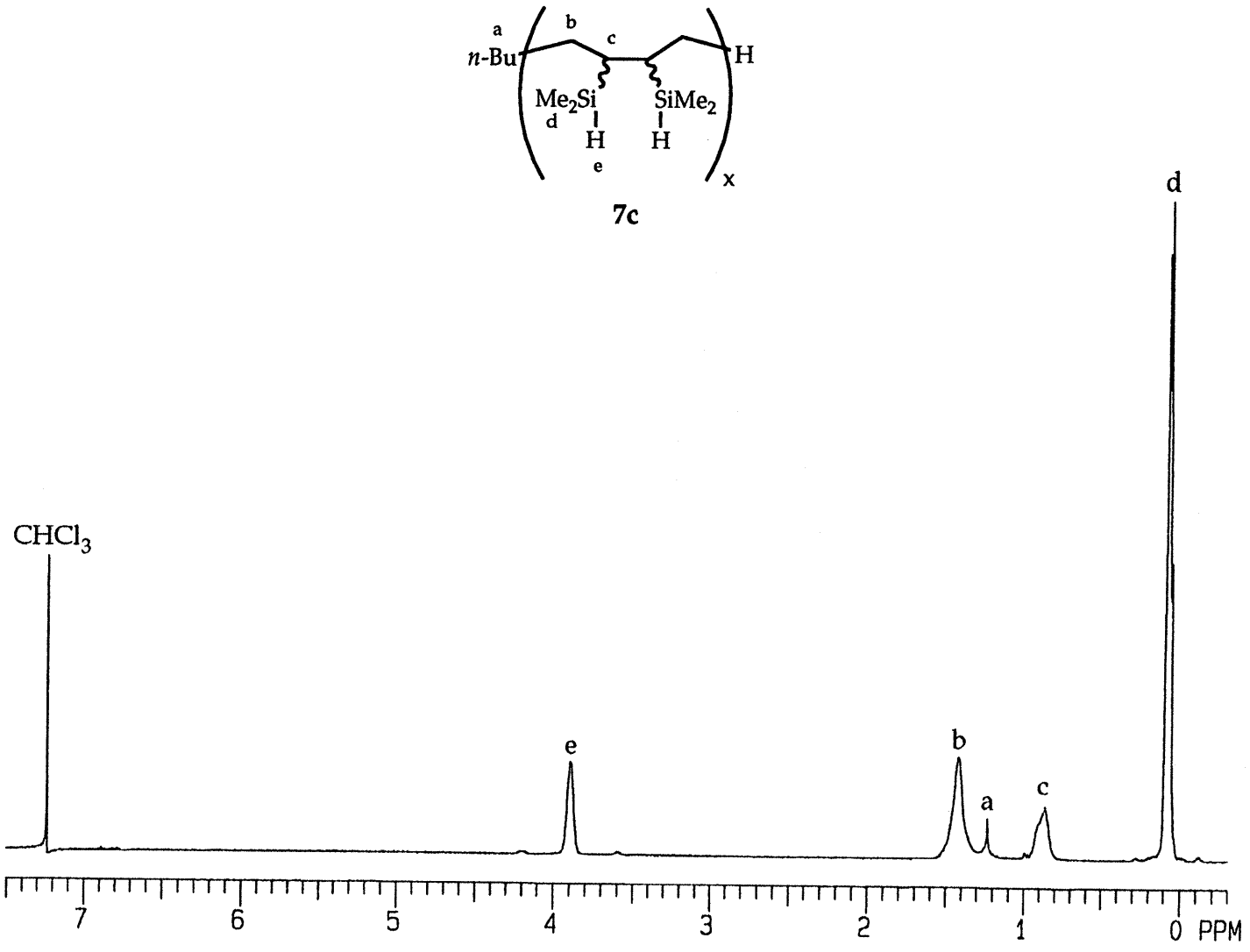


Figure 22. ^{1}H NMR Spectrum of Polymer **7c**.

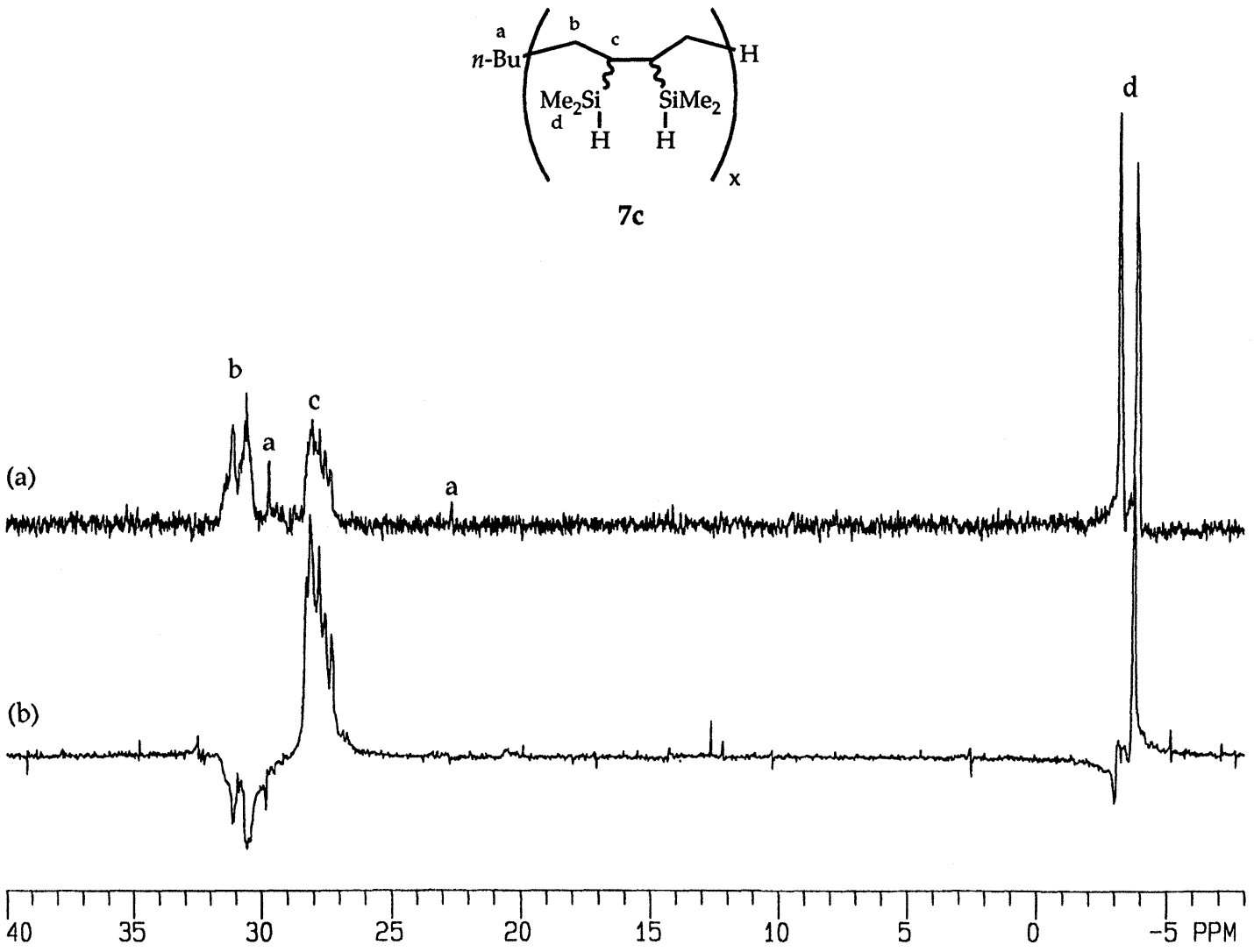


Figure 23. (a) ^{13}C and (b) ^{13}C DEPT (Mult = 1.5; CH, CH_3 up; CH_2 down) NMR Spectra of Polymer **7c**.

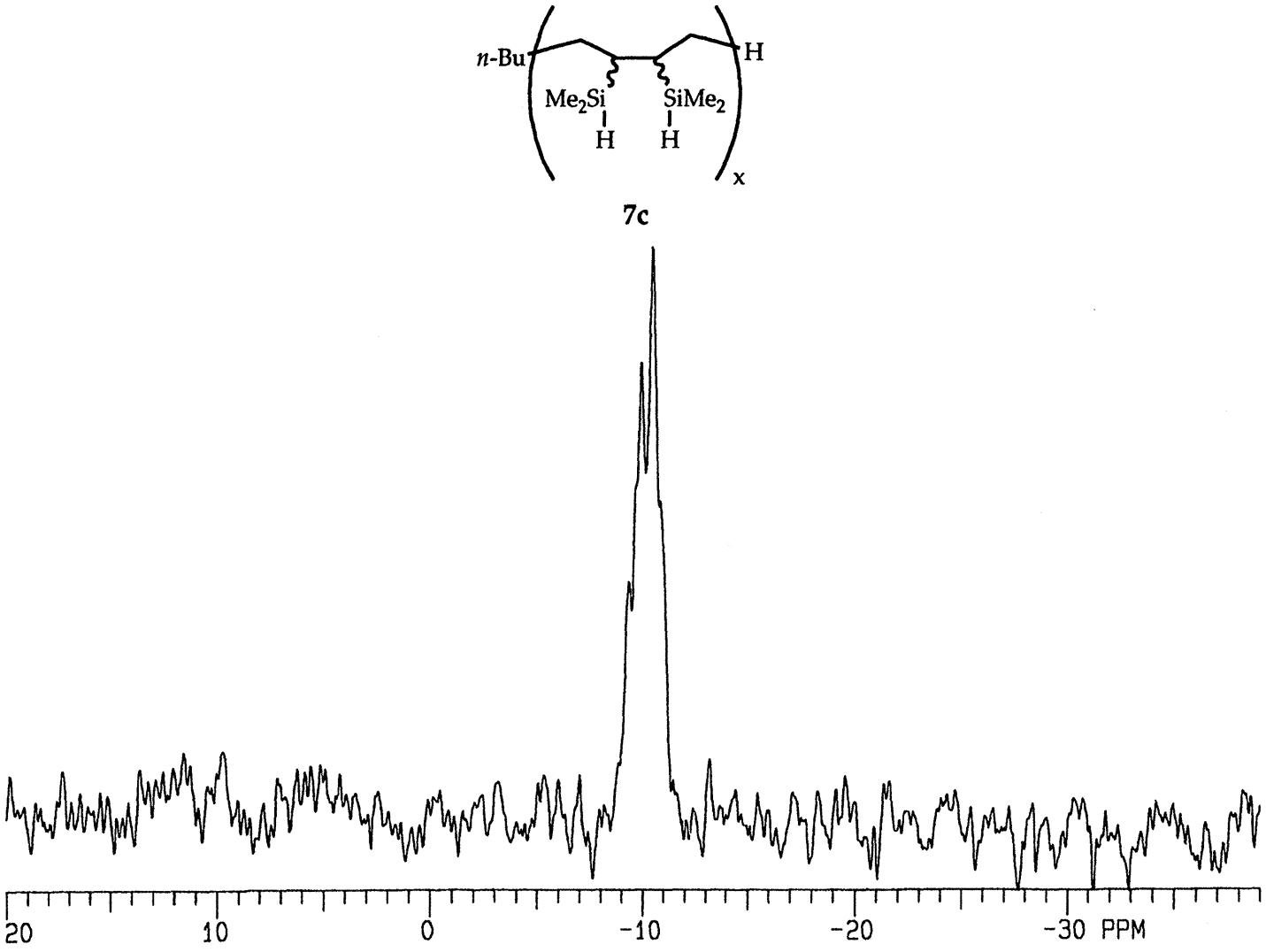
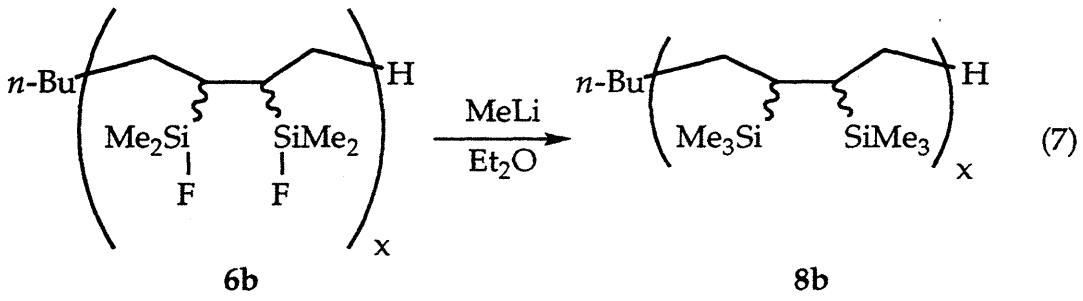


Figure 24. ^{29}Si NMR Spectrum of Polymer **7c**.

resonances formed a common motif for the silicon spectra of all the product polymers **7 - 10** arising from the nucleophilic substitution of polymer **6**.

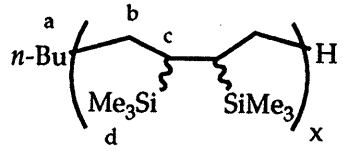
When polymer **6b** was reacted with an excess of methyllithium in diethyl ether at room temperature, poly(vinyltrimethylsilane) **8b** was obtained in high yield as a white powder after precipitation from toluene/methanol (eq. 7). Polymer **8b** possessed a narrow molecular weight distribution which was hardly shifted in molecular weight from that of the parent polymer **6b**, indicating that no crosslinking or backbone degradation reactions had occurred during the functionalization reaction and that polymers **6b** and **8b** had similar hydrodynamic volumes.



6b **8b** (7)

The ^{1}H NMR of **8b** (Figure 25) showed the usual aliphatic signals (similar in appearance to those of **6b**, except shifted approx. 0.2 ppm upfield) and a pair of strong $SiMe_3$ singlets at -0.004 and 0.012 ppm, presumably arising from rac and meso head-to-head monomer sequences. The new $SiMe_3$ signals had completely replaced the $SiMe_2F$ signal at 0.236 ppm for the parent polymer **6b**, indicating complete substitution of the Si-F bonds had occurred; this was supported by the results of combustion analysis.

As was mentioned previously, anionically-generated poly(vinyltrimethylsilane) has been studied by a number of groups for some time. Detailed spectroscopic work by Oku and coworkers established that the



8b

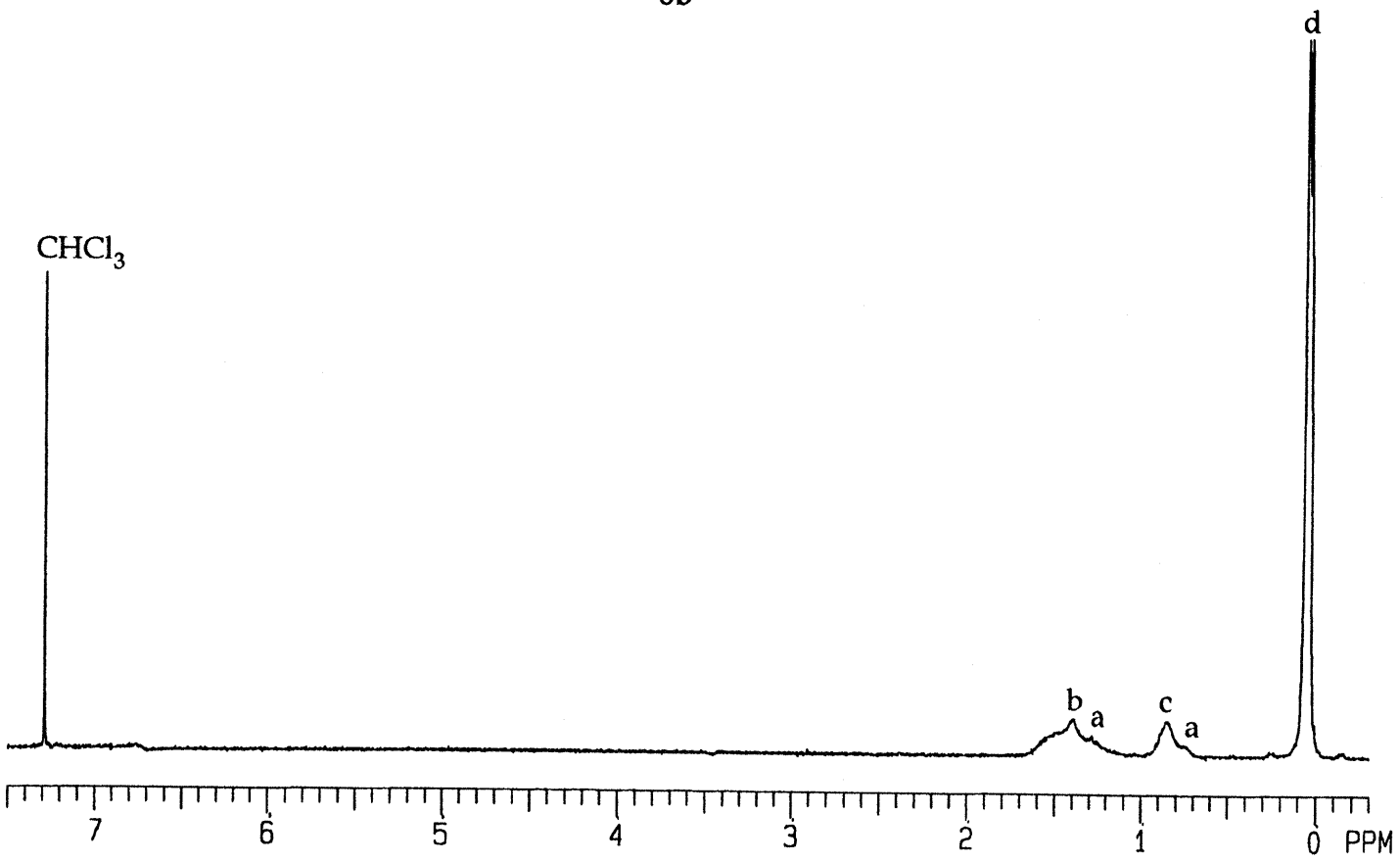


Figure 25. ^{1}H NMR Spectrum of Polymer **8b**.

polymerization of vinyltrimethylsilane in hydrocarbon solvent proceeds for the most part in a head-to-tail fashion. At higher temperatures, and particularly when N,N,N',N'-tetramethylethylenediamine (TMEDA) co-solvent is added, a competitive isomerization reaction occurs in which the propagating silylmethine carbanion migrates to the silylmethyl group of the terminal monomer unit.[56-58] This isomerization manifests itself in the ^{1}H NMR spectrum of the polymer by the disappearance of the silylmethine proton resonance at 0.9 ppm with the concomitant emergence of a silylmethylene resonance at 0.5 ppm.[56] The aliphatic region of the ^{1}H NMR spectrum of **8b** contained no resonances in the 0.5 ppm region and thus resembled very closely the spectrum of poly(vinyltrimethylsilane) prepared in the absence of TMEDA (which contained a low concentration of isomerized units). Hence, this isomerization mechanism, which occurs during the anionic polymerization of vinyltrimethylsilane and other vinyltriorganylsilanes,[59,60] does not operate during the polymerization of the **NTMS** monomer. Also, given the nearly identical ^{1}H NMR spectra of polymers **5** and **6**, it is concluded that polymer **1** does not contain any isomerized units of this sort.

The ^{13}C NMR spectrum of **8b** (Figure 26a) showed one sharp, very intense $SiMe_3$ signal at 0.10 ppm along with much weaker aliphatic signals: two sharp endgroup signals, and four broad backbone resonances. Using a DEPT sequence (Figure 26b), the two higher-field backbone resonances were assigned to silylmethine carbons, and the two lower-field resonances to methylene carbon atoms. The two methylene carbon signals were of roughly equal intensity; their splitting most likely arises from the presence of both rac and mer head-to-head sequences in the polymer backbone.

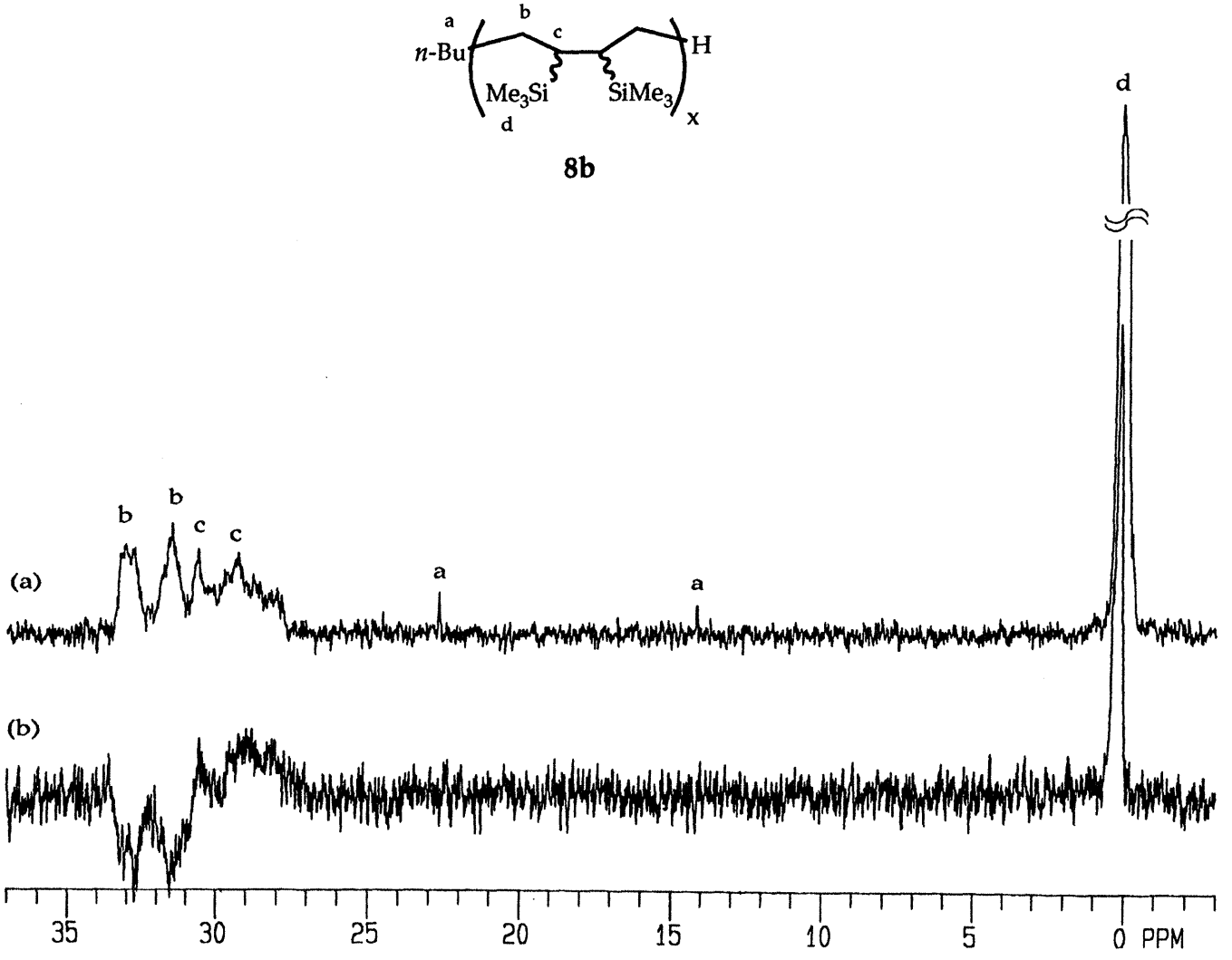


Figure 26. (a) ^{13}C and (b) ^{13}C DEPT (Mult = 1.5; CH, CH_3 up; CH_2 down) NMR Spectra of Polymer **8b**.

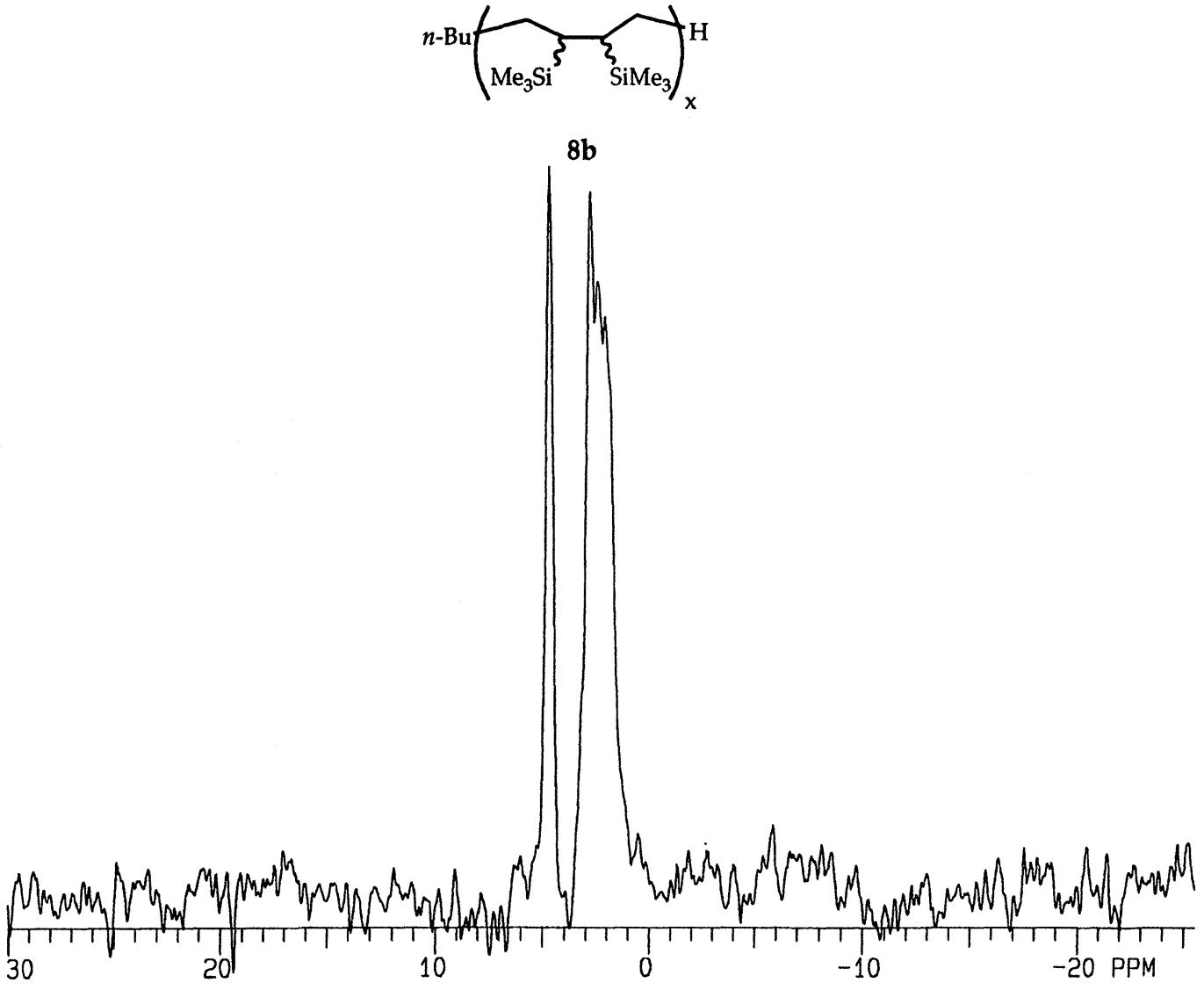
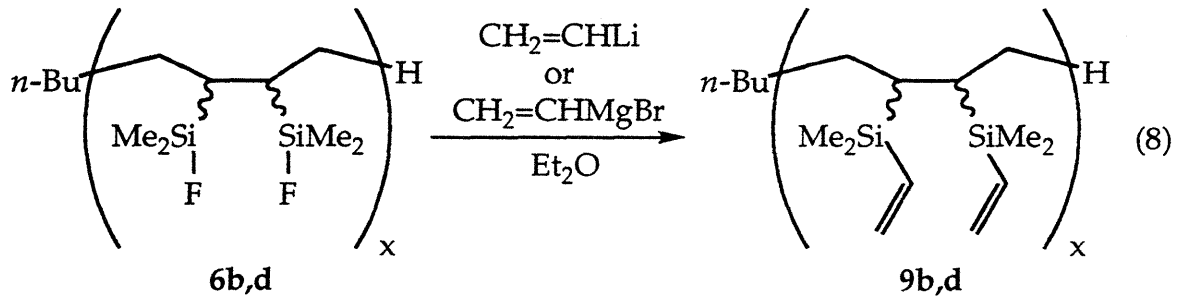


Figure 27. ^{29}Si NMR Spectrum of Polymer **8b**.

Like that of polymer **7c**, the ^{29}Si NMR spectrum of polymer **8b** (Figure 27) displayed a complex pattern of at least four sharp resonances arising from head-to-head and tail-to-tail tacticity effects. In the spectrum of **8b**, however, one of these resonances was shifted ~2 ppm downfield from the others. There were no residual resonances in the R_3SiF region.

The functionalization of polymers **6b** and **6d** with vinyllithium and -magnesium reagents, respectively, led to poly(vinyldimethylvinylsilanes) **9b** and **9d** in good yields. The reaction of the Si-F bonds of polymer **6** with vinyllithium was much more facile than the corresponding reaction with vinylmagnesium bromide, requiring only two days at room temperature to effect complete substitution (vs. seven days at room temperature followed by five days at reflux for vinylmagnesium bromide). Both polymers were obtained as white solids after precipitation of the crude reaction products from a toluene/methanol system. The GPC traces of both polymers showed broad, multi-modal distributions, indicative of cross-linking reactions occurring during the functionalization reaction, most likely involving the radical- or anionic-initiated polymerizations of pendant vinyl groups; the high solubility of these polymers and the GPC traces argue for low numbers of cross-links per polymer chain. The average molecular weight of polymer **9d** was higher than that of **9b**, consistent with the higher molecular weight of its parent polymer **6d**.



6b,d **9b,d** (8)

Polymers **9b** and **9d** exhibited identical IR and NMR (^{1}H, ^{13}C, ^{29}Si) spectra. The vinylsilane moieties gave characteristic absorptions in the IR and NMR spectra. The ^{1}H NMR spectrum of **9b** (Figure 28) shows three multiplets in the 5.5 - 6.5 ppm region arising from the protons on the vinyl groups; these signals integrate to two vinyl groups per monomer unit. The $SiCH_3$ resonance appears as a broad singlet at 0.081 ppm, shifted 0.155 ppm upfield from that of the parent polymer **6b**. The silylmethine and methylene resonances are somewhat broad, but still resolved from one another, appearing at 0.87 and 1.0 - 1.8 ppm, respectively.

The two vinyl carbons appear as sharp singlets at 131.28 and 140.31 ppm in the ^{13}C NMR spectrum of **9b** (Figure 29a). One relatively sharp $SiCH_3$ resonance is observed, along with sharp endgroup signals and broad backbone resonances. Methylene and methine backbone resonances were resolved using a ^{13}C DEPT sequence (Figure 29b) and were similar in appearance to those of other derivatives of **6**. The ^{29}Si NMR spectrum of **9b** (Figure 30) closely resembles that of **8b** (Figure 27), containing one sharp resonance shifted several ppm downfield from a broad cluster of other sharp resonances.

The direct anionic polymerization of divinyldimethylsilane has been reported to give a soluble, low molecular weight polymer in which approximately 70% of the pendant vinyl groups are incorporated into cyclic and cross-linked units.[38] The ^{1}H NMR of this polymer exhibits multiple sharp $SiCH_3$ resonances around 0 ppm and two broad aliphatic backbone resonances at 0.7 and 2.0 ppm in addition to the signals found in the spectrum of **9b**. The absence of these additional signals in the spectrum of **9b** gives further evidence for the low number of cross-linked units present in **9b**.

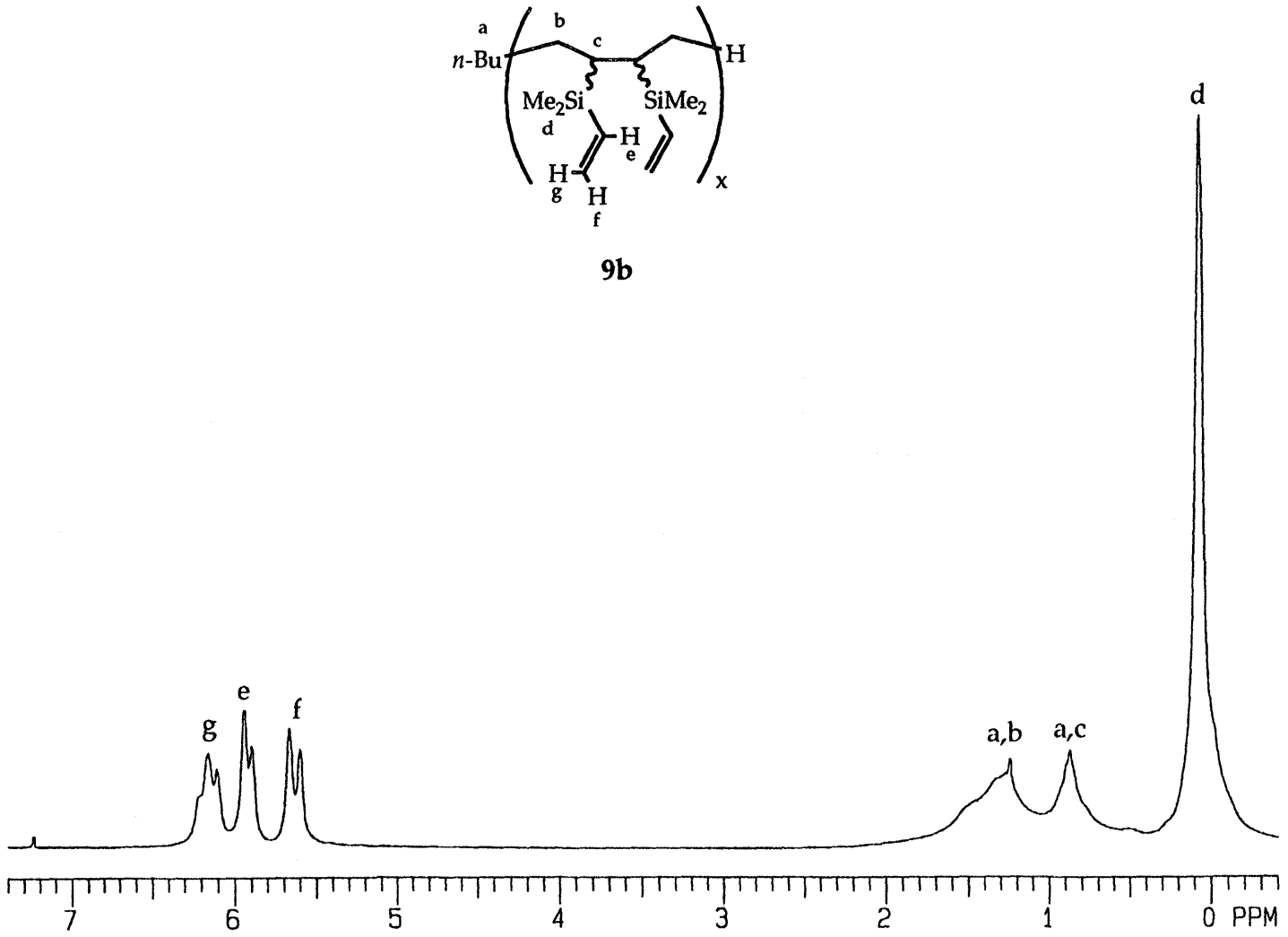


Figure 28. ^{1}H NMR Spectrum of Polymer **9b**.

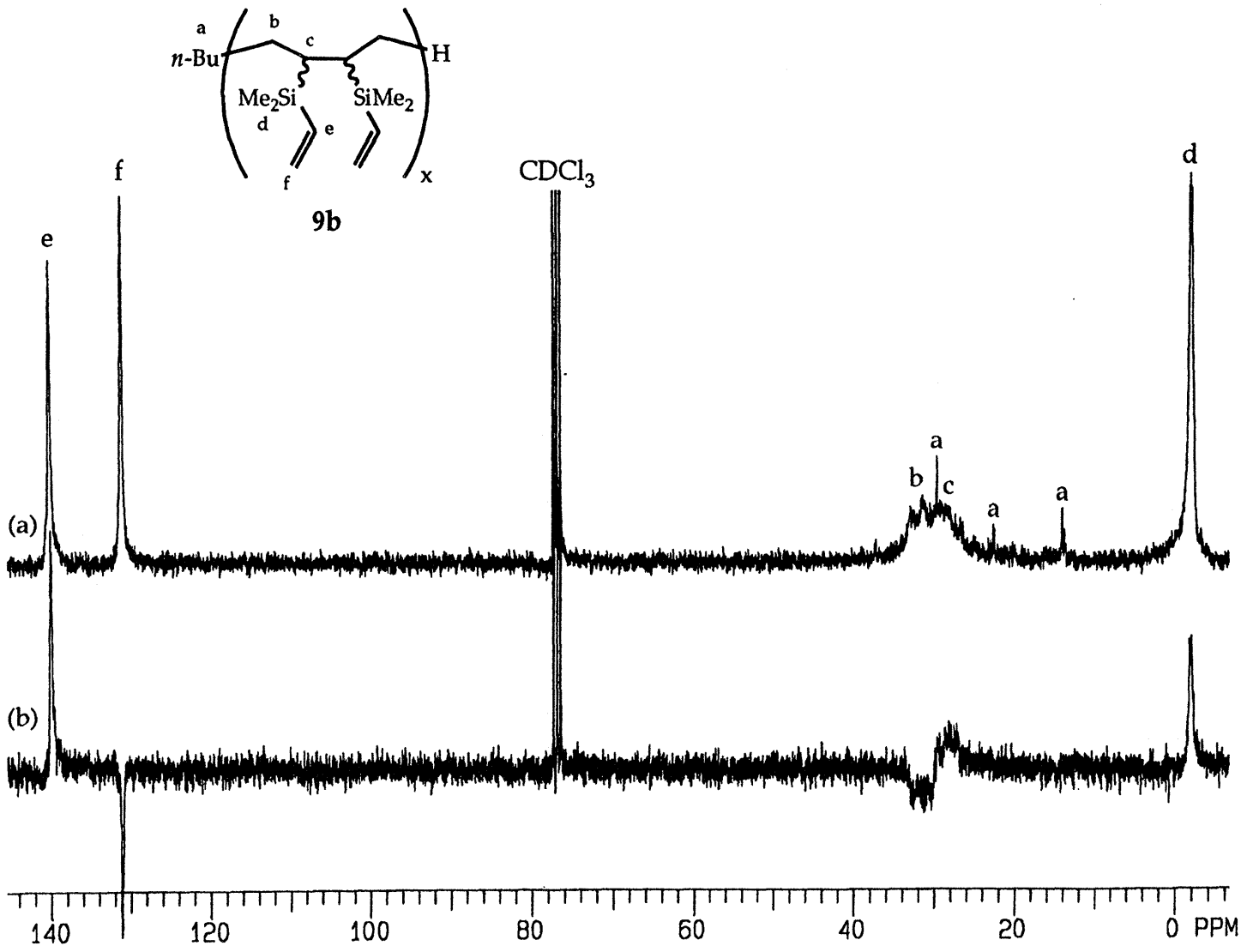


Figure 29. (a) ^{13}C and (b) ^{13}C DEPT (Mult = 1.5; CH, CH_3 up; CH_2 down) NMR Spectra of Polymer **9b**.

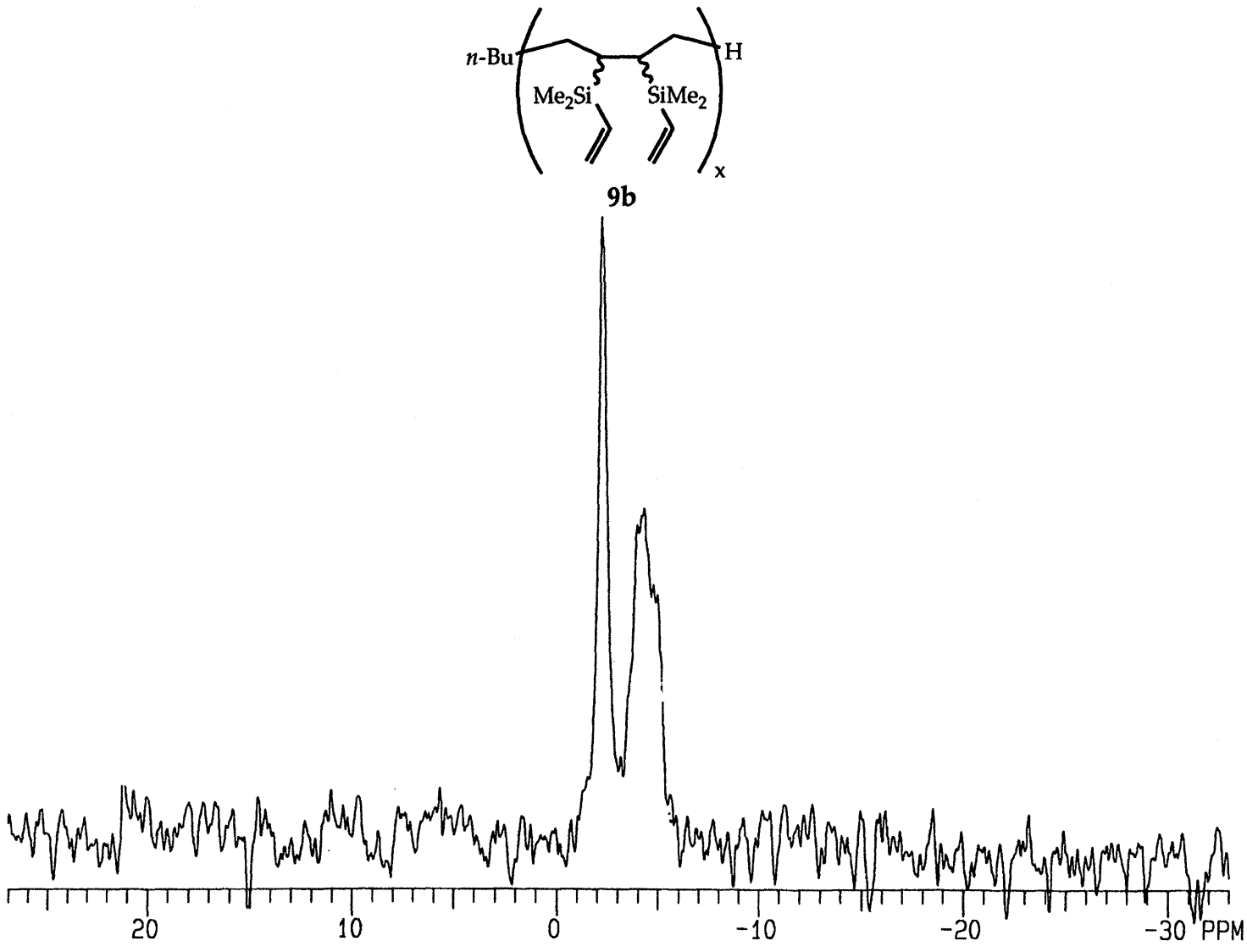
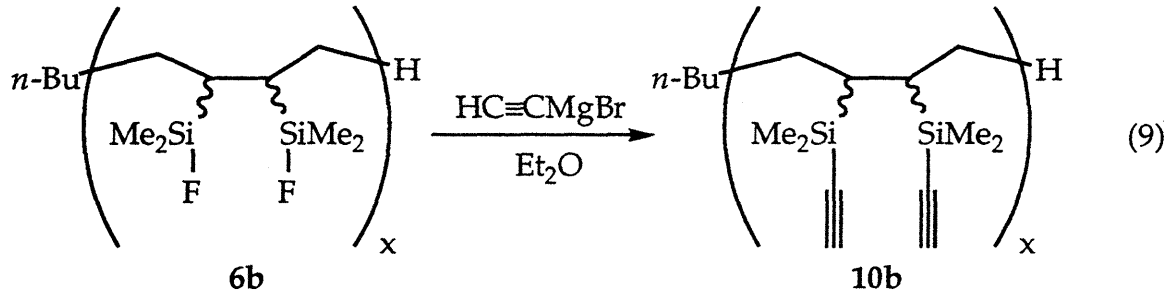


Figure 30. ^{29}Si NMR Spectrum of Polymer **9b**.

The final derivative of polymer **6b** was prepared by its reaction with ethynylmagnesium bromide in ether to give poly(vinylethynyldimethylsilane) **10b** in good yield. The high concentration of pendant polar groups on this polymer rendered it soluble in alcohols; the crude polymer was therefore purified by dissolving it in methanol and precipitating it by addition of water. Analysis by GPC showed a narrow monomodal distribution, indicating that no cross-linking reactions had occurred during its synthesis. The apparent molecular weight of **10b** was significantly lower than that of the parent polymer **6b**, despite the higher monomer molecular weight of **10b** and same average chain length.



6b **10b** (9)

The pendant acetylene groups of **10b** gave strong absorptions at 3290 and 2032 cm^{-1} in its IR spectrum. The acetylene proton appeared in the ^1H NMR spectrum of **10b** (Figure 31) as a broad singlet at 2.40 ppm. The $SiCH_3$ signal, a strong, relatively narrow singlet at 0.237 ppm, was virtually unshifted from its position in the parent polymer. The aliphatic backbone and endgroup signals had a similar appearance to those of the other derivatives of **6**.

Both acetylene carbons of **10b** were clearly visible in its ^{13}C NMR spectrum (Figure 32a), resonating at 90.23 and 95.09 ppm. The $SiCH_3$ signal was a strong, broad singlet. Four sharp endgroup signals appeared along with

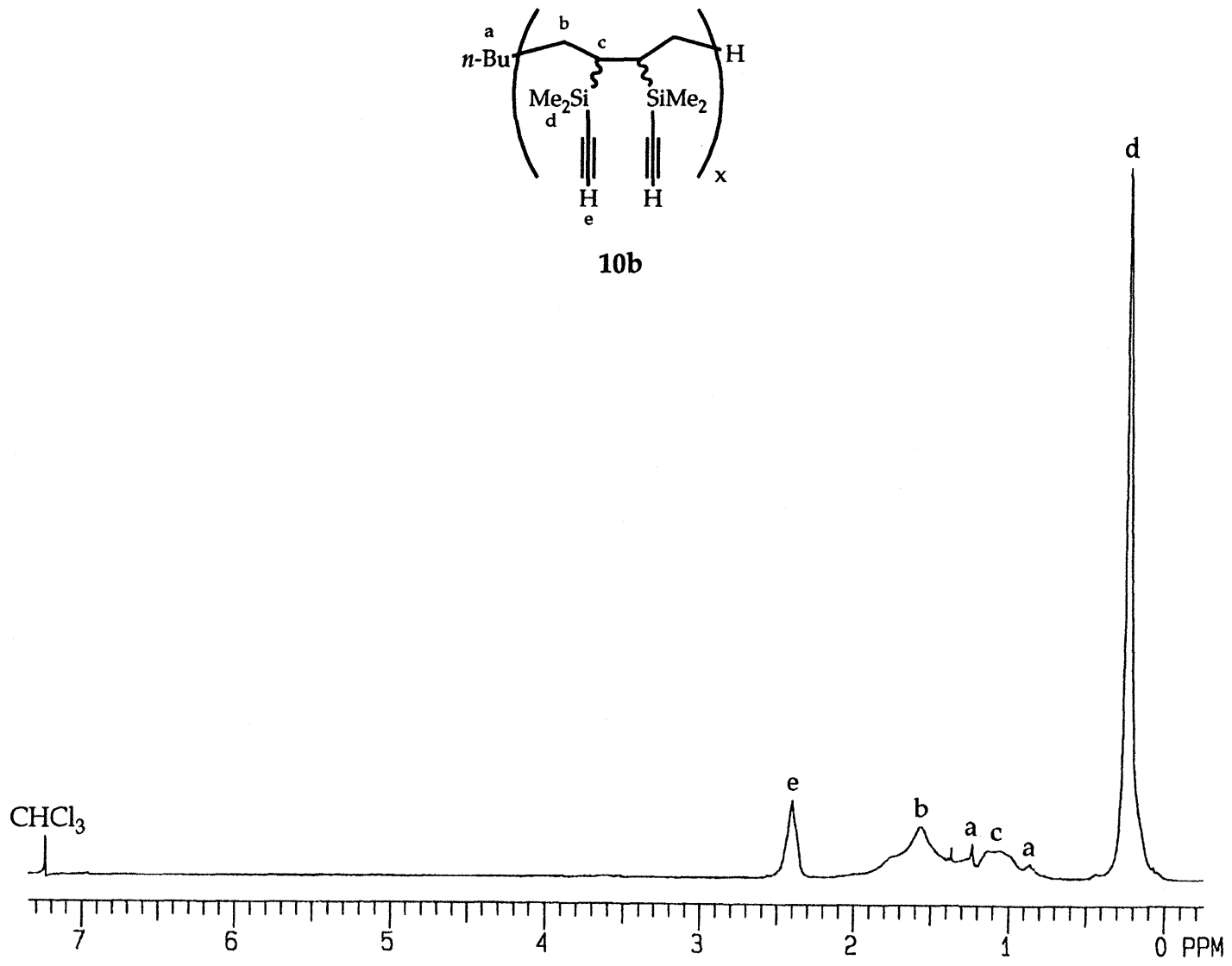


Figure 31. ^{1}H NMR Spectrum of Polymer **10b**.

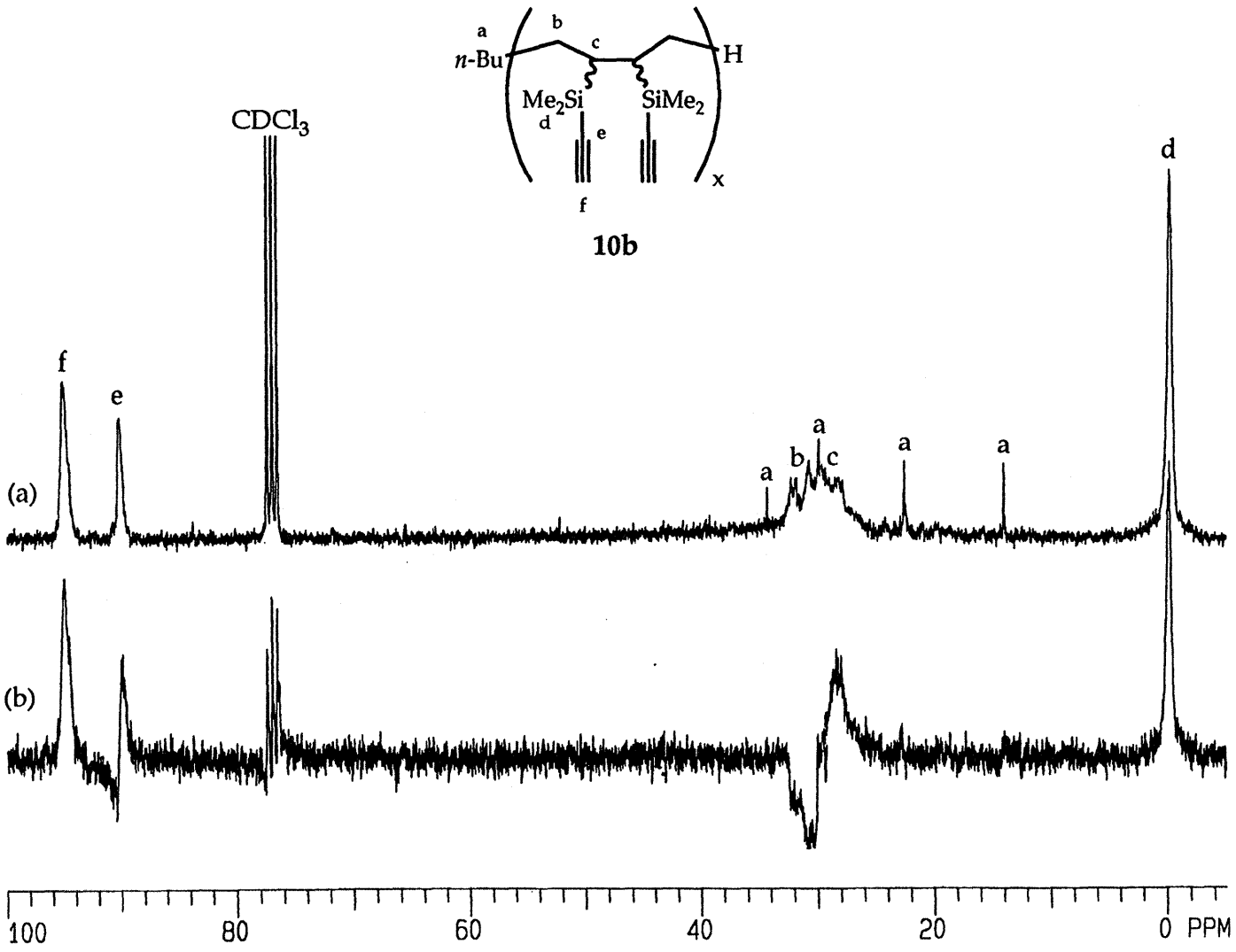
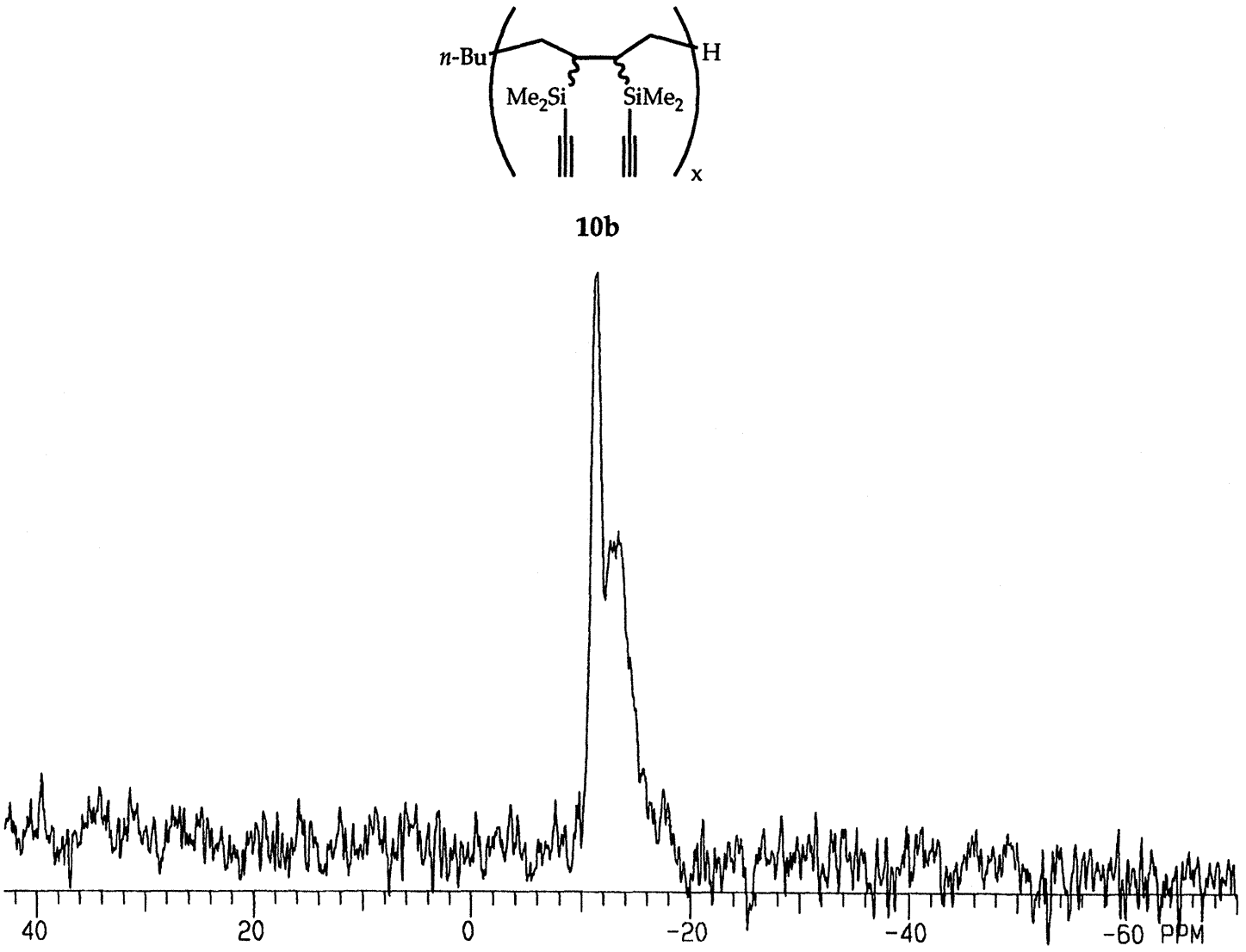


Figure 32. (a) ^{13}C and (b) ^{13}C DEPT (Mult = 1.5; CH, CH_3 up; CH_2 down) NMR Spectra of Polymer **10b**.



10b

Figure 33. ^{29}Si NMR Spectrum of Polymer **10b**.

broad silylmethine and methylene backbone signals in the aliphatic region. The backbone signals, assigned using a DEPT sequence (Figure 32b) were very similar in appearance to those of other derivatives of **6**. The ^{29}Si NMR spectrum of **10b** (Figure 33) exhibited the familiar pattern of a sharp, intense singlet downfield from a broader superposition of sharper resonances. The chemical shift difference between these two signals was less than in the spectra of **8b** (Figure 27) and **9b** (Figure 30).

These derivatization experiments served to demonstrate the usefulness of polymer **2** as an entry into the synthesis of a variety of polymers of the type $(CH_2CHSi(CH_3)_2R)_n$ having a regular microstructure consisting of alternating head-to-head and tail-to-tail monomer sequences. In this sense, the $NSi(CH_3)_3$ linking group in the **NTMS** monomer functions as a protecting group for two fluorosilane functional groups, while at the same time controlling the monomer addition sequence in the polymer. Using polymer **6** as a starting point, the syntheses of many interesting polymers with potentially useful applications should be possible.

CONCLUSIONS

The anionic polymerization of the **NMe** and **NTMS** monomers gives highly regular polymers which consist completely of linked cyclic units with no detectable cross-links or linear segments. The substituent of the nitrogen linking group profoundly affects the ring-size found in the resulting cyclopolymer, and hence the regularity of the polymer backbone: the **NTMS** monomer gives only five-membered rings in the polymer backbone, while the **NMe** monomer forms both five- and six-membered rings. The stereochemistry of the cyclization step was demonstrated for the polymerization of the **NTMS** monomer to be solvent-dependent; the ratio of

trans to *cis* five-membered rings formed increased with solvent composition in the following order: hexane/THF < hexane/triethylamine < hexane. The polymerization of the **NMe** monomer was marked by a termination step which limited the effective average degree of polymerization to approximately ten. The polymerization of the **NTMS** monomer was free from any significant termination reactions, except when the reaction was carried out in a hexane/THF solvent mixture. The polymerizations of the **NMe** and **NTMS** monomers proceeded without the isomerization reaction observed in the anionic polymerizations of other vinylsilanes.

Polymers **1** and **2** could be ring-opened with aqueous hydrofluoric acid to give poly(vinyldimethylfluorosilanes) **5** and **6**. These polymers demonstrated tacticities consistent with those of the parent cyclopolymers. Polymer **6** was derivatized with several nucleophilic reagents to give highly regular, highly functionalized polymers of the type $(CH_2CHSi(CH_3)_2R)_n$.

EXPERIMENTAL SECTION

General Comments

All reactions, unless otherwise noted, were performed under an argon atmosphere using standard Schlenk techniques. Glassware was oven-dried overnight, assembled while hot and cooled *in vacuo* before refilling with Ar. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from United Chemical Technologies and distilled from magnesium turnings before use. 1,3-Divinyltetramethyldisilazane was purchased from United Chemical Technologies and used as received. Organolithium and -magnesium reagents were purchased from Aldrich. The concentration of organolithium reagents was determined by the Gilman double titration method.[82] 1,3-

Divinylpentamethyldisilazane and
Bis(vinyldimethylsilyl)(trimethylsilyl)amine were prepared according to the procedures outlined in the Experimental Section of Chapter 1.

Proton NMR spectra were obtained on a Varian XL-300 NMR spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from tetramethylsilane. ^{13}C NMR spectra, proton decoupled and DEPT sequences, were obtained using a Varian XL-300 NMR spectrometer operating at 75.4 MHz using $CDCl_3/CHCl_3$ as a reference at 77.0 ppm downfield from tetramethylsilane. ^{19}F NMR spectra were obtained using a Varian XL-300 spectrometer operating at 282.2 MHz in $CDCl_3$ using $CFCl_3$ (0.0 ppm) as an external standard. ^{29}Si NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 59.59 MHz in $CDCl_3$ using tetramethylsilane (0.0 ppm) as the external standard. Infrared spectra were obtained on a Perkin Elmer 1600 Series FTIR. Gas chromatography (GC) was performed using an HP 5890 A gas chromatograph (10% SE-30 silicone gum on Chromosorb; thermal conductivity detector). 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) or a two column setup (Waters Ultrastyragel 10^4, 10^3 Å) using toluene as the eluent.

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

Cyclopolymerization Reactions

Cyclopolymerization of 1,3-Divinylpentamethyldisilazane with 10 mol% n-BuLi in Hexane/Triethylamine (SWK VI/38b)

The monomer (2.03 g, 10.2 mmol) was combined with 0.4 mL of dibutylmagnesium (1.0 M in heptane) in a 10 mL round-bottomed flask equipped with a magnetic stir bar and connected through a glass tube to a 50 mL three-necked, round-bottomed flask equipped with a magnetic stir bar and two vacuum line adaptors. Hexane (8 mL), triethylamine (1 mL) and *n*-BuLi (0.6 mL; 2.5 M in hexane) were introduced into a 25 mL round-bottomed flask containing a magnetic stir bar and connected to the three-necked flask through a short length of rubber tubing. The contents of the 10 mL and 25 mL flasks were successively vacuum-transferred into the three-necked flask, which had been cooled to -78 °C. After completion of these transfers, the apparatus was refilled with Ar and warmed to room temperature. *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 three days of stirring at room temperature, the reaction was terminated with 0.5 mL anhydrous methanol. All volatiles were removed at reduced pressure, leaving a white solid which was dissolved in *ca.* 8 mL of toluene and precipitated by adding to 200 mL of well-stirred, anhydrous methanol. The product **1a**, a white powder, was collected by suction filtration and dried for 14 h at 0.005 torr. Yield: 1.83 g (87%). Anal. Calcd for $C_9H_{21}NSi_2$ + 0.1 C_4H_{10} (205.256 g/mol): C, 55.01; H, 10.80%. Found: C, 54.63; H, 10.74%.

^{1}H NMR ($CDCl_3$): δ -0.1 (br), -0.03 (br), 0.05 (br) (12 H, $SiCH_3$); 0.4 - 0.7 (br; CH, CH_2), 0.8 - 2.0 (br; CH, CH_2), 0.87 (m, *n*-pentyl CH_3), 1.24 (br s, *n*-pentyl CH_2) (7 H); 2.39 (s, 3 H, NCH_3).

^{13}C DEPT NMR ($CDCl_3$): δ -5.23 (s), -3.41 (br), -2.0 (br), -0.9 (br), -0.06 (s) ($SiCH_3$); 14.2 (s, *n*-pentyl CH_3); 22.6, 22.7 (s, *n*-pentyl $CH_3\underline{C}H_2$); 25.5 (br), 28.0 (br), 31.5 (br), 34.8 (br) (CH, CH_2); 26.91, 27.02, 28.97 (s, NCH_3); 32.35 (s, *n*-pentyl $CH_3CH_2\underline{C}H_2$).

^{29}Si NMR ($CDCl_3$): δ 7.4 (br s, six-membered rings); 13.7 (br s, *cis* five-membered rings), 14.1 (br s) (overlapped, *trans* five-membered rings).

GPC (10^4, 10^3 Å columns): M_w = 7230, M_n = 4770, D = 1.52.

IR (NaCl disk): 2950 (s, ν_{as} $SiCH_3$), 2905 (s, ν_s $SiCH_3$), 2856 (s, ν_{as} aliphatic CH_2), 2849 (m, ν_s NCH_3), 2805 (m, ν_s NCH_3), 1458 (w, δ_{as} CH_3), 1405 (w, δ_{as} CH_3), 1248 (vs, δ_s $SiCH_3$), 1186 (w, ν NC), 1142 (s), 1075 (s, ρ NCH_3), 908 (vs, ν_{as} SiNSi), 882 (vs, ρ $SiCH_3$), 829 (vs, ρ $SiCH_3$), 790 (m), 767 (vs), 677 (w).

Cyclopolymerization of Bis(vinyldimethylsilyl)(trimethylsilyl)amine with 5 mol% n-BuLi in Hexane/Triethylamine (SWK VI/51a)

The monomer (2.58 g, 10.0 mmol) was charged into a 100 mL Schlenk flask equipped with a magnetic stir bar and vacuum line adaptor. Hexane (8 mL), triethylamine (1 mL) and *n*-BuLi (0.4 mL; 2.5 M in hexane) were introduced into the reaction vessel in the same way as described in the above procedure. *n*-BuLi (0.20 mL; 2.5 M; 0.50 mmol; 5.0 mol %) was added via syringe, resulting in a light yellow solution. After three days of stirring, the reaction was terminated with 0.5 mL of anhydrous methanol. All volatiles were removed at reduced pressure, leaving a white solid which was dissolved in *ca.*5 mL of toluene and precipitated by adding to 150 mL of well-stirred, anhydrous methanol. The product **2b**, a white powder, was collected by suction filtration and dried for 15.5 h at 0.002 torr. Yield: 2.58 g (99%). Anal. Calcd for $C_{11}H_{27}NSi_3$ + 0.05 C_4H_{10} (260.505 g/mol): C, 51.64; H, 10.64%. Found: C, 51.70; H, 10.58%.

^{1}H NMR ($CDCl_3$): δ 0.027 (s, $Si(CH_3)_2$), 0.087 (s, $Si(CH_3)_3$), 0.19 (br, $Si(CH_3)_2$) (21 H); 0.48 (br; 1 H; CH, CH_2); 0.87 (m, *n*-pentyl CH_3), 1.10 (br; CH, CH_2), 1.25 (br, *n*-pentyl CH_2), 1.37 (br; CH, CH_2), 1.64 (br; CH, CH_2), 1.74 (br; CH, CH_2) (5.5 H).

^{13}C NMR ($CDCl_3$): δ -0.3 (br, $Si(CH_3)_2$), 1.2 (br, $Si(CH_3)_2$), 2.9 (br, $Si(CH_3)_2$), 3.75 (s, $Si(CH_3)_3$), 4.2 (br, $Si(CH_3)_2$), 14.2 (s, *n*-pentyl CH_3), 22.6 (s, *n*-pentyl $CH_3\underline{C}H_2$), 25.5 - 30.0 (br; *cis* CH, CH_2), 31.4 - 32.8 (br; *trans* CH, CH_2), 32.3 (s, *n*-pentyl $CH_3CH_2\underline{C}H_2$).

^{29}Si NMR ($CDCl_3$): δ 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).

GPC (10^4, 10^3, 60 Å columns): M_w = 12900 , M_n =12200, D = 1.15 .

IR (NaCl disk): 2953 (s, ν_{as} CH_3), 2905 (m, ν_s CH_3), 2853 (m, ν_{as} aliphatic CH_2), 1405 (w, δ_{as} CH_3), 1251 (vs, δ_s $SiCH_3$), 964 (vs, ν_{as} Si_3N), 899 (vs, ρ $SiCH_3$), 836 (s, ρ $SiCH_3$), 795 (m), 771 (m), 679 (w).

Cyclopolymerization of Bis(vinyldimethylsilyl)(trimethylsilyl)amine with 5 mol% n-BuLi in Hexane (SWK VI/16)

The procedure for the cyclopolymerization of the monomer in hexane/triethylamine was followed, except that 9 mL of hexane was used as solvent in place of the hexane/triethylamine solvent mixture. After three days of stirring, the reaction was terminated with 0.5 mL of anhydrous methanol. All volatiles were removed at reduced pressure, leaving a white solid which was dissolved in *ca.* 10 mL of toluene and precipitated by adding to 200 mL of well-stirred anhydrous methanol. The product **2e**, a white powder, was collected by suction filtration and dried for 17.5 h at 0.002 torr. Yield: 2.57 g (99%).

The spectroscopic data for **2e** are the same as those of **2b**, except for the differences described in the section entitled Co-solvent Dependence in the Polymerization of the **NTMS** Monomer.

GPC (10^4, 10^3, 60 Å columns): M_w = 12200, M_n = 10900, D = 1.12.

Cyclopolymerization of Bis(vinyldimethylsilyl)(trimethylsilyl)amine with 5 mol% n-BuLi in Hexane/THF (SWK VI/19)

The procedure for the cyclopolymerization of the monomer in hexane/triethylamine was followed, except using 2.57 g of monomer (9.98 mmol), and 8 mL of hexane and 1 mL of THF as solvents in place of the hexane/triethylamine solvent mixture. After three days of stirring, the reaction was terminated with 0.5 mL of anhydrous methanol. All volatiles were removed at reduced pressure, leaving a white solid which was dissolved in *ca.* 8 mL of toluene and precipitated by adding to 250 mL of well-stirred anhydrous methanol. The product **2f**, a white powder, was collected by suction filtration and dried for 20.25 h at 0.002 torr. Yield: 2.52 g (97%).

The spectroscopic data for **2f** are the same as those of **2b**, except for the differences described in the section entitled Co-solvent Dependence in the Polymerization of the **NTMS** Monomer.

GPC (10^4, 10^3, 60 Å columns): M_w = 7740, M_n = 6260, D = 1.24.

Model Anionic Cyclization Reactions

Reaction of 1,3-Divinylpentamethyldisilazane with an Excess of n-BuLi (SWK IV/27)

Hexane (350 mL), triethylamine (10 mL) and *n*-BuLi (20.0 mL; 2.0 M in cyclohexane; 40.0 mmol) were combined in a 500 mL Schlenk flask equipped

with a stir bar and a rubber septum. 1,3-Divinylpentamethyldisilazane (4.8 mL, 4.0 g, 20.0 mmol) was added to the mixture via syringe, one drop at a time, over the course of two days. 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, yielding a slightly yellow liquid (0.73 g) boiling at 67.5°C. A second fraction (0.90 g) was collected boiling at 89°C, and a third (1.29 g) at 140°C. A viscous, yellow residue (1.79 g) remained in the distillation pot. Analysis by GC/MS showed the first fraction consisted entirely of the desired monocyclic products (three isomers) and the other fractions contained higher MW compounds. By use of preparative GC (isothermal; column temperature = 200 °C) pure samples of the five- and six-membered rings (**3a** and **3b**, respectively) were isolated for spectroscopic analysis (it was not possible to separate the two five-membered ring isomers). Yield: 0.73 g (14%). Anal. Calcd for $C_{13}H_{31}NSi_2$ (257.566 g/mol) (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* ***3a***

^{1}H NMR ($CDCl_3$): 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, $SiCHC\underline{H}_3$), 0.95 (d, J = 7 Hz, 3 H, $SiCHC\underline{H}_3$), 1.08 (m, 1 H, SiCH), 1.12 - 1.4 (br, 16 H; *n*-pentyl CH_2), 1.4 (br, 4 H, $C\underline{H}_2CH_2CH_2CH_2CH_3$), 1.7 (m, 1 H, SiCH), 2.41 (s, 6 H, NCH_3).

^{13}C DEPT NMR ($CDCl_3$): δ -3.93, -3.80, -3.73, -2.20, -1.65, -1.56, -0.74, -0.27 ($SiCH_3$); 11.62 (*cis* $SiCH\underline{C}H_3$); 14.33 (*trans* $SiCH\underline{C}H_3$); 14.14, 14.20 (*n*-pentyl

CH_3); 18.95 (*cis* Si<u>C</u>HCH_3); 22.80 (*trans* Si<u>C</u>HCH_3); 27.74 (*cis* Si<u>C</u>HCH_2); 31.36 (*trans* Si<u>C</u>HCH_2); 22.67, 22.77 ($CH_2CH_2CH_2\underline{C}H_2CH_3$); 26.97, 27.03 ($NCH_3$); 29.31 (*trans* <u>C</u>$H_2CH_2CH_2CH_2CH_3$); 30.00, 30.53 ($CH_2\underline{C}H_2CH_2CH_2CH_3$); 32.29, 32.45 ($CH_2CH_2\underline{C}H_2CH_2CH_3$).

^{29}Si NMR ($CDCl_3$): 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 3b

^{1}H NMR ($CDCl_3$): 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 (ddd, J^1 = 14 Hz, J^2 = 6 Hz, J^3 = 3 Hz, 1 H, $SiCH_2$), 0.87 (t, 3 H, *n*-pentyl CH_3), 1.05 - 1.35 (br, 9 H, $SiCH_2$, *n*-pentyl CH_2), 1.41 (qm, J^1 = 13 Hz, J^2 = 2 Hz, 2 H, <u>C</u>$H_2CH_2CH_2CH_2CH_3$), 1.87 (m, J = 3 Hz, 1 H), 2.37 (3 H, NCH_3).

^{13}C DEPT NMR ($CDCl_3$): δ -4.97, -2.21, -1.90, -1.12 ($SiCH_3$); 14.14 (*n*-pentyl CH_3); 15.30 (Si<u>C</u>H_2CH_2CHSi); 22.70 ($CH_2CH_2CH_2\underline{C}H_2CH_3$); 23.82 ($SiCH_2$-<u>C</u>$H_2CHSi$); 28.03 (SiCH); 28.69 (<u>C</u>$H_2CH_2CH_2CH_2CH_3$); 28.75 (NCH_3); 30.63 ($CH_2\underline{C}H_2CH_2CH_2CH_3$); 32.14 ($CH_2CH_2\underline{C}H_2CH_2CH_3$).

^{29}Si NMR ($CDCl_3$): 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 Bis(vinyldimethylsilyl)(trimethylsilyl)amine with an Excess of n-*BuLi (SWK IV/32)*

Hexane (350 mL), triethylamine (10 mL) and *n*-BuLi (17.4 mL; 2.0 M in cyclohexane; 34.8 mmol) were combined in a 500 mL Schlenk flask equipped with a magnetic stir bar, rubber septum and pressure-equalizing dropping funnel. Bis(vinyldimethylsilyl)(trimethylsilyl)amine (4.48 g, 17.4 mmol) was charged into the dropping funnel and dissolved in *ca.* 75 mL of hexane, and the resulting solution was added slowly to the vigorously stirred reaction mixture over the course of 8.5 h. Upon completion of the addition, the reaction mixture was stirred for 12 h and then quenched with 1.5 mL (1.2 g, 37 mmol) of anhydrous methanol. The resulting mixture was filtered through a glass frit containing Celite, washing with three 20 mL portions of hexane. Removal of solvents at reduced pressure left a yellow oil which was distilled at 0.005 torr, yielding a colorless liquid (0.59 g) boiling at 99-100°C. A second fraction (0.24 g) was collected boiling at 120°C. A viscous, yellow residue (4.87 g) remained in the distillation pot. Analysis by GC/MS showed the first fraction consisted entirely of the desired monocyclic products **4** (two isomers); the second fraction contained higher MW compounds. Yield: 0.59 g (11%). Anal. Calcd for $C_{15}H_{37}NSi_3$ (315.722 g/mol) (mixture of isomers): C, 57.06; H, 11.81%. Found: C, 57.25; H, 11.82%.

^{1}H NMR ($CDCl_3$): 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, $SiCHC\underline{H}_3$), 1.08 (q, J = 7 Hz, 1 H, $SiC\underline{H}CH_3$), 1.2 - 1.4 (br, 12 H, $CH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 1.42 (br, 4 H, $SiCHC\underline{H}_2$), 1.72 (m, 1 H, SiCH).

^{13}C DEPT NMR ($CDCl_3$): δ -0.89, -0.47, 0.30, 1.59, 1.73, 1.96, 3.43, 4.14 ($Si(CH_3)_2$); 3.65, 3.69 ($Si(CH_3)_3$); 11.11 (*cis* $SiCH\underline{C}H_3$); 14.06 (*trans* $SiCH\underline{C}H_3$); 14.29, 14.33

($CH_2CH_2CH_2CH_2\underline{C}H_3$); 19.63 (*cis* $Si\underline{C}HCH_3$); 24.16 (*trans* $Si\underline{C}HCH_3$); 28.52 (*cis* $Si\underline{C}HCH_2$); 31.82 (*trans* $Si\underline{C}HCH_2$); 22.82, 22.93 ($CH_2CH_2CH_2\underline{C}H_2CH_3$); 26.32 (*cis* $\underline{C}H_2CH_2CH_2CH_2CH_3$); 29.32 (*trans* $\underline{C}H_2CH_2CH_2CH_2CH_3$); 30.12, 30.63 ($CH_2\underline{C}H_2CH_2CH_2CH_3$); 32.44, 32.73 ($CH_2CH_2\underline{C}H_2CH_2CH_3$).

^{29}Si NMR ($CDCl_3$): 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}.

Polymer Derivatization Reactions

*Reaction of Cyclopolymer **1a** with HF(aq) (SWK VI/47a)*

Polymer **1a** (1.59 g, 7.75 mmol) was dissolved in 30 mL of diethyl ether and 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. (**NOTE**: Extreme caution should be exercised (i.e. wearing a lab apron, long rubber gloves and face shield, and having a supply of calcium gluconate lotion nearby) when handling 49% aqueous HF.)[83] After stirring for 1 h, the reaction mixture was transferred into a separatory funnel where it was washed four times with 20 mL portions of sat. $NaHCO_3$(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 **5a** as a clear, colorless, viscous oil. Yield: 1.51 g (91%). Anal. Calcd for C_4H_9FSi + 0.05 C_4H_{10} (107.106 g/mol): C, 47.10; H, 8.94%. Found: C, 47.69; H, 9.05%.

^{1}H NMR ($CDCl_3$): δ 0.20, 0.23 (s, overlapped, 6 H, $SiCH_3$); 0.87 (br t, 0.15 H, *n*-pentyl CH_3); 1.05 (br, 1 H, SiCH); 1.24 (br, *n*-pentyl CH_2), 1.55 (br; $SiCHC\underline{H}_2$) (2.3 H).

^{19}F NMR ($CDCl_3$) δ -161.43 (br), -158.97 (s), -157.69 (s).

^{13}C DEPT NMR ($CDCl_3$): δ -2.36, -0.78 (br s, $SiCH_3$); 14.14 (s, *n*-pentyl CH_3); 22.59 (s, *n*-pentyl $CH_3\underline{C}H_2$); 24.2 (br, CH); 26.3 (br, CH); 27.5 (br, CH); 28.6 (br, CH); 29.8 (br, CH_2); 32.07, 32.28, 32.4 (s, *n*-pent CH_2).

^{29}Si NMR ($CDCl_3$): δ 32.36 (br d, 1Si, J_{SiF} = 287 Hz), 33.61 (br d, ~0.4 Si, J_{SiF} = 286 Hz).

GPC (10^4, 10^3 Å columns): M_w = 4860, M_n = 2750, D = 1.77.

IR (NaCl disk): 2961 (s, ν_{as} CH_3), 2920 (s, ν_s CH_3), 2852 (s, ν_{as} aliphatic CH_2), 1454 (w, δ_{as} CH_3), 1408 (w, δ_{as} CH_3), 1256 (vs, δ_s $SiCH_3$), 1059 (w), 864 (vs, ρ $SiCH_3$), 835 (vs, ρ $SiCH_3$), 784 (vs), 761 (s), 692 (m).

Reaction of Cyclopolymer **2c** *with HF(aq) (SWK V/70)*

Polymer **2c** (1.27 g, 4.89 mmol) was reacted with 5 mL of aqueous HF (49%) according to the procedure outlined above. The product **6c**, a clear, tacky solid, was dried for 13 h at 0.005 torr. Yield: 0.88 g (85%). Anal. Calcd for C_4H_9FSi + 0.02 C_4H_{10} (105.362 g/mol): C, 46.51; H, 8.80%. Found: C, 46.39; H, 8.80%.

^{1}H NMR ($CDCl_3$): δ 0.22, 0.24, 0.26 (s, overlapped, 6 H, $SiCH_3$); 0.87 (m, *n*-pentyl CH_3), 1.01 (br, CH) (1.1 H); 1.20 - 1.70 (br; 2.1 H; CH_2, *n*-pentyl CH_2).

^{19}F NMR ($CDCl_3$) δ -159.45 (br), -158.75 (br s), -157.64 (s), -157.17 (s).

^{13}C DEPT NMR ($CDCl_3$): δ -0.85 (br, $SiCH_3$); 14.2 (s, *n*-pentyl CH_3); 22.6 (s, *n*-pentyl $CH_3\underline{C}H_2$); 28.3 (br, CH); 29.4, 30.0 (br, CH_2); 32.0, 32.3 (s, *n*-pentyl CH_2).

^{29}Si NMR ($CDCl_3$): δ 32.83 (d, 1 Si, J_{SiF} = 285 Hz), 33.92 (d, ~0.78 Si, J_{SiF} = 287 Hz).

GPC (10^4, 10^3, 60 Å columns): M_w = 7850, M_n = 6850, D = 1.15.

IR (NaCl disk): 2959 (m, ν_{as} CH_3), 2925 (m, ν_s CH_3), 2856 (m, ν_{as} aliphatic CH_2), 1463 (w, δ_{as} CH_3), 1406 (w, δ_{as} CH_3), 1256 (vs, δ_s $SiCH_3$), 862 (vs, ρ $SiCH_3$), 840 (vs, ρ $SiCH_3$), 787 (s), 690 (m), 643 (m).

*Reaction of Poly(vinyldimethylfluorosilane) **6c** with $LiAlH_4$ (SWK VI/17)*

A solution of 1.356 g (12.87 mmol) polymer **6c** in 20 mL of diethyl ether was carefully added via cannula to 1.45 g (38.2 mmol) $LiAlH_4$ 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 very carefully hydrolyzed by the slow addition of water to the reaction flask. The organic layer was separated and washed twice with water; 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 **7c**, a clear, colorless oil, was dried for 39.5 h on the vacuum line. Yield: 0.853 g (76%). Anal. Calcd for $C_4H_{10}Si$ + 0.02 C_4H_{10} (87.371 g/mol): C, 56.09; H, 11.77%. Found: C, 56.60; H, 11.69%.

^{1}H NMR ($CDCl_3$): δ 0.082 (d,^{3}J = 4 Hz, 6 H, $SiCH_3$), 0.89 (br; 1.1 H; CH, *n*-pentyl CH_3); 1.25 (br s, 0.2 H, *n*-pentyl CH_2), 1.42 (br s, 2 H, CH_2), 3.90 (br s, J_{SiH} = 182 Hz, 1 H, SiH).

^{13}C DEPT NMR ($CDCl_3$): δ -3.91, -3.25 (s, $SiCH_3$); 14.2 (s, *n*-pentyl CH_3); 22.6 (s, *n*-pentyl $CH_3\underline{C}H_2$); 27.8 (br, CH); 29.8 (s), 30.6 (br), 31.2 (br) (CH_2).

^{29}Si NMR ($CDCl_3$): δ -10.95, -10.63, -10.06, -9.43 (br, overlapped).

GPC (10^4, 10^3, 60 Å columns): M_w = 8740, M_n = 8230, D = 1.06.

IR (NaCl disk): 2954 (s, ν_{as} CH_3), 2914 (s, ν_s CH_3), 2850 (s, ν_{as} aliphatic CH_2), 2104 (vs, ν_s SiH), 1458 (w, δ_{as} CH_3), 1416 (w, δ_{as} CH_3), 1248 (vs, δ_s $SiCH_3$), 885 (vs, ρ $SiCH_3$), 833 (s, ρ $SiCH_3$), 757 (s), 695 (m), 632 (w).

*Reaction of Poly(vinyldimethylfluorosilane) **6b** with MeLi (SWK V/1)*

Polymer **6b** (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 sat. $NaHCO_3$ (aq). The organic layer was separated, washed twice with distilled water, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed at reduced pressure; the residue was dissolved in *ca.* 5 mL of toluene and precipitated by adding to 175 mL of well-stirred anhydrous methanol. The product **8b**, a white powder, was collected by suction filtration and dried *in vacuo* for 18 h. Yield: 0.626 g (93%). Anal. Calcd for $C_5H_{12}Si$ + 0.025 C_4H_{10} (101.689 g/mol): C, 60.24; H, 12.14%. Found: C, 60.12; H, 12.04%.

^{1}H NMR ($CDCl_3$): δ -0.004, 0.012 (s, 9 H, $SiCH_3$); 0.65 - 0.90 (br; 1.1 H; CH, *n*-pentyl CH_3); 1.10 - 1.60 (br; 2.2 H; CH_2, *n*-pentyl CH_2).

^{13}C DEPT NMR ($CDCl_3$): δ 0.10 (br s, $SiCH_3$); 14.2 (s, *n*-pentyl CH_3); 22.8 (s, *n*-pentyl $CH_3\underline{C}H_2$); 27.8, 30.6 (br, CH); 31.5, 33.0 (br, CH_2).

^{29}Si NMR ($CDCl_3$): δ 2.01, 2.36, 2.71(s, overlapped); 4.61 (s).

GPC (10^4, 10^3, 60 Å columns): M_w = 9160, M_n = 8390, D = 1.09.

IR (NaCl disk): 2951 (s, ν_{as} CH_3), 2852 (s, ν_{as} aliphatic CH_2), 1444 (m, δ_{as} CH_3), 1404 (m, δ_{as} CH_3), 1247 (s, δ_s $SiCH_3$), 908 (s, ρ $SiCH_3$), 832 (s, br, ρ $SiCH_3$), 748 (s), 684 (s).

*Reaction of Poly(vinyldimethylfluorosilane) **6b** with CH_2=CHLi (SWK VI/55)*

Vinyllithium was prepared by the reaction of tetravinyltin (2.30 g; 12.1 mmol) with *n*-BuLi (8.10 mL; 2.5 M; 20.3 mmol) in hexane (50 mL) solution at room temperature in a 200 mL Schlenk flask.[84] The white solid product was collected on a Schlenk frit, washed with 20 mL of hexane, dissolved in 60 mL of diethyl ether and added to a 200 mL Schlenk flask containing 0.854 g (8.08 mmol) of polymer **6b** in 20 mL of diethyl ether. The reaction mixture was stirred at room temperature for 2 days. For workup, the reaction was poured into 100 mL of sat. NH_4Cl (aq) and the organic layer was separated and washed twice with 25 mL portions of water. The aqueous layer was back-extracted twice with 30 mL portions of ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and dried at reduced pressure, leaving a white solid which was dissolved in *ca.* 8 mL of toluene and precipitated by adding to 200 mL of well-stirred, anhydrous methanol. The product **9b**, a white powder, was collected by suction filtration and dried for 29 h at 0.02 torr. Yield: 0.81 g (88%). Anal. Calcd for $C_6H_{12}Si$ + 0.025 C_4H_{10} (113.700 g/mol): C, 64.44; H, 10.86%. Found: C, 64.21; H, 10.99%.

^{1}H NMR ($CDCl_3$): δ 0.081 (s, 6 H, $SiCH_3$), 0.87 (br; 1.1 H; CH, *n*-pentyl CH_3), 1.0 - 1.8 (br; 2.2 H; CH_2, *n*-pentyl CH_2), 5.63 (br d, J_{gem} = 19 Hz, 1 H, SiCH=C$\underline{H}_2$ (*trans* to Si)), 5.91 (br d, J_{trans} = 13 Hz, 1 H, SiC$\underline{H}$=CH_2), 6.15 (br dd, 1 H, SiCH=C$\underline{H}_2$ (*cis* to Si)).

^{13}C DEPT NMR ($CDCl_3$): δ -1.88 (br s, $SiCH_3$); 14.2 (s, *n*-pentyl CH_3); 22.8 (s, *n*-pentyl $CH_3\underline{C}H_2$); 25.5 - 30.0 (br, CH); 26.5, 26.9, 29.8 (s, *n*-pentyl CH_2); 31.4, 32.8 (br, CH_2); 131.28 (br s, $SiCH=\underline{C}H_2$);140.31 (br s, $Si\underline{C}H=CH_2$).

^{29}Si NMR ($CDCl_3$): δ -4.2 (br, 1.2 Si), -2.25 (s, 1 Si).

GPC (10^4, 10^3, 60 Å columns): M_w = 23500, M_n = 13300, D = 1.76 (multimodal).

IR (NaCl disk): 3045 (m, ν_{as} $CH=CH_2$), 3007 (w, ν_s $CH=CH_2$), 2952 (s, ν_{as} CH_3), 2852 (m, ν_{as} aliphatic CH_2), 1898 (w, $CH=CH_2$ overtone), 1590 (w, ν_s C=C), 1457 (w, δ_{as} CH_3), 1403 (m; δ_{as} CH_3, δ $CH=CH_2$), 1247 (s, δ_s $SiCH_3$), 1009 (m, δ $CH=CH_2$), 948 (s, ρ $SiCH_3$), 828 (vs, ρ $SiCH_3$), 765 (s), 695 (m), 522 (w).

*Reaction of Poly(vinyldimethylfluorosilane) **6d** with $CH_2=CHMgBr$ (SWK VI/42)*

A solution of 0.95 g (9.06 mmol) polymer **6d** in 5 mL of THF was added to 28.0 mL (0.98 M in THF, 27 mmol) of $CH_2=CHMgBr$ solution in a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa. The mixture was stirred at room temperature and monitored by ^{1}H NMR. After 7 days, the reaction was only 81% complete, so another 9.4 mL (0.98 M, 9.2 mmol) of $CH_2=CHMgBr$ solution was added and the reaction mixture heated to reflux. After 3 days at reflux, an aliquot showed nearly quantitative conversion by ^{1}H NMR. The reaction mixture was heated at reflux for another 2 days, then cooled to room temperature and poured into sat. NH_4Cl (aq). Hexane (100 mL) was added, and the organic layer separated and washed twice with 50 mL portions of distilled water; the aqueous layer was back-extracted once with 50 mL hexane. The organic layers were combined and dried over anhydrous $MgSO_4$, filtered, and dried at reduced pressure. The resulting oil was taken up in 5 mL of toluene and precipitated from 150 mL of well-stirred, anhydrous methanol.

The product **9d**, a white solid, was collected by suction filtration and dried for 17.5 h at room temperature and 0.002 torr. Yield: 0.650 g (112.886 g/mol; 64%).

The spectroscopic properties of polymer **9d** were essentially identical to those of the polymer (**9b**) prepared from the reaction of **6b** with CH_2=CHLi. **GPC** (10^4, 10^3, 60 Å columns): M_W = 26400, M_n = 15800, D = 1.67 (multimodal).

*Reaction of Poly(vinyldimethylfluorosilane) **6b** with HC≡CMgBr (SWK VI/54)*

Polymer **6b** (0.854 g, 8.08 mmol) as a solution in 10 mL of THF was combined with 46.0 mL of HC≡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 hydrolyzed with 100 mL of sat. NH_4Cl (aq). Diethyl ether (50 mL) was added, and the organic layer separated and washed twice with 50 mL portions of distilled water. The aqueous layer was back-extracted twice with 25 mL portions of ether. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. Removal of all volatiles at reduced pressure left a brown solid which was taken up in *ca.* 20 mL of methanol and precipitated from 225 mL of well-stirred water . The product **10b**, a tan powder, was collected by suction filtration and dried for 16.25 h at 0.02 torr. Yield: 0.88 g (98%). Anal. Calcd for $C_6H_{10}Si$ + 0.025 C_4H_{10} (111.684 g/mol): C, 65.60; H, 9.25%. Found: C, 65.14; H, 9.40%.

^{1}H NMR ($CDCl_3$): δ 0.24 (br s, 6 H, $SiCH_3$); 0.87 (m, *n*-pentyl CH_3), 1.05 (br, CH), 1.24 (br s, *n*-pentyl CH_2), 1.55 (br, CH_2) (3.3 H); 2.40 (br s, 1 H, C≡CH).

^{13}C DEPT NMR ($CDCl_3$): δ -0.19 (br s, $SiCH_3$); 14.2 (s, *n*-pentyl CH_3); 22.6 (s, *n*-pentyl $CH_3\underline{C}H_2$); 25.5 - 30.0 (br, CH); 29.67 (s, *n*-pentyl CH_2); 30.7 (br), 32.0 (br) (overlapped, CH_2); 34.3 (s, *n*-pentyl CH_2); 90.23 (br s, $Si\underline{C}{\equiv}CH$); 95.09 (br s, $SiC{\equiv}\underline{C}H$).

^{29}Si NMR ($CDCl_3$): δ -13.27 (br), -11.29 (s) (overlapped).

GPC (10^4, 10^3, 60 Å columns): M_w = 5210, M_n = 4220, D = 1.24.

IR (NaCl disk): 3290 (s, ν_s SiC≡CH), 2957 (s, ν_{as} CH_3), 2922 (s, ν_s CH_3), 2854 (s, ν_{as} aliphatic CH_2), 2032 (s, sh, ν_s C≡C), 1456 (w, δ_{as} CH_3), 1409 (w, δ_{as} CH_3), 1250 (s, δ_s $SiCH_3$), 840 (vs, ρ $SiCH_3$), 774 (s), 672 (s), 576 (w).

REFERENCES

1. *International Symposium on Polymers for Advanced Technologies;* Lewin, M., Ed.; Jerusalem, Israel, 1987; VCH: New York, pp 116-38.
2. National Research Council (U.S.). Committee on Polymer Science and Engineering *Polymer Science and Engineering: The Shifting Research Frontiers;* National Academy Press: Washington, D.C., 1994.
3. Tanner, D.; Fitzgerald, J. A.; Phillips, B. R. *Adv. Mater.* **1989**, *28*, 649-54.
4. Butler, G. B. *Cyclopolymerization and Cyclocopolymerization;* Marcel Dekker: New York, 1992, p 557.
5. Butler, G. B.; Angelo, R. J. *J. Am. Chem. Soc.* **1957**, *79*, 3128-31.
6. Baldwin, J. E. *J. Chem. Soc. Chem. Comm.* **1976**, 734-6.
7. Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc. Chem. Comm.* **1980**, 482-3.
8. Cavallo, L.; Guerra, G.; Corradini, P.; Reconi, L.; Waymouth, R. M. *Macromolecules* **1993**, *26*, 260-7.
9. Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270-1.
10. Coates, G. W.; Waymouth, R. M. *J. Mol. Catal.* **1992**, *76*, 189-94.

11. Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91-8.

12. Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953-4.

13. Resconi, L.; Coates, G. W.; Mogstad, A.-L.; Waymouth, R. M. *J. Macromol. Sci.-Chem.* **1991**, *A28*, 1225-34.

14. Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

15. Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3295-6.

16. Beaman, R. G.: U.S. Patent 3,048,566, 1962; Chem. Abstr. **59**: 782b (1962).

17. Miller, W. L.; Black, W. B. *Polym. Prepr.* **1962**, *3*, 345.

18. Kakuchi, T.; Satoh, T.; Kanai, H.; Umeda, S.; Hatakeyama, T.; Hashimoto, H.; Yokota, K. *Macromolecules* **1996**, *29*, 4490-93.

19. Satoh, T.; Yokota, K.; Kakuchi, T. *Macromolecules* **1995**, *28*, 4762-4.

20. Field, N. D. *J. Org. Chem.* **1960**, *25*, 1006-8.

21. DeWinter, W.; Marvel, C. S.; Abdul-Karim, A. *J. Polym. Sci., Part A, Polym. Chem.* **1963**, *1*, 3261-4.

22. Kodaira, T.; Tanahashi, H. *Macromolecules* **1989**, *22*, 4643-5.

23. Kodaira, T.; Tanahashi, H.; Hara, K. *Polym. J.* **1990**, *22*, 649-59.

24. Kodaira, T.; Urushisaki, M.; Usugaya, M.; Ohora, K.; Okumura, M. *Macromolecules* **1994**, *27*, 1320-4.

25. Kricheldorf, H. R. "Silicon in Polymer Synthesis," In ; Springer-Verlag: Berlin, 1996, pp 494.

26. Butler, G. B.; Stackman, R. W. *J. Org. Chem.* **1960**, *25*, 1643-4.

27. Butler, G. B.; Iachia, B. *J. Macromol. Sci.-Chem.* **1969**, *A3*, 1485-91.

28. Butler, G. B.; Stackman, R. W. *J. Macromol. Sci.-Chem.* **1969**, *A3*, 821-34.

29. Gusel'nikov, L. Y.; Nametkin, N. S.; Polyak, L. S.; Chernysheva, T. I. *Vysokomol. Soedin.* **1964**, *A6*, 2002-7.

30. Marvel, C. S.; Woolford, R. G. *J. Org. Chem.* **1960**, *25*, 1641-.

31. Billingham, N. C.; Jenkins, A. D.; Kronfli, E. B.; Walton, D. R. M. *J. Polym. Sci., Polym. Chem.* **1977**, *15*, 675-81.

32. Cragg, R. H.; Jones, R. G.; Swain, A. C. *Eur. Polym. J.* **1991**, *27*, 785-8.

33. Jones, R. G.; Cragg, R. H.; Swain, A. C. *Eur. Polym. J.* **1992**, *28*, 651-5.

34. Saigo, K.; Tateishi, K.; Adachi, H. *J. Polym. Sci., Part A, Polym. Chem.* **1988**, *26*, 2085-97.

35. Kusumoto, T.; Hiyama, T. *Chem. Lett.* **1988**, 1149-52.

36. Kim, Y.-H.; Gal, Y.-S.; Kim, U.-Y.; Choi, S.-K. *Macromolecules* **1988**, *21*, 1991-5.

37. Kim, Y.-H.; Kwan, S.-K.; Gal, Y.-S.; Choi, S.-K. *J. Macromol. Sci.—Pure Appl. Chem.* **1992**, *A29*, 589-97.

38. Oku, J.-i.; Hawegawa, T.; Takaki, M. *Chem. Technol. Silicon Tin, Proc. Asian Network Anal. Inorg. Chem. Int. Chem. Conf. Silicon Tin, 1st;* Kumar Das, V. G., Ng, S. W. and Gielen, M., Eds.; Kuala Lumpur, Malaysia, 1992; Oxford Univ. Press: Oxford, pp 440-5.

39. Robison, J. L. *Synthesis and Reactivity of Silicon Containing Linear and Cyclic Monomers and Polymers;* Ph.D. Dissertation, Massachusetts Institute of Technology: Cambridge, MA, 1992.

40. Seyferth, D.; Robison, J. *Macromolecules* **1993**, *26*, 407-18.

41. Speier, J. L.; Dow Corning Corporation: U.S. Patent 3,485,857, 1969.

42. Stober, M. R.; Michael, K. W.; Speier, J. L. *J. Org. Chem.* **1967**, *32*, 2740-4.

43. Suga, Y.; Oku, J.-i.; Takaki, M. *Macromolecules* **1994**, *27*, 7930-1.

44. Bassindale, A. R.; Taylor, P. G. "Activating and Directive Effects of Silicon," In *The Chemistry of Organic Silicon Compounds;* Patai, S. and

Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 2, pp 893-963.

45. Lebedev, B. V.; Rabinovich, I. B.; Lebedev, N. K.; Tsvetkov, V. G.; Durgar'yan, S. G.; Khotimskii, V. S. *Vysokomol. Soedin.* **1977**, *A19*, 513-8.

46. Nametkin, N. S.; Topchiev, A. V.; Dourgar'yan, S. G. *J. Polym. Sci., Part C* **1963**, *4*, 1053-9.

47. Nametkin, N. S.; Durgar'yan, S. G.; Kopkov, V. I.; Khotimskii, V. S. *Dokl. Akad. Nauk SSR (Chemistry)* **1969**, *185*, 366-8.

48. Nametkin, N. S.; Durgar'yan, S. G.; Kopkov, V. I.; Chernyakov, I. E.; Piryatinskii, V. M.: U.K. Patent 1,256,472, 1971.

49. Nametkin, N. S.; Semenov, O. B.; Durgar'yan, S. G.; Filippova, V. G.; Rukin, N. M. *Dokl. Akad. Nauk SSR (Chemistry)* **1974**, *215*, 861-4.

50. Lebedev, B. V.; Lebedev, N. K.; Khotimskii, V. S.; Durgar'yan, S. G.; Nametkin, N. S. *Dokl. Akad. Nauk SSR (Physical Chemistry)* **1981**, *259*, 629-33.

51. Bryantseva, I. S.; Rukin, N. M.; Vorontsov, V. M.; Khotimskii, V. S.; Semenov, O. B.; Durgar'yan, S. G.; Nametkin, N. S. *Vysokomol. Soedin.* **1978**, *B20*, 730-4.

52. Bryantseva, I. S.; Khotimskii, V. S.; Durgar'yan, S. G.; Nametkin, N. S. *Dokl. Akad. Nauk SSR (Chemistry)* **1980**, *251*, 878-82.

53. Bryantseva, I. S.; Khotimskii, V. S.; Durgar'yan, S. G.; Petrovskii, P. V. *Vysokomol. Soedin.* **1985**, *B27*, 149-52.

54. Parsamyan, I. L.; Chernyakov, I. E.; Durgar'yan, S. G.; Nametkin, N. S. *Dokl. Akad. Nauk SSR (Chemistry)* **1978**, *244*, 116-8.

55. Parsamyan, I. L.; Semenov, O. B.; Nametkin, N. S. *Dokl. Akad. Nauk SSR (Chemistry)* **1980**, *252*, 123-5.

56. Asami, R.; Oku, J.-i.; Takeuchi, M.; Nakamura, K.; Takaki, M. *Polym. J.* **1988**, *20*, 669-702.

57. Oku, J.-i.; Hasegawa, T.; Nakamura, K.; Takeuchi, M.; Takaki, M.; Asami, R. *Polym. J.* **1991**, *23*, 195-9.

58. Oku, J.-i.; Hasegawa, T.; Takeuchi, T.; Takaki, M. *Polym. J.* **1991**, *23*, 1377-82.

59. Oku, J.-i.; Hasegawa, T.; Kawakita, T.; Kondo, Y.; Takaki, M. *Macromolecules* **1991**, *24*, 1253-6.

60. Oku, J.-i.; Hasegawa, T.; Kubota, Y.; Takaki, M.; Asami, R. *Polym. Bull.* **1992**, *28*, 505-9.

61. Rickle, G. K. *J. Macromol. Sci.-Chem.* **1986**, *A23*, 1287-97.

62. Rickle, G. K. *J. Macromol. Sci.-Chem.* **1987**, *A24*, 93-104.

63. Pawlenko, S. *Organosilicon Chemistry*; Walter de Gruyter: New York, 1986.

64. Eaborn, C. *Organosilicon Compounds*; Butterworths: London, 1960.

65. Flatt, D. V.: U.S. Patent 3,453,233, 1969; C.A. **71**: 71748b (1969).

66. Auner, N. *J. Organomet. Chem.* **1987**, *336*, 59-81.

67. Bovey, F. A. *High Resolution NMR of Macromolecules*; Academic Press: New York, 1972, p 462.

68. Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron* **1990**, *46*, 1385-489.

69. Bailey, W. F.; Punzalan, E. R. *J. Am. Chem. Soc.* **1994**, *116*, 6577-80.

70. Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K.; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 5720-7.

71. Bailey, W. F.; Gavaskar, K. V. *Tetrahedron* **1994**, *50*, 5957-70.

72. Kriegsmann, H. *Z. Elektrochem.* **1957**, *61*, 1088.

73. Goubeau, J.; Jiménez-Barberá, J. *Z. Anorg. Allg. Chem.* **1960**, *303*, 222 ?

74. Smith, A. L. *Spectrochim. Acta* **1960**, *16*, 87-105.

75. Williams, E. A.; Cargioli, J. D. "Silicon-29 NMR Spectroscopy," In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1979; Vol. 9, pp 221-318.

76. Szwarc, M.; Van Beylen, M. *Ionic Polymerization and Living Polymers*; Chapman & Hall: New York, 1993, p 380.

77. Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker, Inc.: New York, 1996; Vol. 34, p 727.

78. Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy: High-Resolution Methods and Applications in Organic Chemistry and Biochemistry*; 3rd ed.; VCH: New York, 1987, p 515.

79. Lancaster, J. E.; Baccei, L.; Panzer, H. P. *J. Polym. Sci. Pt. B.* **1976**, *14*, 549-54.

80. Berlin, A. A.; Yenikolopyan, N. S. *Vysokomol. Soedin.* **1968**, *A10*, 1475-95.

81. Fields, R. "Fluorine-19 Nuclear Magnetic Resonance Spectroscopy," In *Annual Reports on NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: New York, 1972; Vol. 5A, pp 99-304.

82. Gilman, H.; Klein, R. A.; Winkler, J. S. *J. Org. Chem.* **1961**, *26*, 2474.

83. Muriale, L.; Lee, E.; Genovese, J.; Trend, S. *Ann. Occup. Hyg.* **1996**, *40*, 705-10.

84. Seyferth, D.; Weiner, M. *J. Am. Chem. Soc.* **1961**, *83*, 3583-6.

CHAPTER THREE

New Approaches to the Functionalization of Carbosilane Dendrimers

INTRODUCTION

The development of methods for the directed synthesis of macromolecules with precisely defined structures has generated considerable excitement in the polymer science community in recent years. One of the most widely studied classes of these new, highly regular macromolecules are the hyperbranched polymers known as dendrimers.[1-4] Dendrimers, as their name implies, resemble trees with their highly branched topologies (Figure 1). Dendrimers, unlike trees, possess a regular exponential branching pattern; this is exploited in their synthesis to control molecular weight and structure with a degree of precision normally associated with small molecule syntheses.

The advent of these highly symmetrical, highly regular polymers has opened up new realms of possibilities for polymer scientists. Proposed applications include drug-delivery systems,[5] catalyst supports, ingredients in photocopier toners,[6] medical imaging agents[7] and building blocks for nanostructured materials.[1]

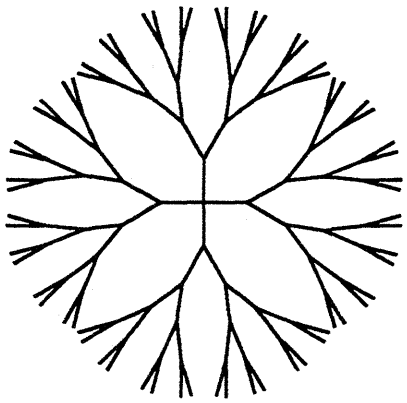
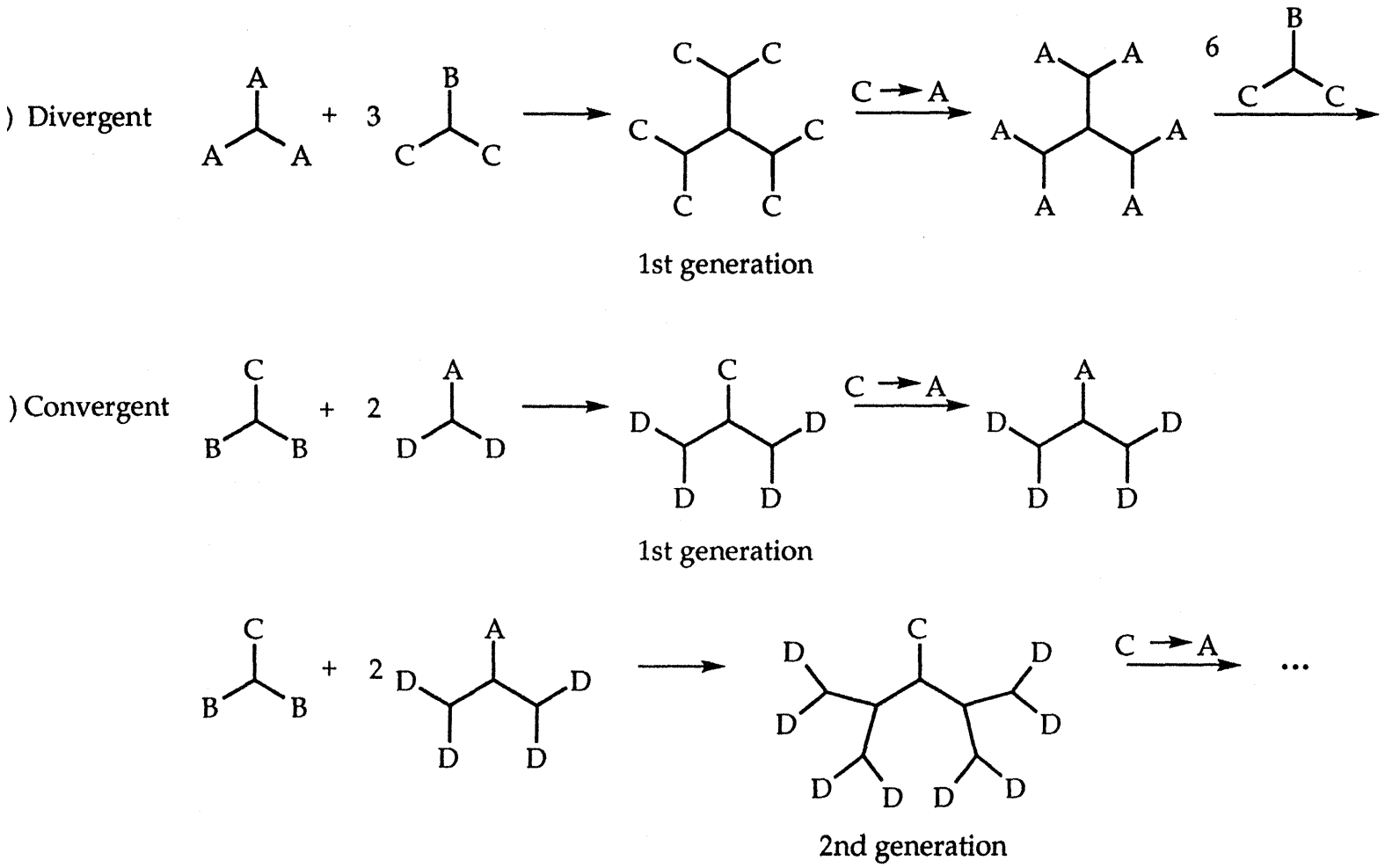


Figure 1. Dendrimer

Dendrimer Construction

Techniques for the controlled synthesis of dendrimers invariably employ iterative reaction sequences and fall into two general categories, convergent and divergent; these are illustrated in Scheme 1 for a trifunctional monomer. In the divergent strategy (Scheme 1a) the polymer grows from the core outward by adding successive layers of monomers to form each new *generation* of dendrimer. The convergent method (Scheme 1b) differs from the divergent in that the branches of the dendrimer are grown essentially from the outside in. Several variations on these methods have been developed, such as the "double-exponential growth" approach which combines aspects of both convergent and divergent strategies.[8]

Key to the success of any strategy for producing highly regular dendrimers is the reaction which couples monomer units to the ends of the branches of the growing polymer. In order to obtain dendrimers of a single, well-defined structure, this reaction must proceed quantitatively and selectively. Even small amounts of defects will result in a mixture of products whose components may not be separable from one another. Equation 1 gives the expected ratios of these components if the defects are randomly distributed among the branches of the dendrimer (i.e. the reactivities of each of the endgroups is the same toward all reactions).[9] In this equation, the P identical reactive endgroups of a dendrimer undergo a chemical transformation which converts them to n different types of groups $a_1, a_2, \ldots a_n$ present in the final product mixture in the proportions $q_1, q_2, \ldots q_n$. The composition of each of the possible product dendrimers may then be expressed by $a_1^{k_1}a_2^{k_2}\ldots$ where $k_1, k_2, \ldots$ are the numbers of endgroups in the product dendrimer bearing the groups $a_1, a_2, \ldots$ ($k_1 + k_2 + \ldots = P$). Equation 1



Scheme 1. Divergent and Convergent Strategies for Dendrimer Synthesis.

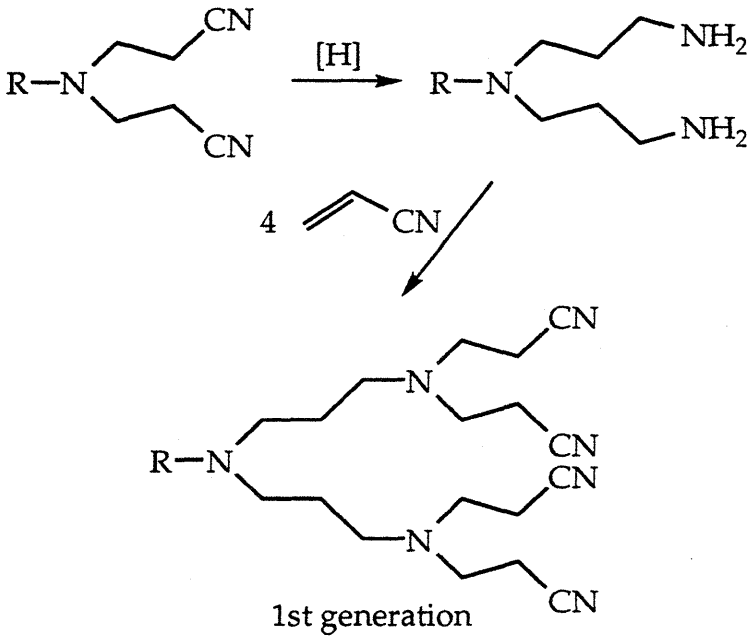
allows one to calculate $X_{a_1k_1a_2k_2...}$, the mole fraction of the dendrimer with the configuration $a_1^{k_1}a_2^{k_2}...$ in the final product mixture.

$$X_{a_1^{k_1}a_2^{k_2}..} = \left(\frac{P!}{k_1!k_2!...}\right) q_1^{k_1}q_2^{k_2}... \qquad (1)$$

An example of the application of equation 1 illustrates the necessity of quantitative-yield reactions in dendrimer synthesis. During the divergent construction of a second generation dendrimer, a first generation dendrimer with eight reactive endgroups (P = 8) is reacted with the next layer of monomer units (a_1). If this reaction occurs with 97% conversion ($q_1 = 0.97$); the remaining 3% of the original endgroups (a_2) remain unreacted ($q_2 = 0.03$). If these unreacted groups are randomly distributed among the branches of the dendrimer, eq. 1 predicts the product mixture will contain 78% of the desired dendrimer with no unreacted endgroups ($X_{a_18a_20} = 0.78$), 19% of the dendrimer with one unreacted endgroup ($X_{a_17a_21} = 0.19$), 4% of the dendrimer with two unreacted endgroups ($X_{a_16a_22} = 0.04$), and so on. Hence, a reaction which proceeds in 97% yield produces a product with only 78% purity; this problem becomes even worse for higher generation dendrimers which possess more reactive groups (the above reaction would give the desired product in only 61% purity if the starting dendrimer possessed 16 reactive endgroups). Factor in the potential difficulties of separating products that differ by only one or two functional groups out of many, and the problem can quickly become intractable.

Even in light of these strict requirements, quite a number of successful strategies have been developed for dendrimer synthesis. The earliest controlled synthesis of a dendrimer, reported by Vögtle in 1978, employed

Michael additions of amines to acrylonitrile followed by reduction (Scheme 2).[10] Since that time, literally hundreds of different dendrimers have been synthesized, with backbones constructed of amino acids, amidoamines, ethers, esters, saturated hydrocarbons, arylacetylenes, quaternary ammonium salts, phosphonium salts, aminophosphine sulfides, siloxanes, carbosilanes and platinum bipyridyl complexes, just to name a few.[4]



Scheme 2. First Controlled Synthesis of Dendrimers.

The poly(amidoamine) (PAMAM) starburst dendrimers of Tomalia (Figure 2) were one of the first classes to be synthesized and are probably the most studied and best characterized of all the known types of dendrimers.[1,11,12] Their popularity is such that they are now available commercially.[13] Numerous physical and theoretical studies have established their spatial dimensions and topology as a function of generation as well as their purity (i.e. the presence of defects).[1] These structural parameters exert

significant influence over the dendrimers' physical properties. Other well-studied systems include the poly(arylethers) of Fréchet grown by convergent methods[14] and Newkome's arborols and related dendrimers.[15]

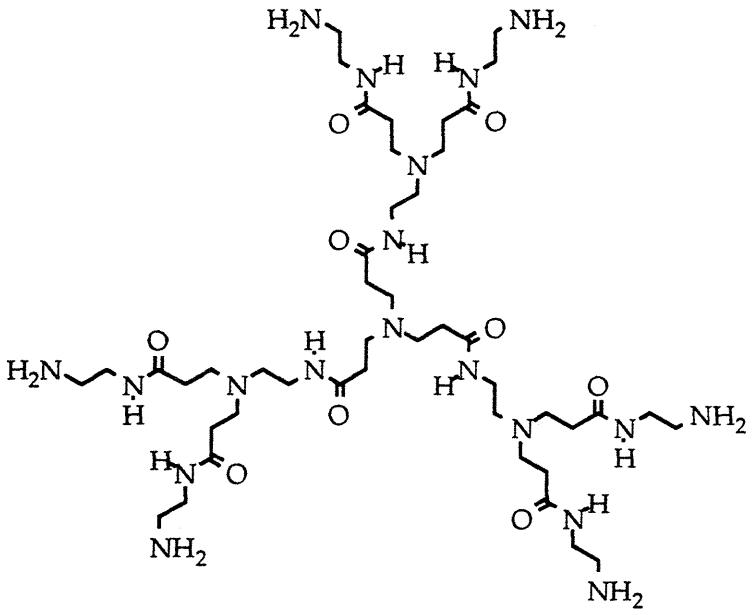
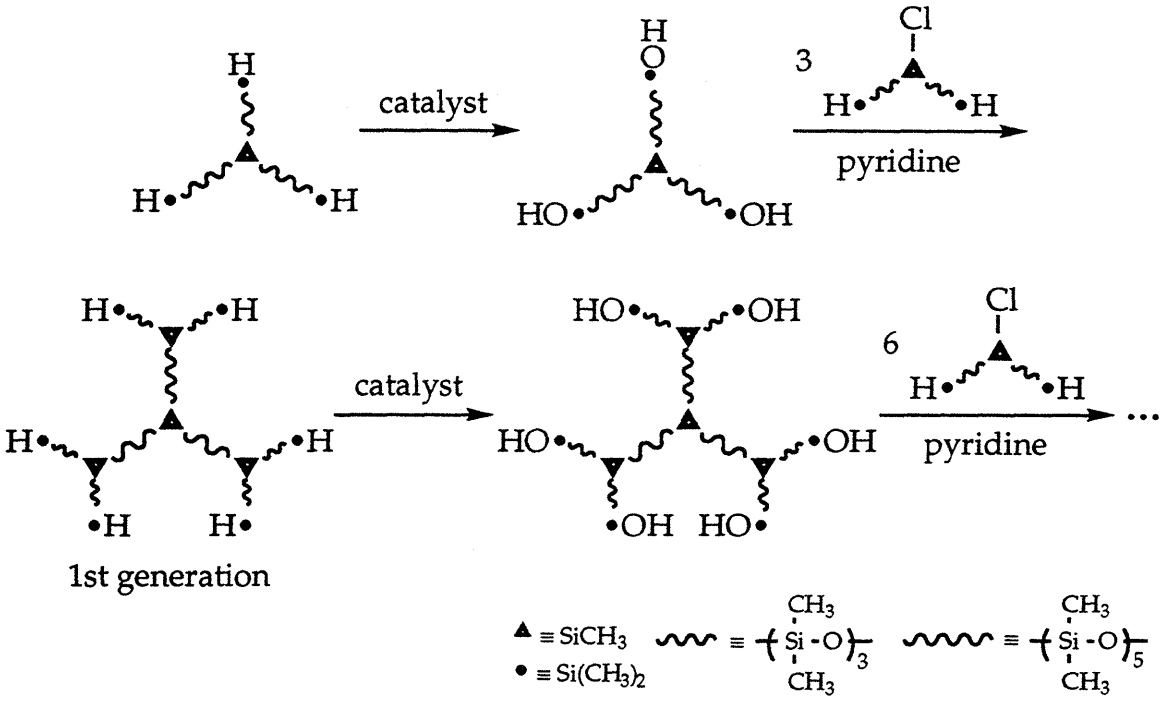


Figure 2. First Generation Poly(amidoamine) (PAMAM) Dendrimer.

Organosilicon chemistry offers a number of high yield, selective reactions which are suitable for dendrimer construction.[16-18] Among these are the reactions of silicon-halide bonds with nucleophiles (e.g., the displacement of Cl^- from Si-Cl bonds by Grignard reagents or silanolates) and hydrosilylations[19] (which, depending on the substrates and conditions, can be quantitative and highly selective). Stepwise couplings of silanols or silanolates with halosilanes gave the first examples of organosilicon dendrimers in 1990 and 1991 (Scheme 3).[20,21] Also around that time, the hydrosilylation reaction was first used in the production of hyperbranched macromolecules, in this case a cascade synthesis of irregular hyperbranched

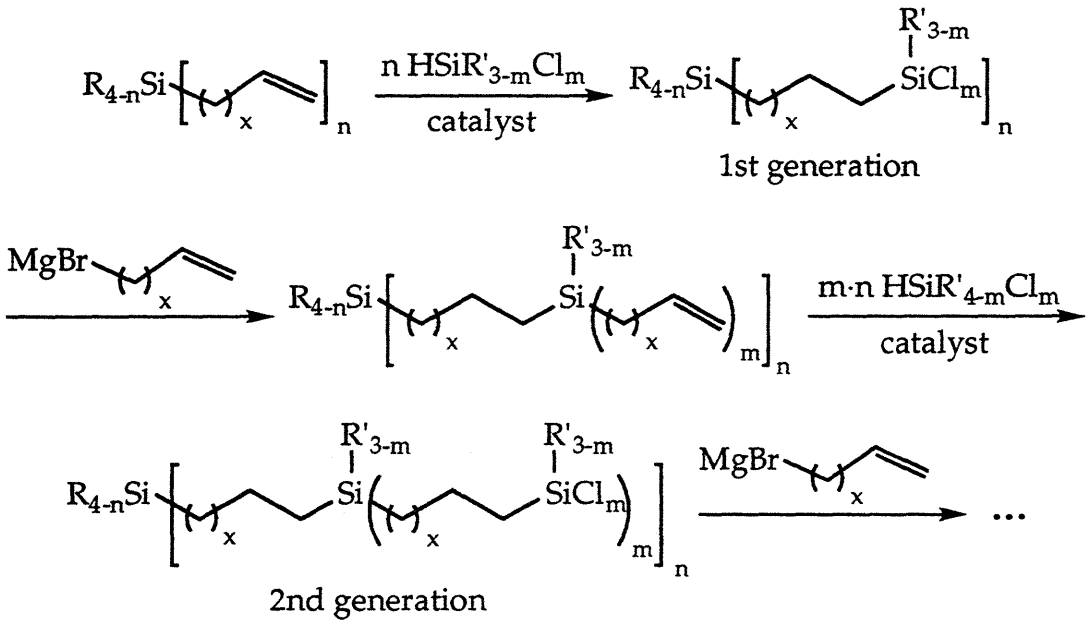
poly(siloxysilanes).[22] Later work by Muzafarov et. al. demonstrated the preparation of hyperbranched polycarbosilanes by a similar cascade hydrosilylation reaction.[23]



Scheme 3. Divergent Synthesis of Dendrimeric Siloxanes (see ref. 20).

The first example of the controlled use of the hydrosilylation reaction for the construction of dendrimers came in 1992 from van der Made and van Leeuwen.[24,25] These authors employed sequences of alternating hydrosilylations with substituted chlorosilanes and alkenylations with Grignard reagents to form several generations of carbosilane dendrimers (Scheme 4). Although the authors reportedly synthesized several different types of dendrimers having varying alkenyl chain lengths (Scheme 4; x = 0, 1, 8) and dendrimer core and branch multiplicities (n = 3, 4; m = 2, 3), only limited experimental and characterization data were provided, mainly for the

allylsilane-based dendrimer with tetrafunctional core and trifunctional branch points.[24] A more complete account was published by Zhou and Roovers in 1993 which detailed the use of tetravinylsilane as a core (n = 4), vinylmagnesium bromide as alkenylating agent (x = 0) and methyldichlorosilane as branch point (m = 2).[26] According to these authors, this system gives dendrimers having a regular structure up to the fourth generation. Soon thereafter, Seyferth and Son described the synthesis of four generations of vinylsilane-based (x = 0) dendrimers possessing core and branch points with four- and three-fold multiplicity, respectively (n = 4; m = 3).[27]



Scheme 4. Divergent Synthesis of Carbosilane Dendrimers

A more recent application of organosilicon chemistry to dendrimer synthesis involves the construction of regular hyperbranched polysilanes, which contain a framework of Si-Si bonds.[28-31] The first reported synthesis of

a first generation polysilane dendrimer was published by Lambert et. al.[28] in early 1995 and was soon followed by a communication from the Sakurai group detailing the syntheses of first and second generation dendritic polysilanes.[29] These polysilane dendrimers evoke considerable interest in terms of their electronic and optical properties,[28] which appear to be measurably different from those of linear oligosilanes.[32]

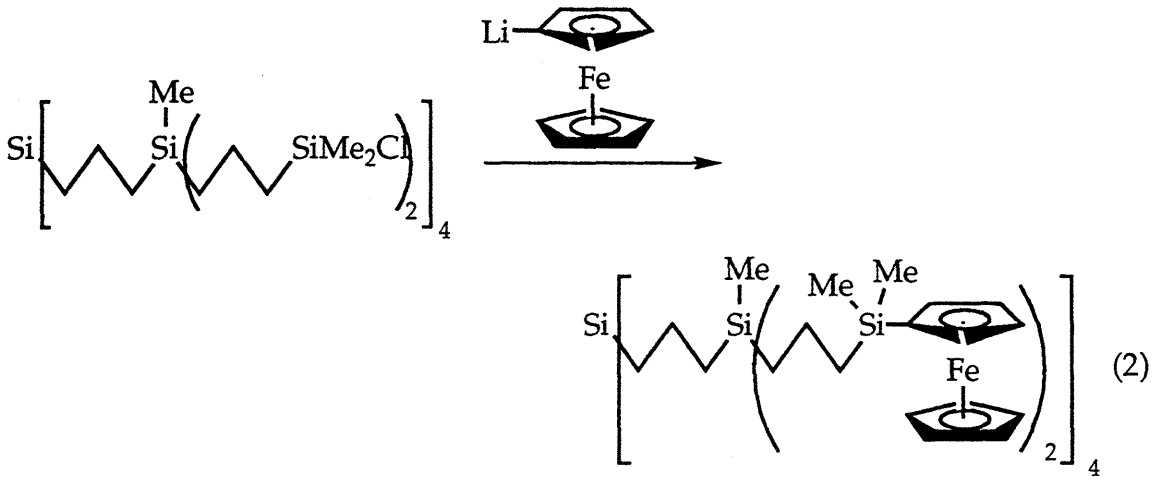
Dendrimer Functionalization

As the science of dendrimer backbone synthesis continues to mature, current research efforts are focusing increasingly on the modification of the terminal branches and interior sites of dendrimers with an eye toward exploiting their unique topology for specific technological applications.[33] One of the most creative and exciting demonstrations of the power of this approach has come from a series of reports from Meijer and coworkers on the entrapment of organic molecules in the interior of poly(propylene imine) dendrimers by the functionalization of the surface sites of the dendrimers with sterically bulky amino acid derivatives.[34-36] These so-called "dendritic boxes" can be made to release their contents in a size-selective fashion by the partial removal of some of the surface-blocking agents.

Another area of active interest involves the attachment of amphiphilic groups to the outer surfaces of dendrimers in order to generate water-soluble derivatives.[2] Because of their spheroidal shape, hydrophobic interiors and charged external surfaces, these systems mimic the structure of micelles; this topic will be discussed further in Chapter 4. Dendrimers are also being explored as multi-site catalyst support systems with the attachment of catalytic and electroactive groups at their surfaces and interiors.[2,37]

The chemically inert framework of carbosilane dendrimers is well-suited for applications as a support for catalyts and electroactive moieties. In addition, the alkenylsilyl and halosilyl endgroups of these dendrimers allow moieties of interest to be easily grafted on the polymers' outer surfaces. A number of studies so far have demonstrated the attachment of various transition metal-containing groups to carbosilane dendrimers.

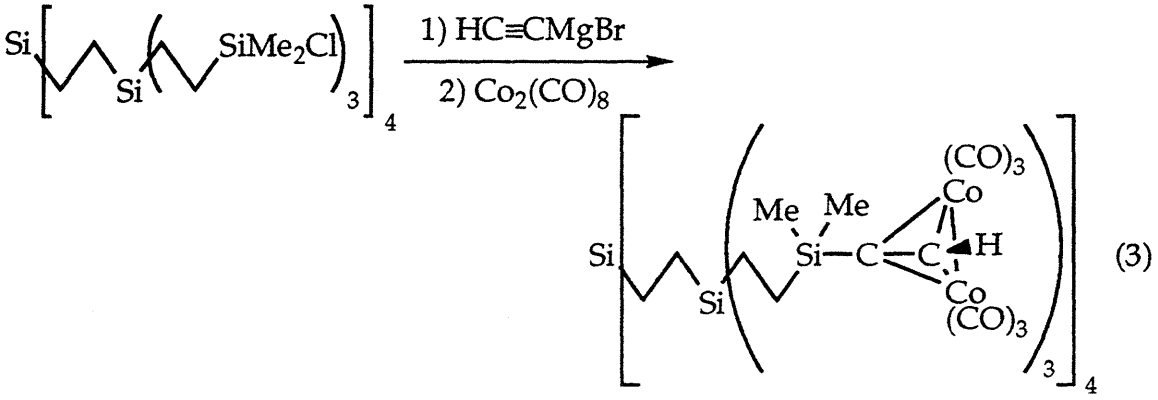
One commonly used method for attaching reactive groups to the surface of carbosilane dendrimers involves nucleophilic displacement reactions of terminal Si-Cl groups. In 1994, a group led by Cuadrado and Morán utilized this approach to synthesize first and second generation carbosilane dendrimers bearing pendant ferrocenyl groups: after capping with $HSiMe_2Cl$, the allylsilane arms were reacted with ferrocene-containing nucleophiles such as ferrocenyllithium (eq. 2).[38] Films of these electroactive dendrimers deposited on gold and glassy carbon disk electrodes showed reversible oxidation behavior.[39]



(2)

That same year, Knapen et. al. used a similar reaction to prepare first and second generation carbosilane dendrimers with attached nickel(II)

complexes which were effective catalysts for the Kharasch reaction.[40] In 1995, Seyferth and Kugita employed this method to synthesize cobalt-containing carbosilane dendrimers.[41] First and second generation dimethylchlorosilyl-terminated dendrimers, upon reaction with ethynylmagnesium bromide, gave silylacetylene-terminated dendrimers which could be further reacted with dicobalt octacarbonyl to furnish dendrimeric cobalt complexes in good to excellent yields (eq. 3). More recently, Cuadrado et. al. applied this approach to functionalize a first generation carbosilane dendrimer with terminal cyclopentadienyl substituents which were further reacted with dicobalt octacarbonyl to furnish the corresponding half-sandwich complexes.[42] In this same report, they also described the synthesis of first generation dendrimers with Si-Fe and Si-Co σ-bonds prepared by the reactions of terminal Si-Cl and Si-H bonds, respectively, with $Na^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ and $Co_2(CO)_8$.

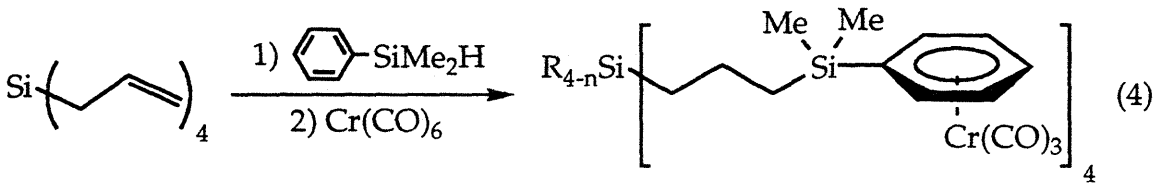


(3)

Two other examples of the use of nucleophilic displacement reactions to functionalize carbosilane dendrimers have been reported. Roovers et. al. in 1993 synthesized hyperbranched star polymers by reacting chlorosilyl-terminated carbosilane dendrimers with excess poly(butadienyl)lithium; these impressive macromolecules were used as models for polymeric

micelles.[43] Krasovskii et. al. prepared carbosilane dendrimers with the fluorescent probe molecule pyrene attached at the core; steady-state fluorescence and quenching studies provided insight into the steric hindrance present at the cores of the dendrimers.[44]

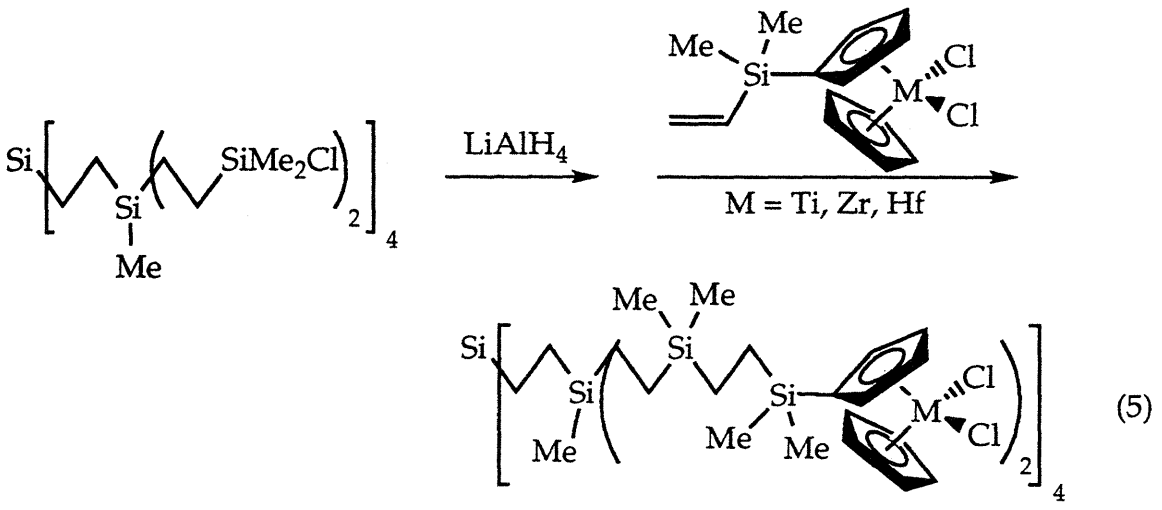
Ligands for transition metal fragments can also be attached to the carbosilane dendrimer framework via addition reactions to C=C bonds. In 1994, Miedaner et. al. synthesized a first generation carbosilane dendrimer bearing four tridentate phosphine ligands by the addition of a P-H bond of the ligand to each of the C=C bonds of tetravinylsilane.[45] Additions of Si-H bonds to C=C bonds (i.e. hydrosilylation) have also been used to attach reactive moieties to carbosilane dendrimers. Cuadrado and coworkers functionalized zero and first generation allylsilane-based dendrimers by hydrosilylation with phenyldimethylsilane.[46] Further reaction with excess chromium hexacarbonyl converted the attached ligands to the corresponding (arene)chromium tricarbonyl complexes. While a complete conversion was acheived for all four phenyl groups of the first generation dendrimer (eq. 4), 50% of the phenyl groups of the eight-armed second generation dendrimer remained unreacted, presumably due to steric crowding.



(4)

Recent work from these laboratories extended this hydrosilylation approach to attach entire pre-formed transition metal complexes to the arms of carbosilane dendrimers. Reduction of the Si-Cl bond of dimethylchlorosilyl-terminated carbosilane dendrimers gave Si-H bonds to

which were added transition metal complexes bearing vinyl-substituted ligands . In this way, dendrimer-supported group 4 metallocene complexes were synthesized (eq. 5), some of which were catalytically active for the MAO-promoted polymerization of ethylene.[47]



(5)

One additional approach to the functionalization of of carbosilane dendrimers has been described. In 1995, Lorenz et. al. reported that hydroboration/oxidation of the terminal allyl groups of allylsilane-based carbosilane dendrimers gave dendritic polyols.[48] In later studies, the terminal OH groups of these dendrimers were esterified with mesogen-containing acid chlorides.[49] The liquid crystalline properties of thin films of these dendrimers deposited on mica substrates were extensively investigated.[50] Similar mesogen-functionalized carbosilane dendrimers have been prepared recently by hydrosilylation of allyl-terminated carbosilane dendrimers with mesogens containing reactive Si-H groups.[51]

The above examples illustrate the utility of carbosilane dendrimers for providing stable frameworks for the attachment of various reactive moieties. At present, the methods available for attaching these moieties are essentially

limited to the addition of E-H (E = B, Si, P) bonds to alkenyl C=C bonds and nucleophilic displacements of terminal Si-X (X = halogen) bonds. The former technique shows promise for becoming a fairly general method for functionalizing carbosilane dendrimers; the usefulness of the latter, however, is limited by the instability of most silicon-heteroatom (e.g. Si-N, Si-OR, Si-S) bonds toward moisture and Lewis acids.[16,17]

In order to further extend the utility of carbosilane dendrimers as building blocks for advanced materials, new methods must be sought for selectively and quantitatively attaching reactive functional groups via chemically robust (e.g. moisture-stable) linkages. The present study concerns the development of one such method, employing (chloromethyl)dimethylsilyl endgroups. (Chloromethyl)silyl substituents demonstrate versatile reactivity, functioning both as nucleophiles, through the readily formed magnesium or lithium reagents, and as electrophiles.[52] Moreover, their nucleophilic reactions with transition metal halides lead to complexes with exceptionally stable metal-alkyl bonds.[53]

The present studies resulted in the development of a facile, effective method for attaching (chloromethyl)silyl substituents to the branch terminii of carbosilane dendrimers. Dendrimers functionalized in this way exhibited both nucleophilic and electrophilic reaction chemistry, leading to heretofore unknown derivatives. During the course of these studies, many of the subtleties concerning the synthesis of carbosilane dendrimers were brought to light, in particular the types and amounts of defects produced during divergent growth sequences as well as methods for their elimination. As a result of these discoveries, the purities of various types of carbosilane dendrimers (e.g. vinyl- or allylsilane-based; with two- or three-fold branch

multiplicities) could be accurately assessed, and a critical comparison of the various methods for their generation could be made.

RESULTS AND DISCUSSION

Synthesis and Purification of Carbosilane Dendrimers

As mentioned in the Introduction, a number of systems of carbosilane dendrimers exist which possess differing degrees of branching at the silicon centers and varying lengths of alkyl segments connecting them (Scheme 4). These will be represented throughout the following discussion using the notation **aG$_{Alkenyl}$-bEndgroup** where **aG** represents the generation of the dendrimer (e.g. **1G** and **2G** for first and second generations, respectively), the subscript **$_{Alkenyl}$** denotes the alkenylating agent used in building the backbone (i.e. vinyl- or allylmagnesium bromide) and **-bEndgroup** gives the total number and type of endgroups (besides methyl groups) attached to the terminal silicon atoms of the dendrimer arms (e.g. **-16Vinyl**). For purposes of this discussion, the generation number **aG** of the carbosilane dendrimer will be determined by the number of successive hydrosilylation sequences which have taken place (see Scheme 4). For a given dendrimer system, the number of endgroups **b** will increase exponentially with generation. As an illustrative example, a second generation dendrimer constructed from a tetravinylsilane core by two sequences of hydrosilylation with trichlorosilane followed by vinylation with vinylmagnesium bromide would be abbreviated as **2G$_{Vinyl}$-36Vinyl**.

Two systems were utilized in the present study: the first is that reported by Zhou and Roovers which consists of **1G$_{Vinyl}$-8Vinyl** and **2G$_{Vinyl}$-16Vinyl** constructed from a tetravinylsilane core, methyldichlorosilane in the hydrosilylation step and vinylmagnesium bromide in the alkenylation step;[26]

the other is that of van der Made and van Leeuwen which uses trichlorosilane and allylmagnesium bromide to construct **1G$_{Allyl}$-12Allyl** and **2G$_{Allyl}$-36Allyl** from a tetraallylsilane core.[24,25] The characteristics of these two systems will be compared to those of a third system which has been extensively studied in these laboratories previously, consisting of **1G$_{Vinyl}$-12Vinyl** and **2G$_{Vinyl}$-36Vinyl** prepared from a tetravinylsilane core using trichlorosilane as branch-point and vinylmagnesium bromide as alkenylating agent.[27]

The facility of synthesis of these various systems depends on several factors:

- The density of packing of branches at the dendrimer surface.
- The reactivity of the alkenylsilane/hydrosilane pair in the hydrosilylation reaction.
- The prevalence of side reactions, and the ease of their suppression.
- The ease of removal of defects and side products.

Each of these parameters is discussed individually below for the various systems of carbosilane dendrimers under consideration in the present study.

Dendrimer Size and Surface Congestion

The multiplicity of silicon branch points, the length of alkyl spacer units and the generation number together dictate the congestion of branches at a carbosilane dendrimer's surface. For a given system (i.e., branch point multiplicity and alkyl spacer length), after a certain number of generations this crowding will reach a critical point at which further growth will be accompanied by the presence of defects in the form of missing (unreacted) branches. Previous studies provide a measure of this surface-crowding

phenomenon and allow comparisons between the different systems to be made.

For the allylsilane-based dendrimers of van der Made and van Leeuwen, the highest attainable defect-free generation was reported to be five,[24,25] although later studies by Lorenz et. al. using matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry revealed the presence of significant amounts (20%) of missing branches for the second generation dendrimer **$2G_{Allyl}$-36Allyl** and even higher amounts for **$3G_{Allyl}$-108Allyl**.[48] For the vinylsilane-based system of Seyferth and Son, acheiving growth beyond the third generation **$3G_{Vinyl}$-108Vinyl** required heating the hydrosilylation reaction mixture in a sealed tube.[27] For the less-hindered system of Zhou and Roovers, however, the defect-free fourth generation dendrimer **$4G_{Vinyl}$-64Vinyl** was reportedly synthesized under the same mild conditions as for lower generations.[26]

Reactivities of Alkenyl- and Hydrosilanes Towards Hydrosilylation

In the present studies, the reactivity observed during the hydrosilylation step showed a strong dependence on the chlorosilane used, decreasing in the order $HSiMe_2Cl$ > $HSiMeCl_2$ > $HSiCl_3$. Hydrosilylations of vinylsilane-based dendrimers with $HSiMe_2Cl$ in THF using the Karstedt catalyst were so rapid and exothermic that they required slow addition of the silane to avoid explosions. The use of $HSiMeCl_2$ (instead of $HSiMe_2Cl$) under the same conditions resulted in strongly exothermic reactions which gave quantitative conversions in reasonably short reaction times (e.g., 18 h). Reactions of allylsilane- and vinylsilane-based dendrimers with $HSiCl_3$ in THF using the Karstedt catalyst generally exhibited weak exotherms. In general, reactions of allylsilane-based dendrimers were much more sluggish

than those of their vinylsilane counterparts and often required multiple catalyst additions and the use of rigorously purified $HSiCl_3$ to reach completion.

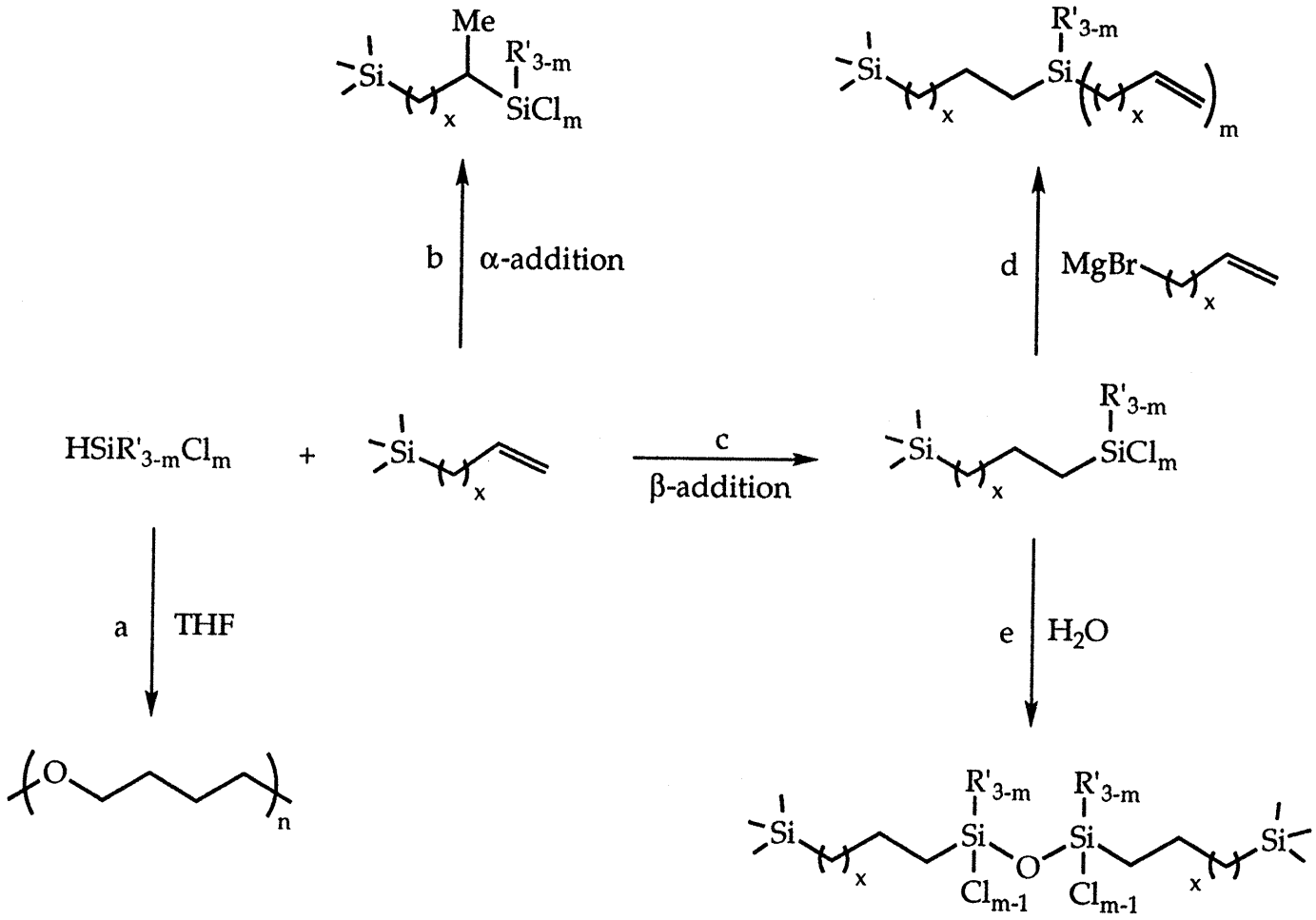
Side Reactions

As discussed in the Introduction, the occurrence of side reactions in a dendrimer synthesis often leads to intractable mixtures of products, thus destroying the most attractive feature of the target macromolecule, namely its precisely defined, uniform structure. As illustrated in Scheme 5, the syntheses of carbosilane dendrimers are prone to several side reactions:

- Incomplete hydrosilylation, leaving unreacted alkenyl groups.
- Cationic ring-opening polymerization of THF catalyzed by chlorosilanes (Scheme 5a).
- α-Addition reactions (Scheme 5b).
- Formation of oligomeric products through hydrolytic coupling of Si-Cl groups (Scheme 5e).

Fortunately, each of these side reactions can either be suppressed through careful control of reaction conditions, or its corresponding impurity removed during the purification of the dendrimeric product.

Incomplete hydrosilylation of the alkenyl groups of the dendrimer will ultimately lead to missing branches and distributions of dendrimer sizes and therefore must be completely suppressed. In the present studies, this was effectively accomplished by simply monitoring the hydrosilylation reaction mixture by ^1H NMR for the presence of unreacted vinyl or allyl groups. More catalyst and/or silane was added as needed until the reaction reached completion. Because of variations in the reactivity of different batches of hydrosilylation catalysts, this procedure was followed for every



Scheme 5. Side Reactions in the Synthesis of Carbosilane Dendrimers.

hydrosilylation reaction. Because of their low reactivity, it was especially critical to monitor the hydrosilylations of allylsilane-containing dendrimers. Failure to take this precaution may have led to the types of defects noted by Lorenz et. al.[48]

Extended hydrosilylation reaction times and excessive heating had the effect of polymerizing large quantities of the solvent (THF) through cationic ring-opening processes catalyzed by the chlorosilanes present in the reaction mixture (Scheme 5a).[54] This side reaction was increasingly favored as the number of Cl groups attached to the chlorosilane increased (giving a more Lewis-acidic silicon center), being the most troublesome for hydrosilylations involving $HSiCl_3$. Due to the long reaction times needed for hydrosilylations of allylsilane-containing dendrimers with $HSiCl_3$, crude product mixtures sometimes contained two to three times the theoretical mass of dendrimer in THF oligomers. Fortunately, this impurity was easily detected by ^1H NMR (Figure 2a) and easily removed by column chromatography after the alkenylation reaction.

In general, the regioselectivity of hydrosilylations varies strongly with the nature of the alkene, silane and solvent.[19] For carbosilane dendrimer syntheses, non-regiospecific hydrosilylation reactions (Scheme 5b) will produce products having statistical mixtures of regioisomeric branches; such dendrimers will all possess the same mass and number of branches, but with slightly different overall shapes.

Hydrosilylations of allylsilane-containing dendrimers in all cases gave products arising from exclusive β-addition of the Si-H bond of the chlorosilane to the C=C bond of the allyl group. For vinylsilane-based dendrimers, however, the choice of chlorosilane and reaction solvent proved to be critical to obtaining uniform dendrimers. Seyferth and Son reported

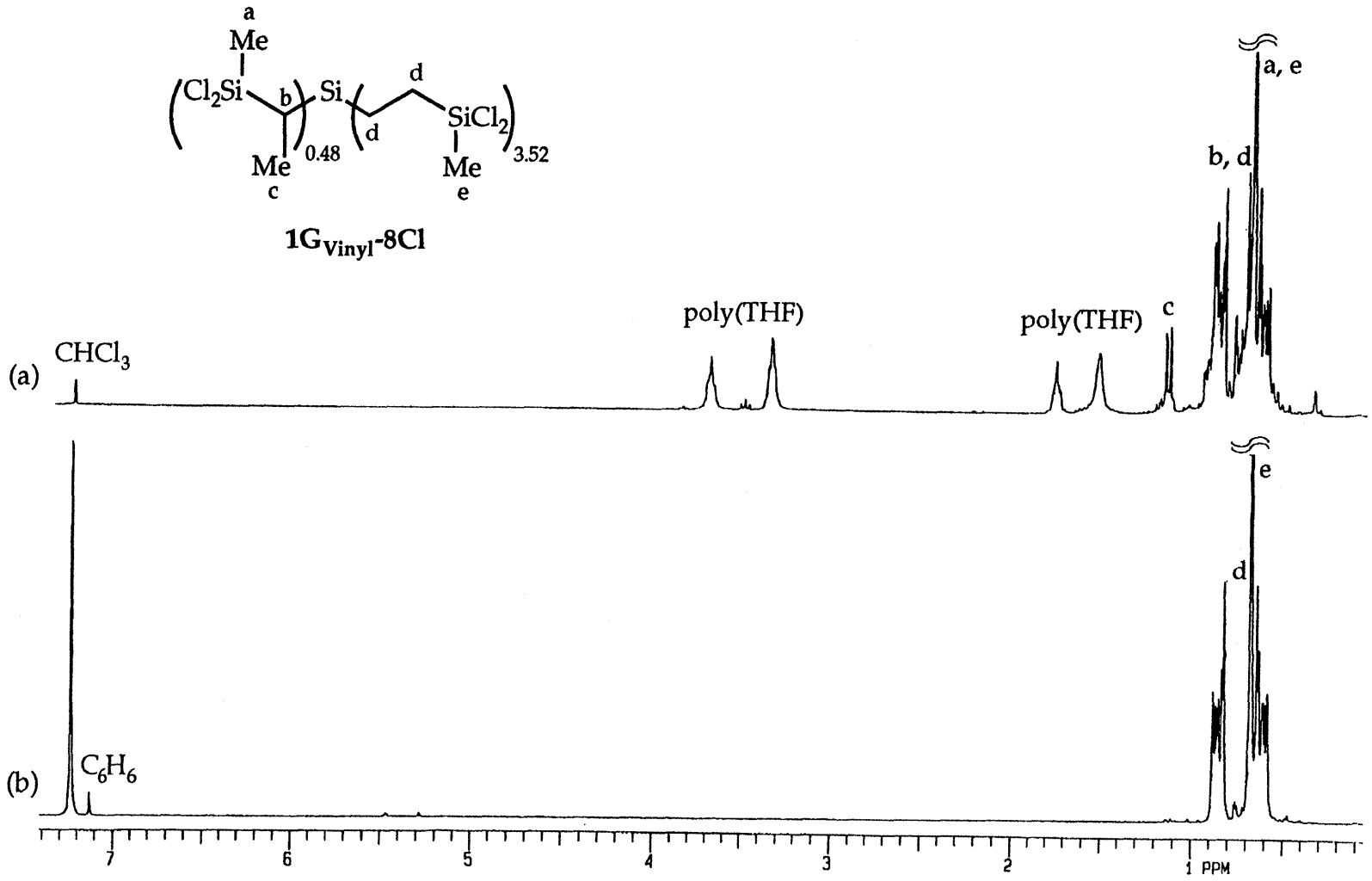
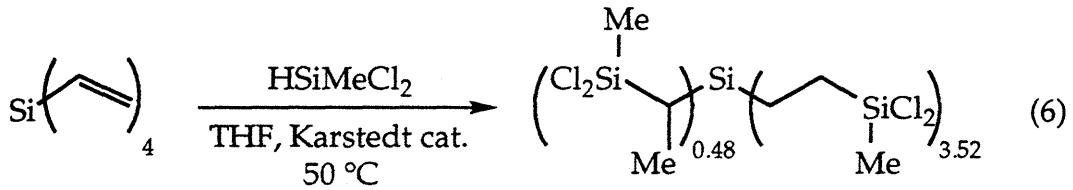


Figure 2. ^{1}H NMR Spectra of Samples of **1G$_{Vinyl}$-8Cl** Prepared in (a) THF with No Cocatalyst and in (b) Benzene with Ph_3P Cocatalyst.

that hydrosilylations of vinylsilane-based dendrimers with $HSiCl_3$ gave mixtures of α- and β-addition products unless the reaction was carried out in the coordinating solvent THF, in which case only β-addition occurred.[27] Zhou and Roovers reported that hydrosilylations of vinylsilane-based dendrimers with $HSiMeCl_2$ in THF also gave exclusively the β-addition isomers.[26] However, numerous attempts to repeat their synthesis of **$1G_{Vinyl}$-8Cl** (eq. 6) resulted in products containing 7 - 12% α-addition isomers by ^1H NMR (Figure 2a). Varying the catalyst (i.e., using solutions of hexachloroplatinic acid (CPA) in place of the Karstedt catalyst, or using samples of Karstedt catalyst from different batches or vendors), reaction temperature and rates of chlorosilane addition did not improve the regioselectivity. Switching the solvent to diethyl ether degraded the selectivity (to 17% α-addition).



$1G_{Vinyl}$-8Cl (6)

Reaction of the impure intermediate **$1G_{Vinyl}$-8Cl** with vinylmagnesium bromide gave, after purification, the product **$1G_{Vinyl}$-8Vinyl** (eq. 7) whose ^1H NMR spectrum (Figure 3a), unlike that reported by Zhou and Roovers for the same compound,[26] contained signals attributable to the α-addition isomers. This result ruled out the possibility that α-addition isomers present in the chlorosilane-terminated dendrimer intermediate could be somehow removed during the process of purification of the vinylated product.

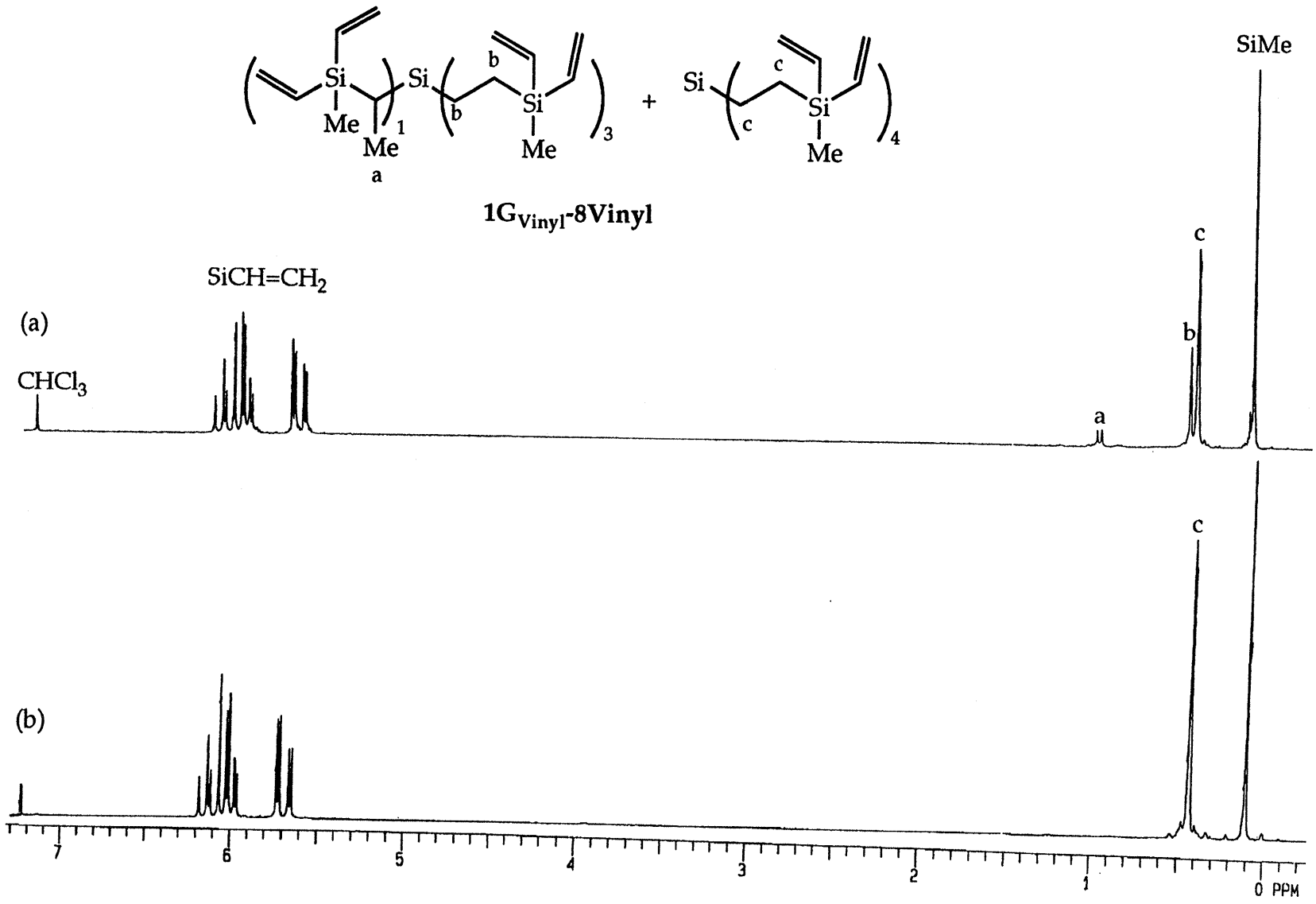
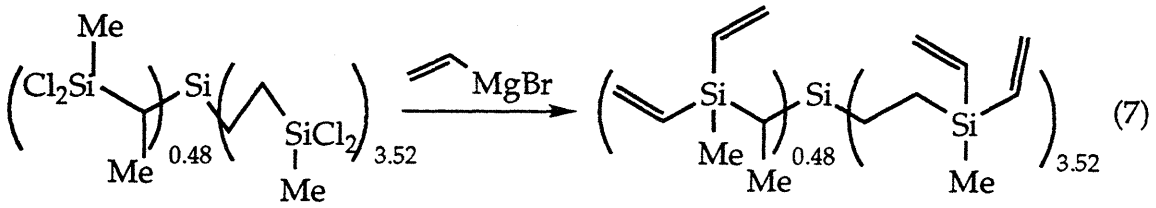


Figure 3. ^{1}H NMR Spectra of Samples of **1G$_{Vinyl}$-8Vinyl** Prepared from Samples of **1G$_{Vinyl}$-8Cl** Containing (a) 8% and (b) No α-Addition Products.

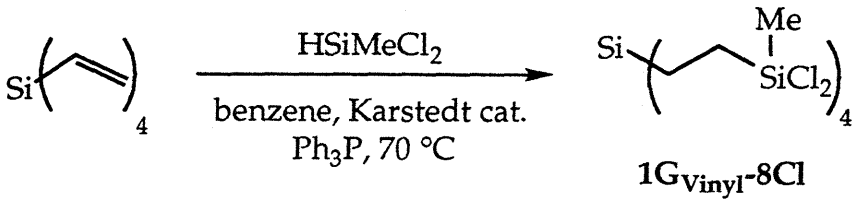


(7)

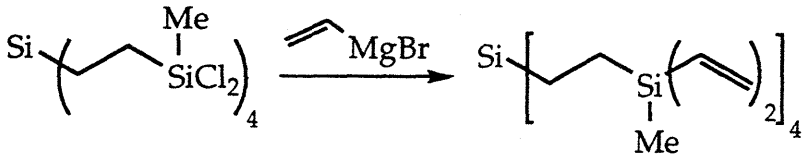
1G$_{Vinyl}$-8Cl **1G$_{Vinyl}$-8Vinyl**

An early study by Musolf and Speier showed that β-selectivities of hydrosilylations using $HSiCl_3$ were enhanced to a much greater degree than those of reactions employing $HSiMeCl_2$ when THF was added to the reaction mixtures.[55] This result explains why Seyferth and Son were able to obtain dendrimers free from α-addition products by using THF as reaction solvent in the hydrosilylation step[27] and why this approach failed in the present study. Studies by Čapka et. al. demonstrated dramatic improvements in the β-selectivity of the hydrosilylation of styrene with $HSiMeCl_2$ when bulky Lewis bases were added to the reaction mixture.[56] Triphenylphosphine gave the best results, resulting in complete selectivity for β-addition.

When tetravinylsilane was reacted with $HSiMeCl_2$ in benzene solvent in the presence of triphenylphosphine and the Karstedt catalyst (or CPA), the **1G$_{Vinyl}$-8Cl** which formed contained only traces of α-addition by ^1H NMR (eq. 8; Figure 2b). Vinylation as before with vinylmagnesium bromide gave **1G$_{Vinyl}$-8Vinyl** (eq. 9) whose ^1H NMR spectrum (Figure 3b) contained none of the α-addition signals found in the previously synthesized sample and was identical to that reported by Zhou and Roovers.

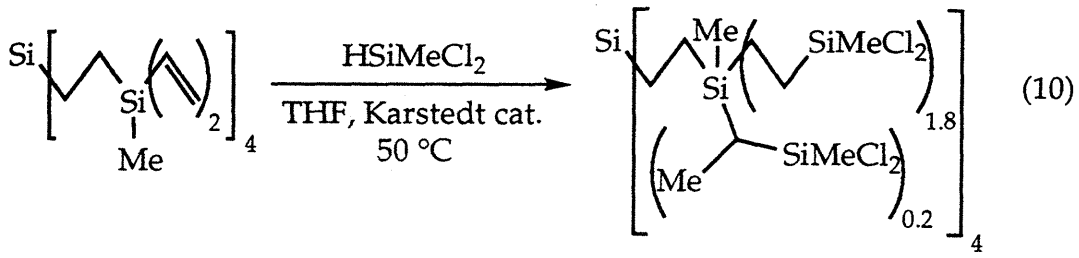


$1G_{Vinyl}$-8Cl (8)



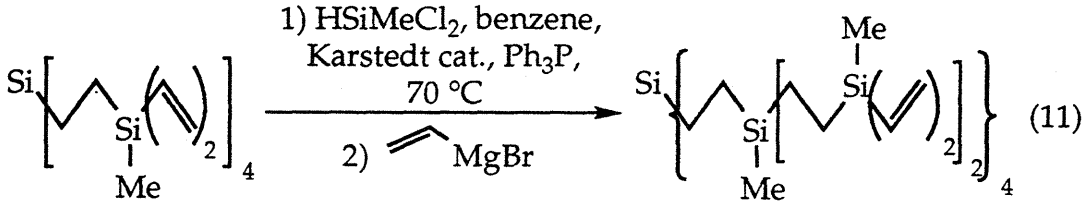
$1G_{Vinyl}$-8Cl $1G_{Vinyl}$-8Vinyl (9)

The simplest explanation for the origin of the observed improvement in regioselectivity involves the increased steric congestion of the catalytically active Pt species upon coordination by one or more molecules of triphenylphosphine which favors the sterically less-hindered β-insertion of the vinyl C=C bond into the Pt-H bond. Following this line of reasoning, it might be predicted that hydrosilylations of vinyl groups attached to first generation dendrimers would show inherently higher β-selectivities than those employing tetravinylsilane as a result of the increased steric bulk of the former. This was not the case, however. When **$1G_{Vinyl}$-8Vinyl** was reacted with $HSiMeCl_2$ according to the procedure of Zhou and Roovers, the product **$2G_{Vinyl}$-16Cl** contained 10% α-addition isomers (eq. 10). Fortunately, the methodology developed for the synthesis of **$1G_{Vinyl}$-8Vinyl** also worked in this case, giving **$2G_{Vinyl}$-16Vinyl** as a colorless, crystalline solid with no detectable α-addition products (eq. 11).



(10)

$1G_{Vinyl}$-8Vinyl **$2G_{Vinyl}$-16Cl**



(11)

$1G_{Vinyl}$-8Vinyl **$2G_{Vinyl}$-16Vinyl**

The final type of defect present in carbosilane dendrimer product mixtures arose from hydrolysis of the terminal Si-Cl bonds of the chlorosilane-terminated dendrimer intermediates (Scheme 5e), either due to traces of adventitious moisture in the hydrosilylation reaction mixture or incomplete alkenylation of all the terminal Si-Cl bonds. These hydrolysis products primarily consisted of dimeric species in which two dendrimers were linked together through one arm. Using large excesses of the alkenylating agent and heating the reaction mixture for extended periods of time reduced, but did not wholly eliminate, the presence of these impurities. Since these types of defects involved only a small fraction of the total number of endgroups of the dendrimers, in most cases they were not detectable by spectroscopic techniques. The only reliable method for routinely determining their presence and amount involved observing the molecular weight profiles of the product mixtures by GPC. As shown in Figure 4a for **$1G_{Vinyl}$-8Vinyl**, the dimeric product eluted sufficiently ahead of the desired product to give a well-resolved peak. Since the two substances were expected to have

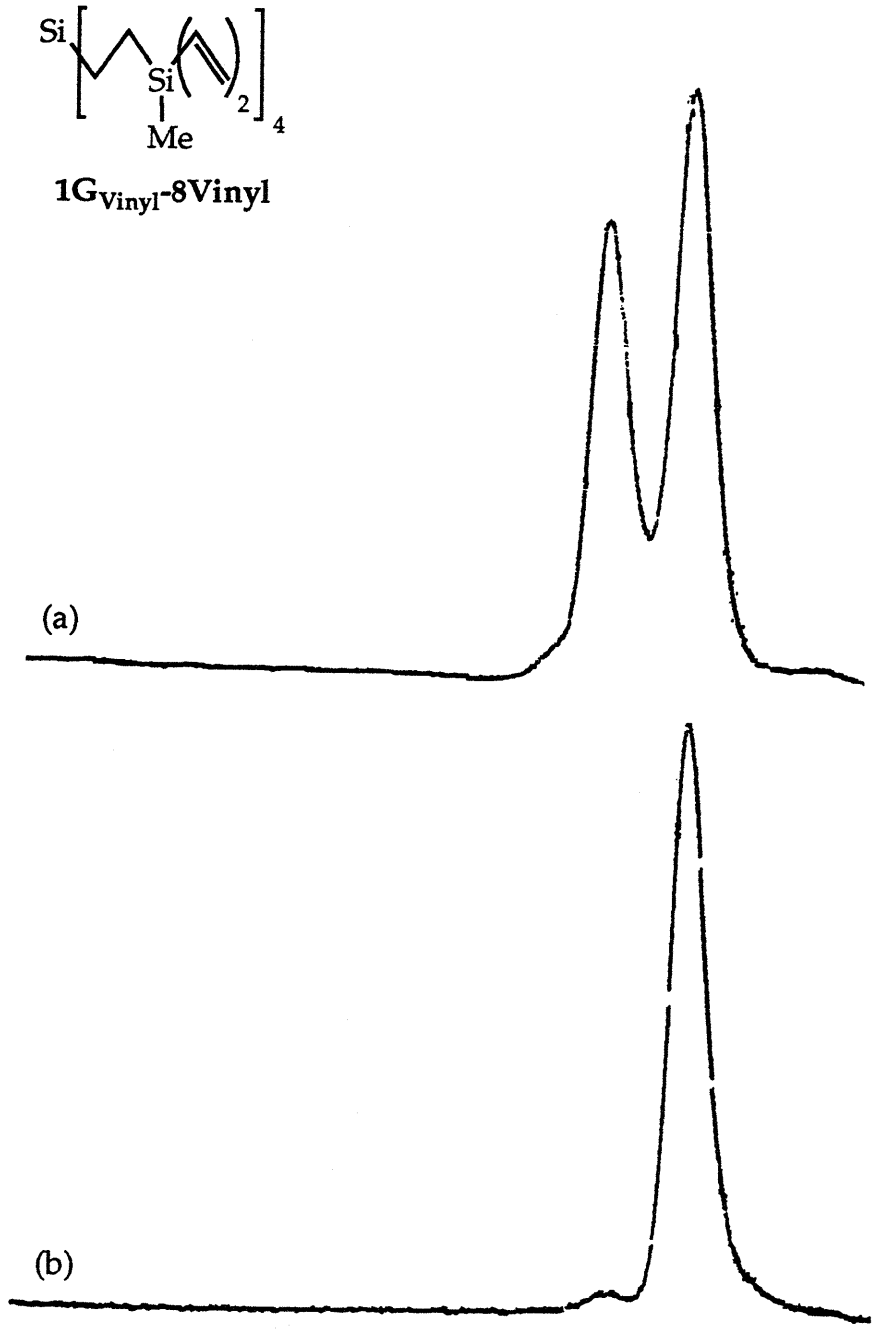


Figure 4. GPC Traces of (a) Late and (b) Early Fractions Taken from the Column Chromatographic Purification of **1G$_{Vinyl}$-8Vinyl**.

essentially identical refractive indices, comparison of integrated peak areas gave a quantitative determination of the amount of dimeric products present (bearing in mind that the dimeric product should give twice the signal intensity per mole as the monomeric product).

In contrast to the elution profile on the GPC column, on typical silica gel columns the dimeric products eluted more slowly than their monomeric counterparts. The resolution between desired product and impurity bands varied according to the dendrimer system and the generation. For allylsilane-based dendrimers, complete removal of dimeric products could be acheived after two successive purifications by column chromatography: the first column essentially removed all the poly(THF), and the second the dimeric products. For **1G$_{Vinyl}$-8Vinyl**, crude product mixtures contained approximately 10% dimeric impurities but no THF polymer, since the hydrosilylation reaction was conducted in benzene. When this crude product was purified by column chromatography, 77% of the theoretical yield of the product eluted first from the column; this fraction contained less than 4% (w/w) dimeric impurities by GPC (Figure 4b), corresponding to a molar purity of > 98%. Later fractions contained significantly higher proportions of the dimeric product (Figure 4a). Purification of **2G$_{Vinyl}$-16Vinyl** in a similar manner as the first generation dendrimer gave a lower yield of product (34%), but without any detectable traces of dimeric products by GPC.

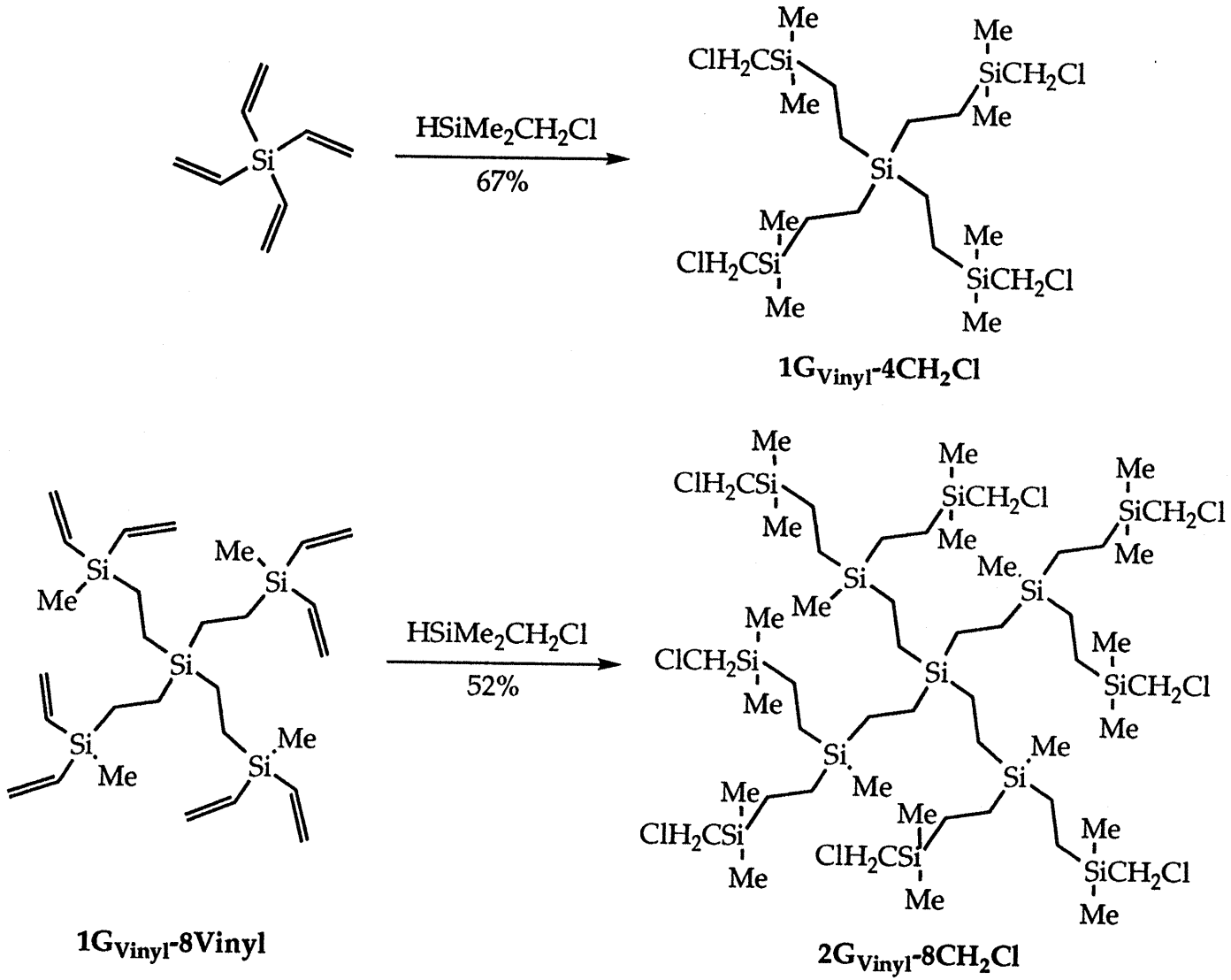
Introduction of (Chloromethyl)dimethylsilane Capping Groups

Dendrimers with terminal (chloromethyl)dimethylsilyl groups were prepared from vinylsilane- and allylsilane-based dendrimers by hydrosilylation with $HSiMe_2CH_2Cl$. This hydrosilylation reaction was strongly effervescent and exothermic, necessitating in many cases the slow

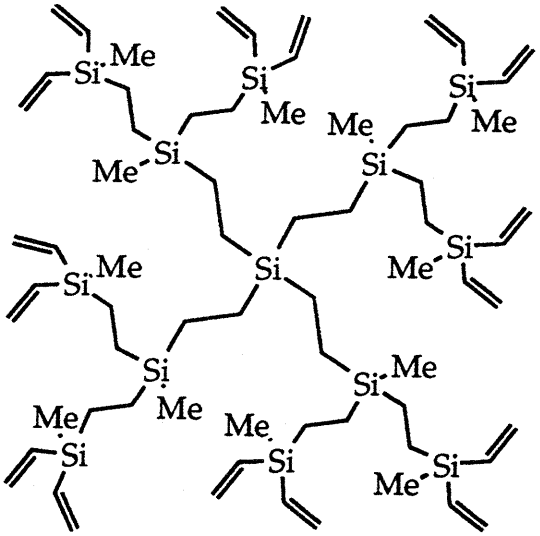
addition of the silane to the reaction mixture in order to avoid explosions. As the reaction progressed, the solution often developed a deep green color which was destroyed by prolonged heating.

For vinylsilane-based dendrimers, in all cases the terminal vinyl groups reacted completely with the (chloromethyl)dimethylsilane, furnishing chloromethyl-terminated dendrimers **$1G_{Vinyl}$-$4CH_2Cl$**, **$2G_{Vinyl}$-$8CH_2Cl$** and **$3G_{Vinyl}$-$16CH_2Cl$** in good yields (Scheme 6). The first and second generation dendrimers were crystalline solids, but the third generation was an oil. Each of these dendrimers gave monodisperse GPC traces. The lower yields obtained for the first and second generation dendrimers (67% and 52%, respectively) compared to the third (90%) arose from the presence of α-addition isomers in the products. Crude product mixtures of **$1G_{Vinyl}$-$4CH_2Cl$** and **$2G_{Vinyl}$-$8CH_2Cl$** contained 4% and 7%, respectively, α-addition isomers. Dendrimers containing one or more α-addition arms were less crystalline than the all-β-isomers and tended to form oils during recrystallization. Thus, recrystallized samples of **$1G_{Vinyl}$-$4CH_2Cl$** and **$2G_{Vinyl}$-$8CH_2Cl$** contained < 1% and 3.5 % α- addition products, respectively. Since the third generation dendrimer **$3G_{Vinyl}$-$16CH_2Cl$** was not crystalline, there was no way to remove the 9% α-addition products present in its terminal branches. Therefore, **$3G_{Vinyl}$-$16CH_2Cl$** was obtained as a mixture of products bearing differing amounts of α-addition isomers on the terminal branches: eq. 1 predicts the relative amounts of dendrimers having 0, 1, 2, 3, 4 and 5 α-addition isomers to be 22, 35, 26, 12, 4 and 1%, respectively.

Attempts to employ Ph_3P as cocatalyst in hopes of inhibiting the α-addition reaction resulted in the formation of a white precipitate (presumably $Ph_3PCH_2SiMe_2H^+$ Cl^-) and immediate termination of the hydrosilylation

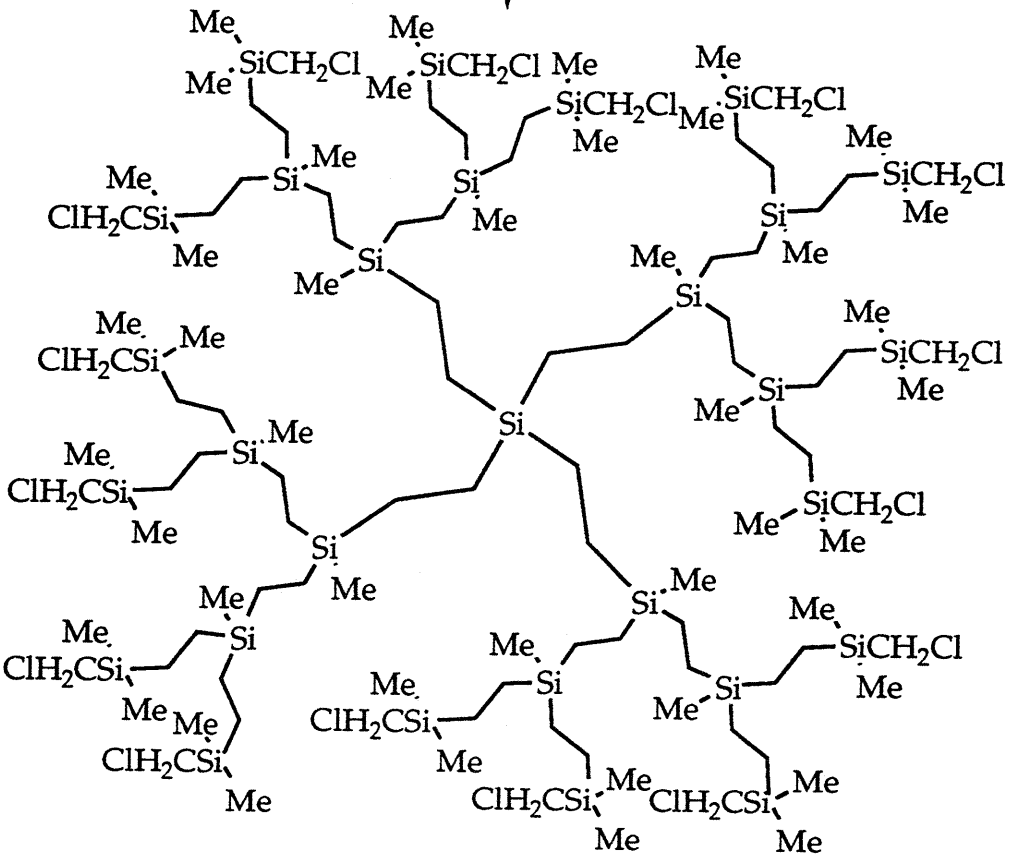


Scheme 6. Synthesis of Vinylsilane-Based, Chloromethyl-Terminated Dendrimers.



$2G_{Vinyl}$-16Vinyl

$HSiMe_2CH_2Cl$
90%



$3G_{Vinyl}$-16CH_2Cl

Scheme 6. (continued).

reaction. Amines such as pyridine and triethylamine also reacted with (chloromethyl)dimethylsilane to form insoluble salts. Substituting the sterically more hindered 2-methyltetrahydrofuran for THF as reaction solvent also gave no improvement in the β-selectivity.

The ^{1}H NMR spectra of **1G$_{Vinyl}$-4CH$_2$Cl**, **2G$_{Vinyl}$-8CH$_2$Cl** and **3G$_{Vinyl}$-16CH$_2$Cl** (Figure 5) were very similar, showing sharp singlets for the methyl and methylene protons of the terminal SiMe$_2$CH$_2$Cl units. Ethylene spacer units next to the terminal groups appeared as complex multiplets, while those in the interior of the second and third generation dendrimers gave broad singlets. Silicon-methyl groups at interior branch points of the second and third generation dendrimers appeared as a small singlet upfield from the methyl signals of the terminal groups.

Analysis by ^{13}C NMR spectroscopy (Figure 6) confirmed the regular structures of all three dendrimers. All carbon atoms, except those closest to the core of the third generation dendrimer, exhibited sharp, distinct resonances. The innermost carbon atoms of **3G$_{Vinyl}$-16CH$_2$Cl** appeared as broad signals (Figure 6c). The ^{29}Si NMR spectra of the three dendrimers (Figure 7) showed distinct signals for each type of silicon atom present in the molecule; their chemical shifts varied according to the number of carbon atoms attached β to the silicon atoms, in line with the generally established trend for tetralkylsilanes:[57] in all cases, the core silicon resonated the furthest downfield, followed by the internal silicon atoms bearing one methyl substituent; the terminal silicon atoms bearing one chloromethyl and two methyl groups were found at the highest frequencies. For the two internal silicon atoms of **3G$_{Vinyl}$-16CH$_2$Cl**, each bearing one methyl and three ethylene groups, the silicon atom closest to the core experienced a greater degree of shielding and resonated at higher field.

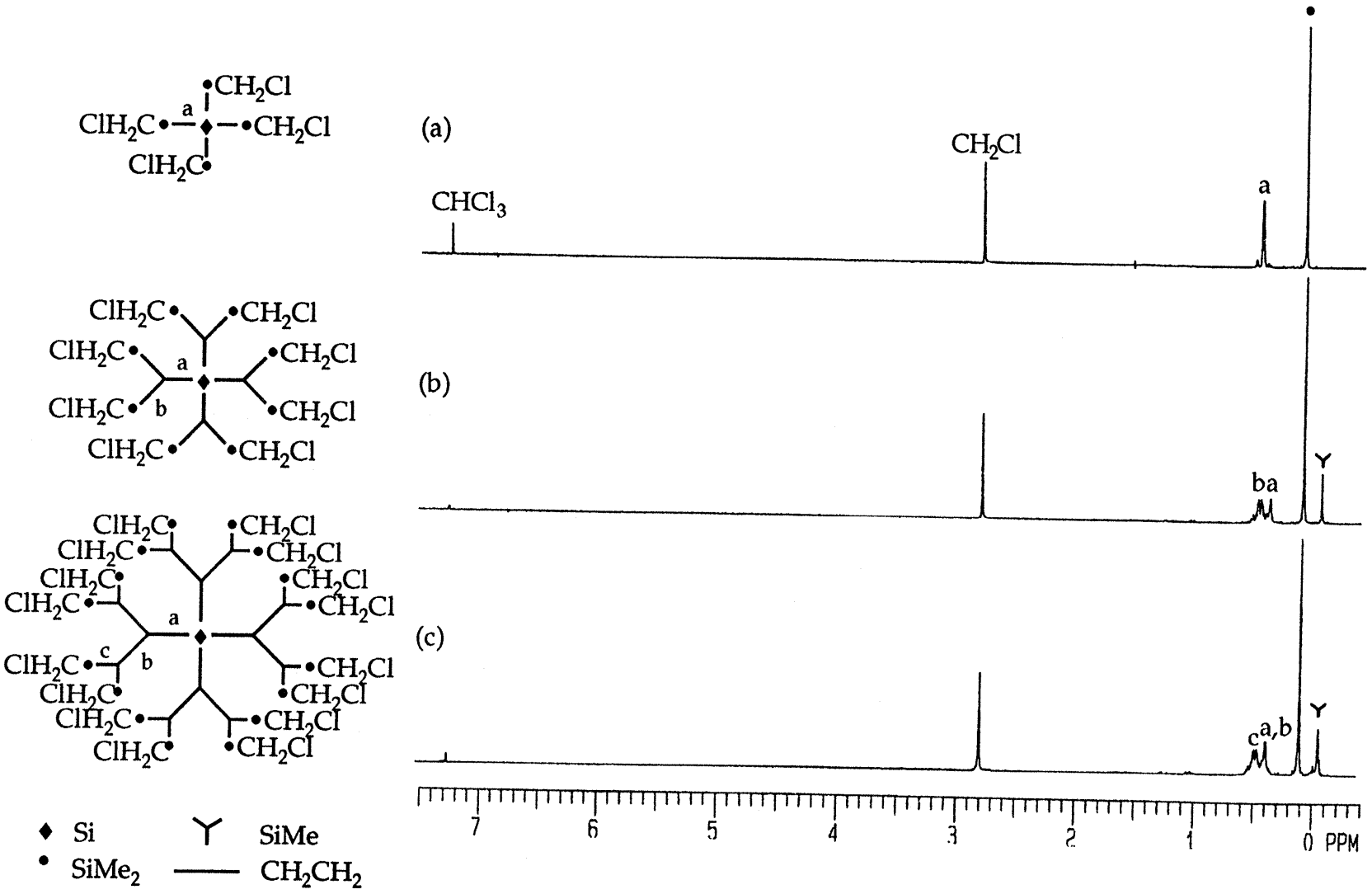


Figure 5. ^{1}H NMR Spectra of (a) **1G$_{Vinyl}$-4CH$_2$Cl**, (b) **2G$_{Vinyl}$-8CH$_2$Cl** and (c) **3G$_{Vinyl}$-16CH$_2$Cl**.

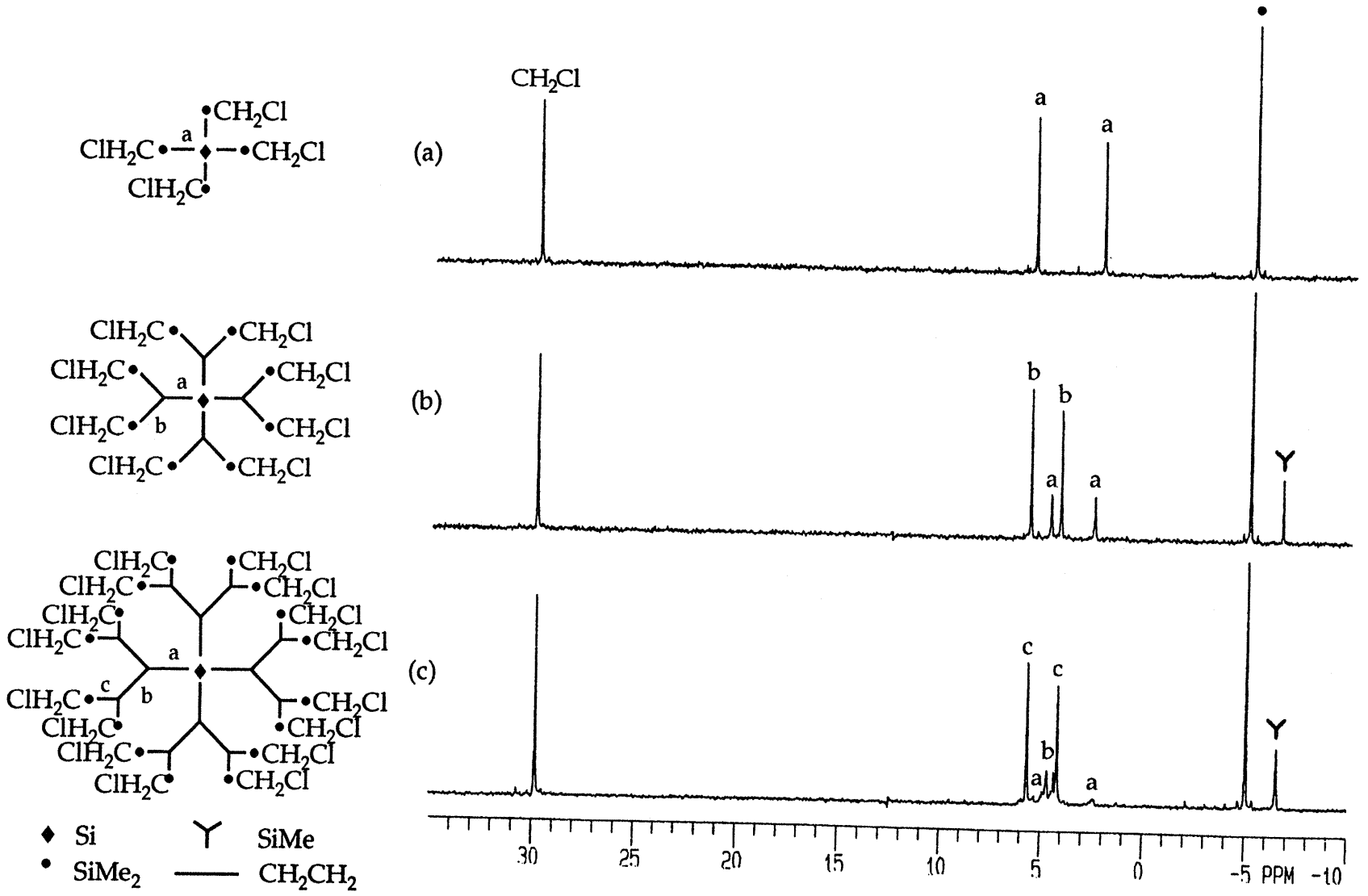


Figure 6. ^{13}C NMR Spectra of (a) $\mathbf{1G_{Vinyl}\text{-}4CH_2Cl}$, (b) $\mathbf{2G_{Vinyl}\text{-}8CH_2Cl}$ and (c) $\mathbf{3G_{Vinyl}\text{-}16CH_2Cl}$.

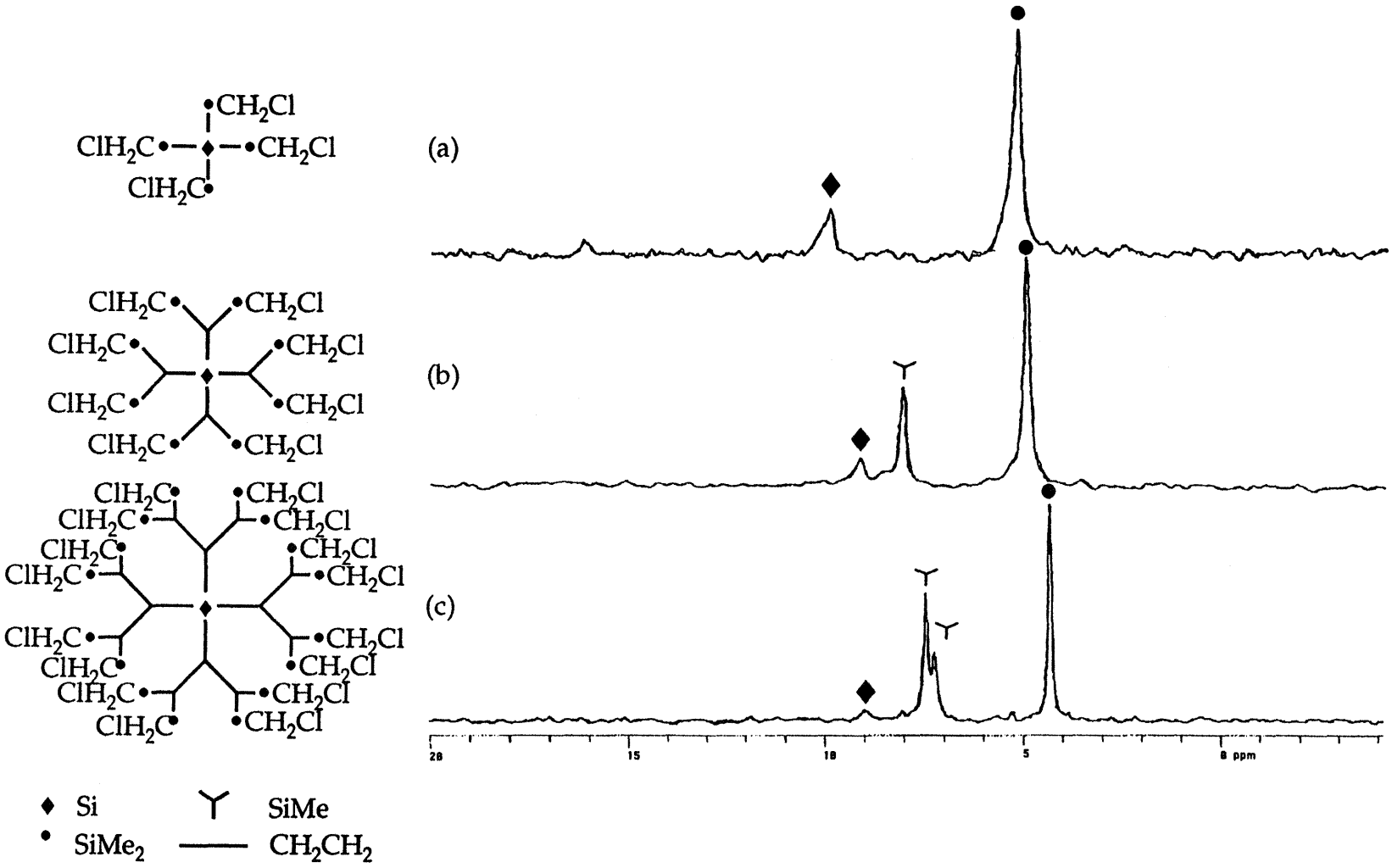


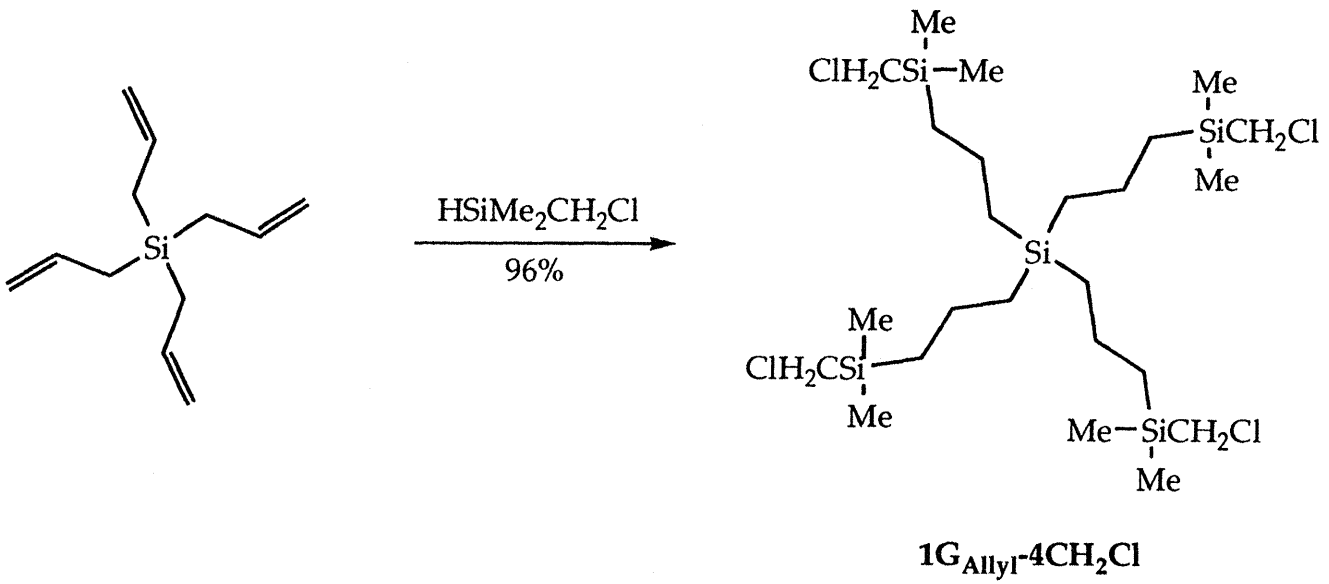
Figure 7. ^{29}Si NMR Spectra of (a) **1G$_{Vinyl}$-4CH$_2$Cl**, (b) **2G$_{Vinyl}$-8CH$_2$Cl** and (c) **3G$_{Vinyl}$-16CH$_2$Cl**.

Preparations of allylsilane-based, chloromethyl-terminated dendrimers (Scheme 7) proceeded analogously to those of the vinylsilane-based dendrimers, with two exceptions. First of all, the hydrosilylations proceeded without α-addition side reactions. Secondly, because of the lower reactivity of the allyl groups towards hydrosilylation, complete substitution with chloromethyl groups could be achieved only for tetraallylsilane and **$1G_{Allyl}$-12Allyl**. The hydrosilylation of **$2G_{Allyl}$-36Allyl** under the same conditions used for all the other dendrimers gave only 90% substitution. Even when the reaction mixture was heated in a sealed tube, the reaction left 3.4% of the allyl groups unreacted. This tendency for incomplete substitution has been observed by other workers for allylsilane-based dendrimers, and represents a serious deficiency of this particular carbosilane dendrimer system.

The first and second generation dendrimers **$1G_{Allyl}$-$4CH_2Cl$** and **$2G_{Allyl}$-$12CH_2Cl$** were fully characterized. Their ^{1}H (Figure 8), ^{13}C (Figure 9) and ^{29}Si (Figure 10) NMR spectra were consistent with their proposed structures. In contrast to what was observed in the ^{29}Si NMR for the vinylsilane-based dendrimers (Figure 7), the interior silicon atoms of the allylsilane-based dendrimers resonated at higher field than the terminal silicon atoms (Figure 10). The GPC trace of **$2G_{Allyl}$-$12CH_2Cl$** showed a monodisperse distribution; that of **$1G_{Allyl}$-$4CH_2Cl$** contained lower molecular weight peaks which are presumed to be artifactual given the high purity of the product indicated by spectroscopic and combustion analysis.

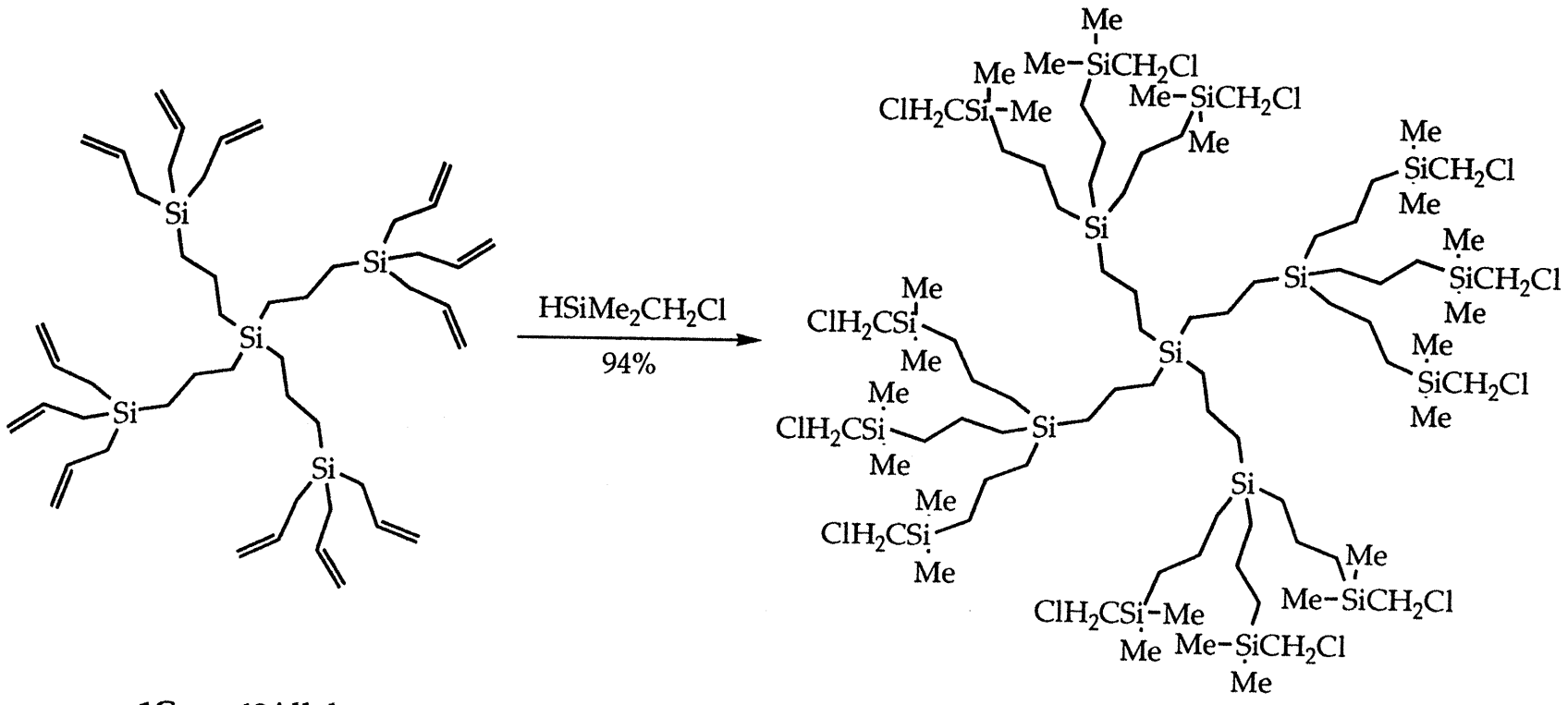
Chloromethyl-Terminated Carbosilane Dendrimers as Nucleophiles

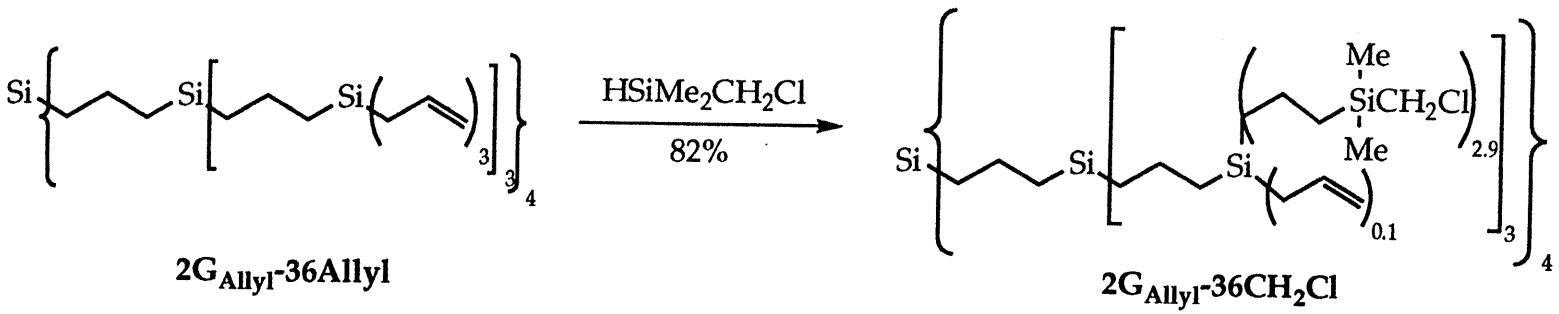
In order to test the possibility of using chloromethyl-terminated dendrimers as nucleophilic reagents in derivatization reactions, the dendrimeric Grignard reagent **$1G_{Vinyl}$-$4CH_2MgCl$** was prepared from the first



$1G_{Allyl}$-$4CH_2Cl$

Scheme 7. Synthesis of Allylsilane-Based, Chloromethyl-Terminated Dendrimers.





Scheme 7. (continued).

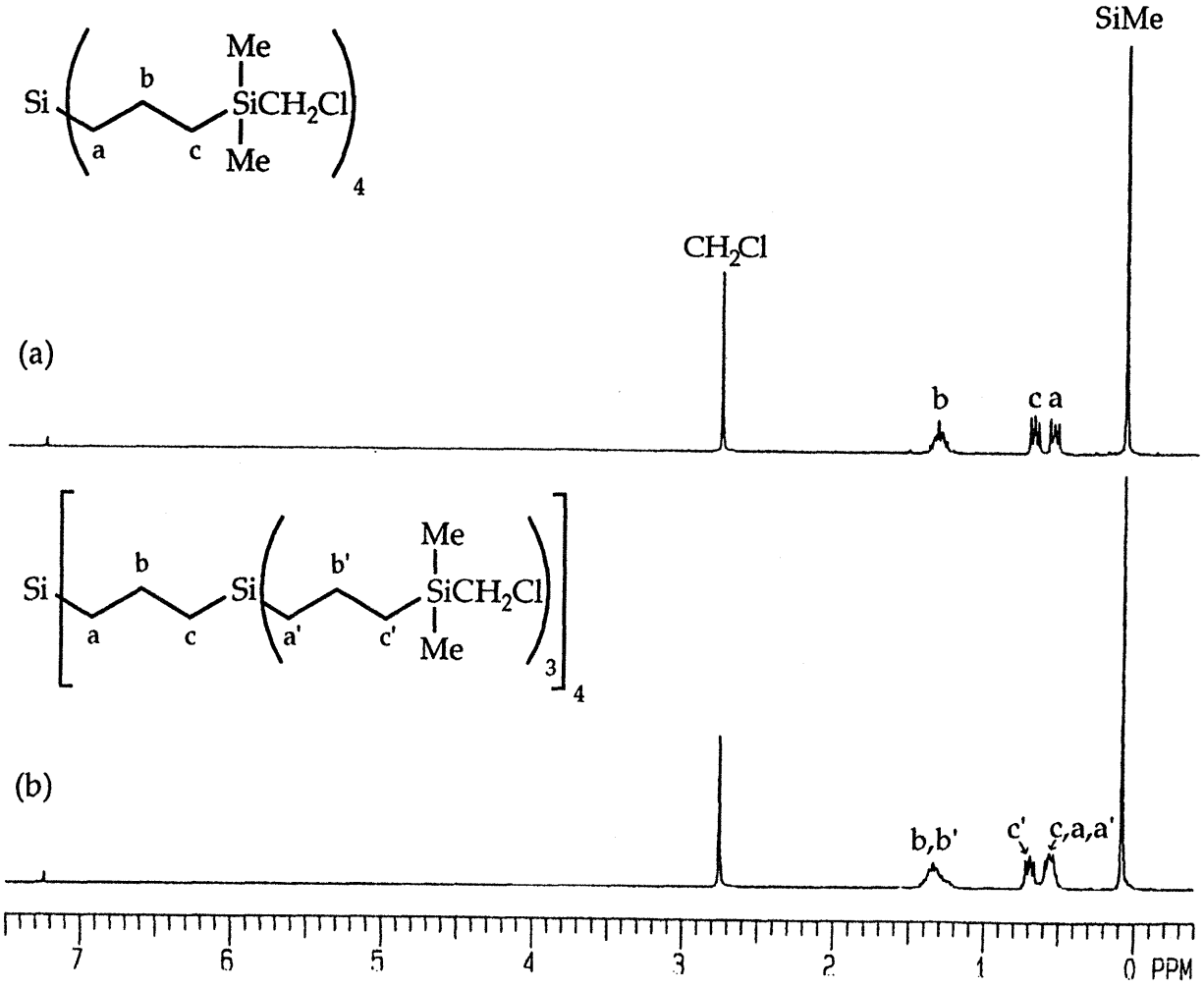


Figure 8. ^{1}H NMR Spectra of (a) **1G$_{Allyl}$-4CH$_2$Cl** and (b) **2G$_{Allyl}$-12CH$_2$Cl**.

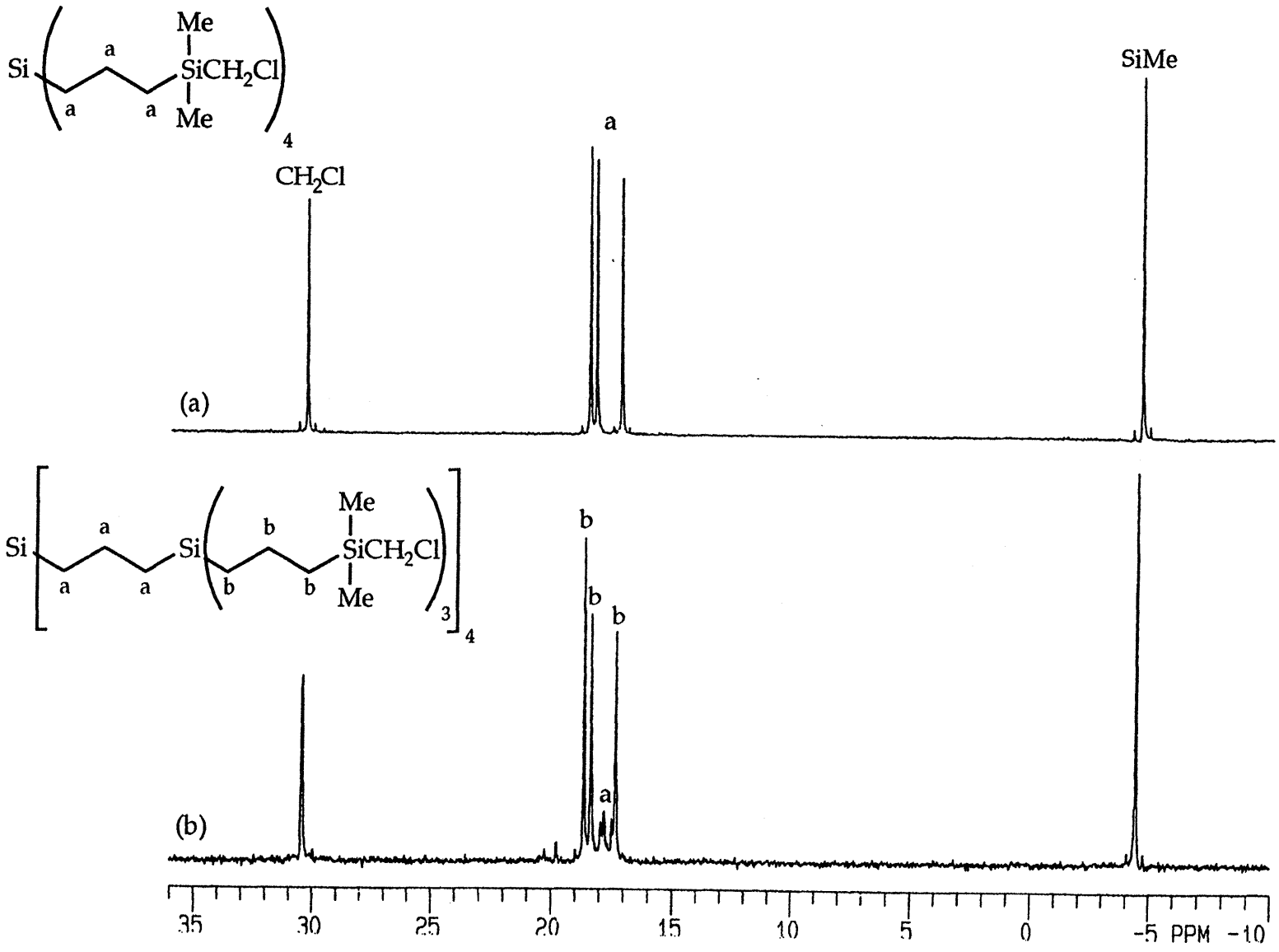


Figure 9. ^{13}C NMR Spectra of (a) **$1G_{Allyl}$-$4CH_2Cl$** and (b) **$2G_{Allyl}$-$12CH_2Cl$**.

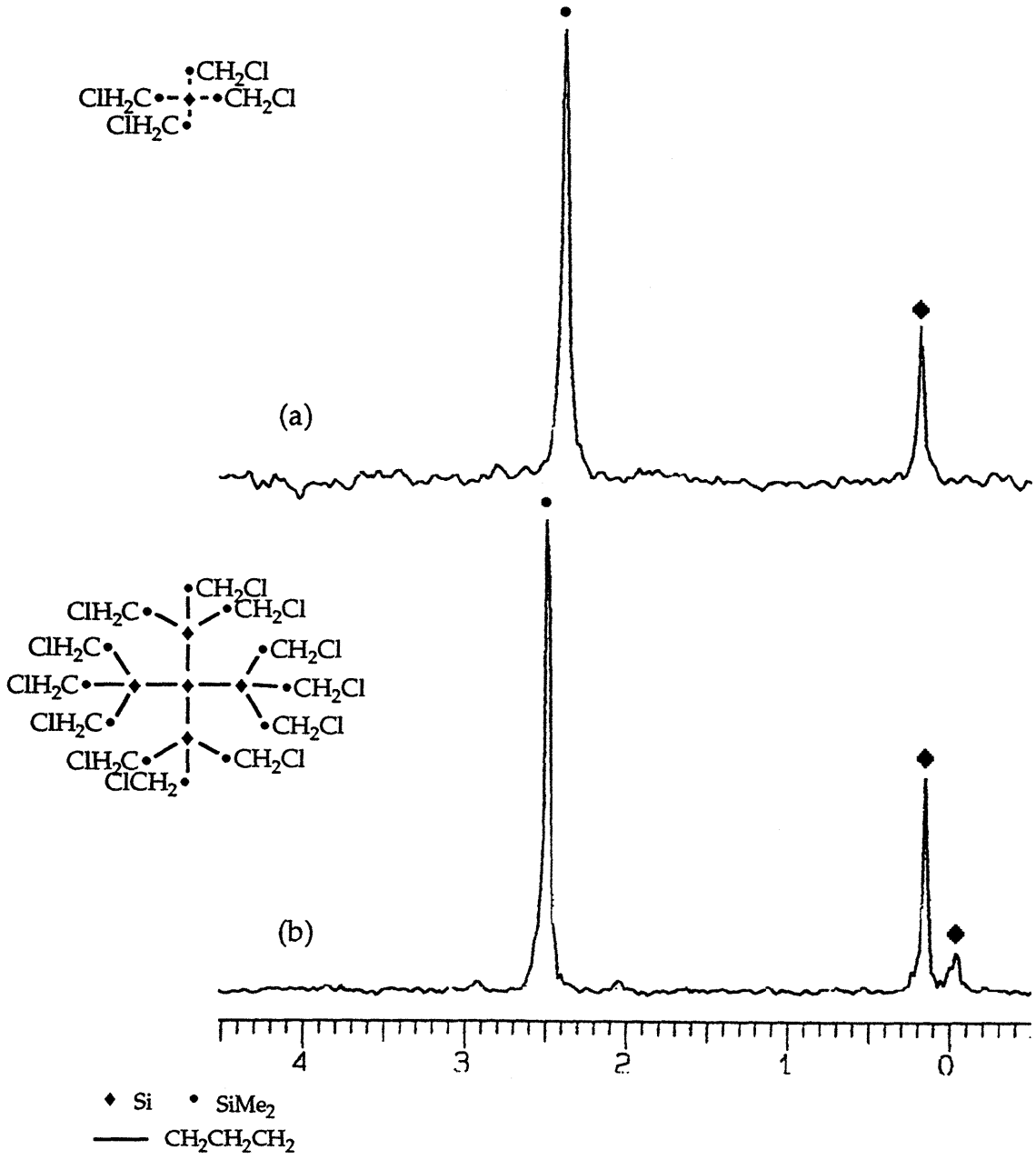
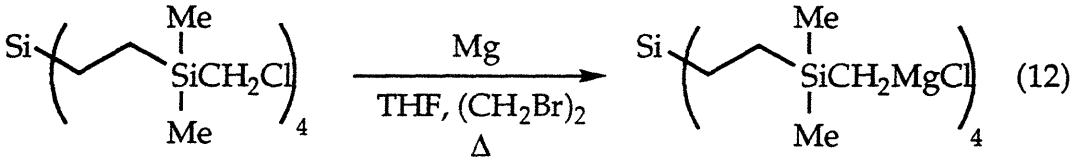


Figure 10. ^{29}Si NMR Spectra of (a) **1G$_{Allyl}$-4CH$_2$Cl** and (b) **2G$_{Allyl}$-12CH$_2$Cl**.

generation dendrimer **1G$_{Vinyl}$-4CH$_2$Cl** by its reaction with a slight excess of Mg turnings in dry THF (eq. 12). The reaction progressed very slowly, often requiring several days heating at reflux and several additions of ethylene dibromide to reach completion. The reaction was monitored by hydrolyzing aliquots and observing the disappearance of the methlyene peak of the chloromethyl group in the ^{1}H NMR spectrum. When diethyl or di-*n*-butyl ether were used in place of THF as the solvent, a viscous oil (presumably the Grignard reagent) precipitated from the reaction mixture, and all further reaction ceased.



(12)

1G$_{Vinyl}$-4CH$_2$Cl **1G$_{Vinyl}$-4CH$_2$MgCl**

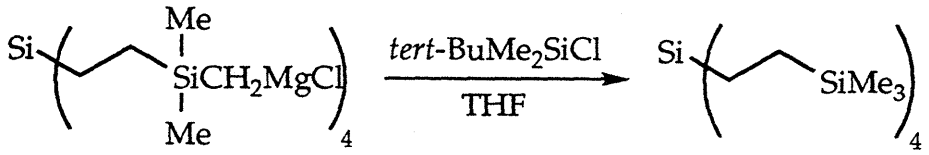
Once formed, **1G$_{Vinyl}$-4CH$_2$MgCl** was reacted with several metalloid and metal halides (Table 1) to give new dendrimers with terminal organometallic functionalities. The extent of the conversion depended upon the particular organometallic halide used; the balance of the silylmethylmagnesium chloride functionalities were converted to trimethylsilyl groups, which in most cases were visible as a sharp singlet at -0.048 ppm in the ^{1}H NMR spectra of the products. Because of the similar polarities of the trimethylsilyl and other organometallic groups, attempted chromatographic separations of dendrimers bearing mixtures of these substituents in most cases failed.

Table 1. Reactions of **1G$_{Vinyl}$-4CH$_2$MgCl** with Metal and Metalloid Halides.

Metal (Metalloid) Halide	React. Time/ Temp.	Conversion (%)[a]	Product
tert-BuMe$_2$SiCl	17 h 65 °C	0	**1G$_{Vinyl}$-12CH$_3$**
CH$_2$=CHMe$_2$SiCl	120 h R.T.	> 95	**1G$_{Vinyl}$-4CH$_2$SiMe$_2$CH=CH$_2$**
Me$_3$SnCl	24 h 65 °C	96[b]	**1G$_{Vinyl}$-4CH$_2$SnMe$_3$**
(COD)Pt(Cl)CH$_2$SiMe$_3$	39 h R.T.	> 95	**1G$_{Vinyl}$-4CH$_2$Pt(COD)(CH$_2$SiMe$_3$)**
(2,4,6-Me$_3$C$_6$H$_2$)$_2$BF	48 h 65 °C	87	**1G$_{Vinyl}$-4CH$_2$BMes$_2$**
Me$_3$SiCH$_2$HgCl	72 h R.T.	75	**1G$_{Vinyl}$-4CH$_2$HgCH$_2$SiMe$_3$**

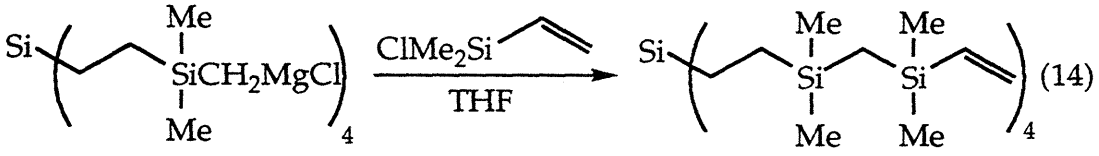
[a]Estimated from integrated areas of ^{1}H NMR spectrum.
[b]Estimated from results of combustion analysis.

No reaction occurred between **1G$_{Vinyl}$-4CH$_2$MgCl** and the sterically hindered *tert*-BuMe$_2$SiCl; instead, the completely reduced **1G$_{Vinyl}$-12CH$_3$** bearing four trimethylsilyl substituents was isolated in good yield (eq. 13). This product was completely characterized and served as a useful spectroscopic model compound for detecting the presence of trimethylsilyl groups in the products of the other Grignard reactions.



$1G_{Vinyl}$-$4CH_2MgCl$ **$1G_{Vinyl}$-$12CH_3$** (13)

Reaction of **$1G_{Vinyl}$-$4CH_2MgCl$** with the less-hindered chlorosilane CH_2=$CHMe_2SiCl$ (eq. 14) proceeded with > 95% conversion by ^1H NMR. The product **$1G_{Vinyl}$-$4CH_2SiMe_2CH$=CH_2** was fully characterized by elemental analysis and ^1H, ^{13}C and ^{29}Si NMR spectroscopy.



$1G_{Vinyl}$-$4CH_2MgCl$ (14)

$1G_{Vinyl}$ -$4CH_2SiMe_2CH$=CH_2

In the case of the reaction of **$1G_{Vinyl}$-$4CH_2MgCl$** with trimethyltin chloride (eq. 15), the spectroscopic features of the product **$1G_{Vinyl}$-$4CH_2SnMe_3$**, such as its ^1H NMR spectrum (Figure 11), suggested complete substitution of all silylmethylmagnesium chloride functionalities with trimethyltin groups; accordingly, **$1G_{Vinyl}$-$4CH_2SnMe_3$** was fully characterized. Combustion analysis repeatedly gave unsatisfactorily high percentages for both carbon and hydrogen. The calculated and experimentally determined carbon and hydrogen percentages could be reconciled by assuming incorporation of 4% trimethylsilyl groups (which contain much higher percentages of carbon and hydrogen than do the trimethyltin-substituted groups) into the product. Apparently, the NMR resonances for these groups were obscured by those of the trimethyltin-functionalized arms.

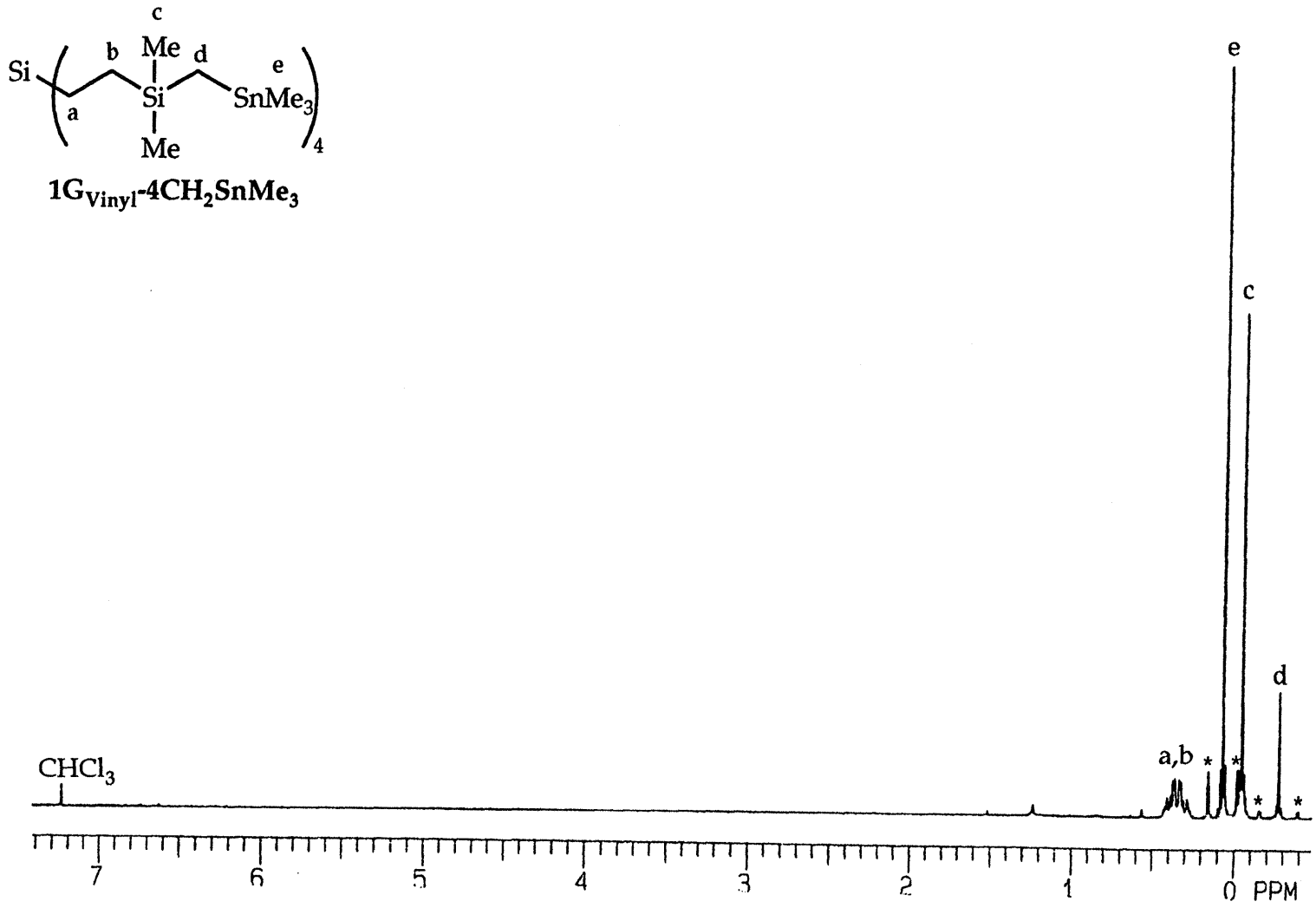
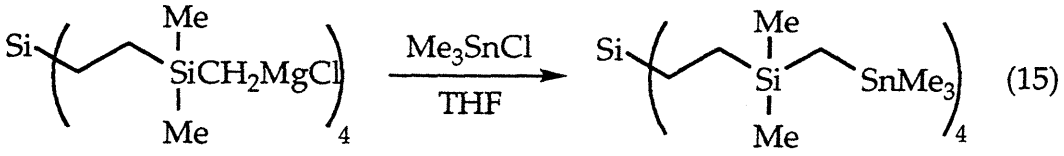


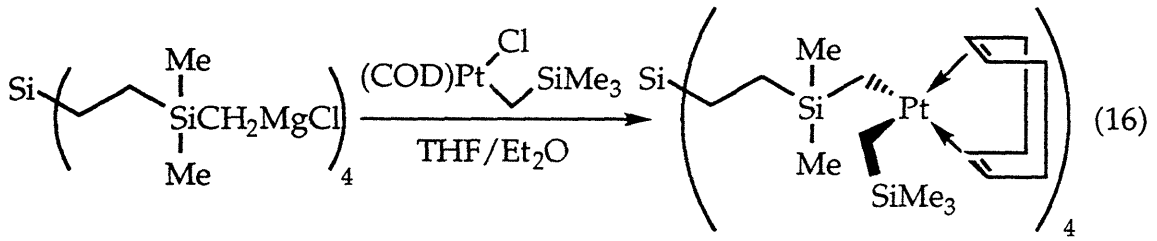
Figure 11. ^{1}H NMR Spectrum of **$1G_{Vinyl}$-$4CH_2SnMe_3$** ($^{117,119}Sn$ Satellites Are Marked with an Asterisk).



(15)

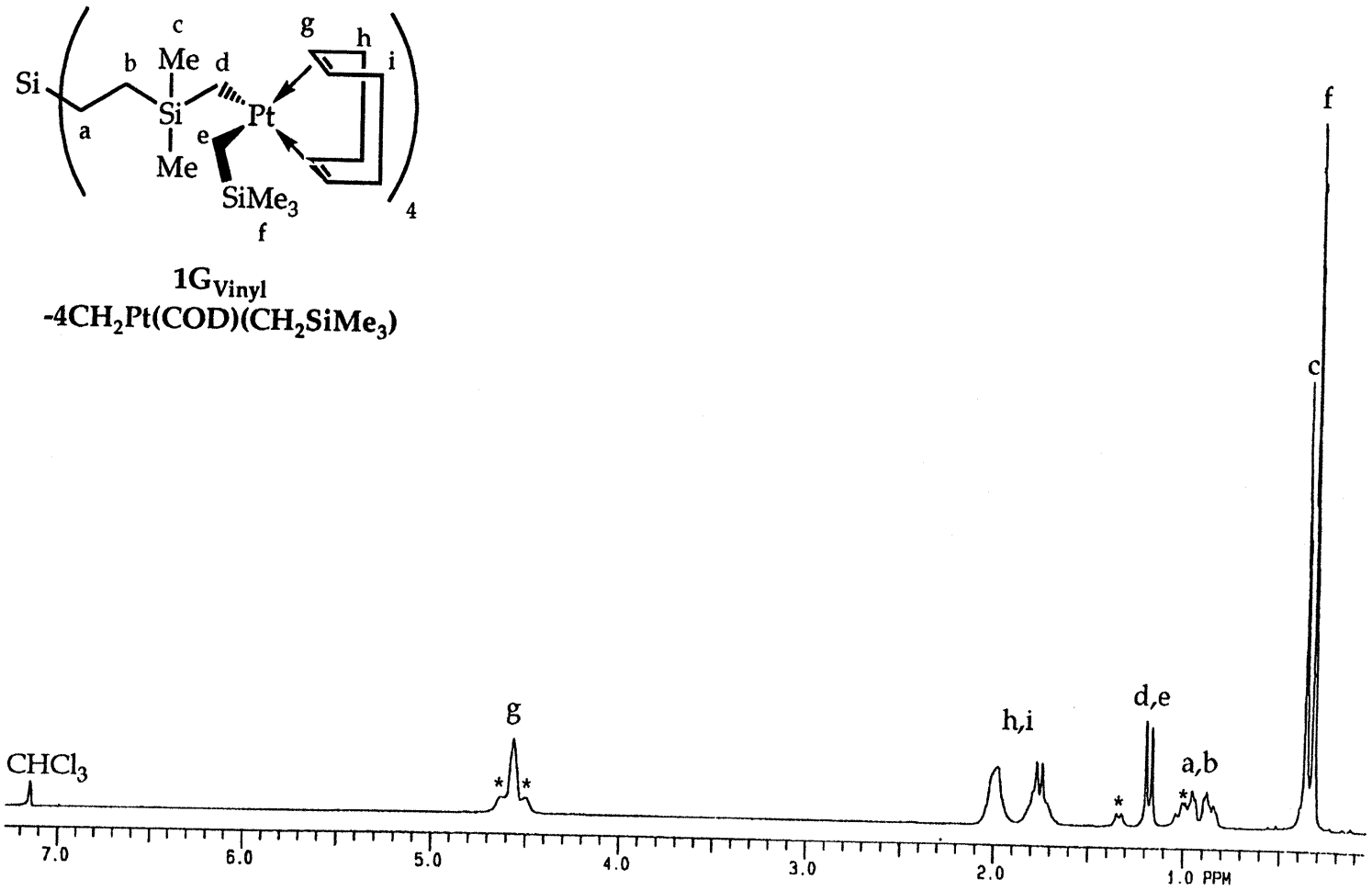
$1G_{Vinyl}$-$4CH_2MgCl$ **$1G_{Vinyl}$-$4CH_2SnMe_3$**

Ankianiec, et. al. in 1994 reported the high-yield preparation of a cycloocta-1,4-dienyl complex of Pt(II) bearing mixed silylmethyl ligands.[58] Their procedure involved the reaction of $PtCl(CH_2SiMe_3)(COD)$ (COD = 1,4-cyclooctadiene) with a functionalized silylmethyl Grignard reagent. Reaction of **$1G_{Vinyl}$-$4CH_2MgCl$** with $PtCl(CH_2SiMe_3)(COD)$ (eq. 16) gave dendrimer **$1G_{Vinyl}$-$4CH_2Pt(COD)(CH_2SiMe_3)$** which was purified by column chromatography. The ^1H (Figure 12), ^{13}C, ^{29}Si and ^{195}Pt NMR spectra of this product indicated that it was free from impurities. However, as was the case with **$1G_{Vinyl}$-$4CH_2SnMe_3$** , the carbon and hydrogen percentages of **$1G_{Vinyl}$-$4CH_2Pt(COD)(CH_2SiMe_3)$** determined by combustion analysis were higher than those calculated from the molecular formula. These differences could be accounted for by incorporation of as little as 4% trimethylsilyl groups in the product, an amount too low to be detected by spectroscopic means.



(16)

$1G_{Vinyl}$-$4CH_2MgCl$ **$1G_{Vinyl}$ -$4CH_2Pt(COD)(CH_2SiMe_3)$**



$1G_{Vinyl}$-$4CH_2Pt(COD)(CH_2SiMe_3)$

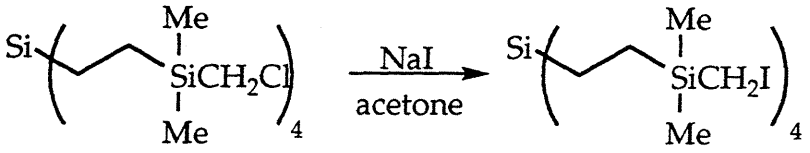
Figure 12. ^{1}H NMR Spectrum of **$1G_{Vinyl}$-$4CH_2Pt(COD)(CH_2SiMe_3)$** (^{195}Pt Satellites Are Marked with an Asterisk).

The last two examples using this method listed in Table 1 gave products with higher percentages of trimethylsilyl groups. Extended reaction times and rigorous drying of reagents and solvents did not improve the conversions, and attempted chromatographic purifications were not successful. As suggested by the first entry in Table 1, the steric hindrance and intrinsic reactivity of the organometallic halides towards Grignard reagents may have inhibited their complete reaction with **1G$_{Vinyl}$-4CH$_2$MgCl**. It is also very likely that traces of the Grignard reagent became hydrolyzed during the course of its formation through reactions with the solvent[59] or adventitious moisture. Taken together, these factors suggest that this method of derivatization in general is not expected to produce highly uniform functionalized dendrimers. On the other hand, given that the dendrimer's reactive sites which do not become functionalized with the organometallic moiety are protonated to give chemically inert trimethylsilyl groups, this system could still provide an entry into dendrimeric catalyst support systems for cases when strict uniformity is not an issue.

Chloromethyl-Terminated Carbosilane Dendrimers as Electrophiles

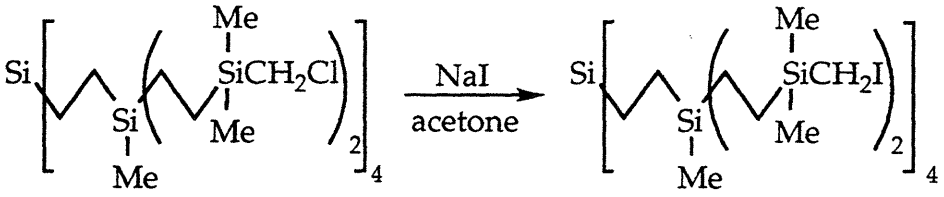
As a means of testing an alternative method for functionalizing chloromethyl-terminated carbosilane dendrimers, **1G$_{Vinyl}$-4CH$_2$Cl** and **2G$_{Vinyl}$-8CH$_2$Cl** were reacted with NaI under conditions of the well-known Finkelstein Reaction (eqs. 17, 18).[60] The iodide nucleophiles cleanly substituted all the C-Cl bonds of the chloromethyl-terminated dendrimers, giving the products **1G$_{Vinyl}$-4CH$_2$I** and **2G$_{Vinyl}$-8CH$_2$I** as analytically pure, colorless, crystalline solids in high yields. Spectroscopic data for the iodomethyl-substituted dendrimers were consistent with their proposed structures. The success of these reactions suggested that other derivatizations

with nucleophilic reagents might be successful. Chapter 4 describes one such series of experiments leading to carbosilane dendrimers functionalized with amphiphilic groups.



(17)

$1G_{Vinyl}$-$4CH_2Cl$ $1G_{Vinyl}$-$4CH_2I$



(18)

$2G_{Vinyl}$-$8CH_2Cl$ $2G_{Vinyl}$-$8CH_2I$

CONCLUSIONS

These studies imparted significant insight into the synthesis of defect-free carbosilane dendrimers. By closely examining each of the possible side reactions and its associated defect or impurity, methods were developed to detect and remove these impurities, giving dendrimers suitable for applications requiring highly regular structures. These studies also allowed the critical evaluation of the advantages and limitations inherent in each of the common carbosilane dendrimer backbone systems. Syntheses of carbosilane dendrimers based on allylsilane units possessed the advantage of regiospecificity during the hydrosilylation reaction; this reaction, however, proceeded to completion only with difficulty, leading in some cases to missing branches and distributions of molecular weights. Hydrosilylations of

vinylsilane-based dendrimers occurred much more readily; establishing control over regioselectivy, however, required modification of the reaction conditions. Both systems of dendrimers formed dimeric products through hydrolysis reactions of terminal Si-Cl bonds. Removal of these products by column chromatography proceeded more easily, in general, for the allylsilane-based dendrimers.

Through use of the hydrosilylation reaction, a new functional group, the $SiCH_2Cl$ moiety, was introduced to the terminal branches of the carbosilane dendrimers and tested as a means of introducing additional functionality through chemically stable linkages. Conversion of these chloromethyl groups to the corresponding magnesium reagents followed by reaction with organometallic halides led, in most cases, to partial incorporation of organometallic moieties on the terminii of the branches. A more promising strategy for derivatization was demonstrated by the reaction of the terminal C-Cl bonds with NaI, furnishing the iodomethyl-substituted products in high purities and yields.

EXPERIMENTAL SECTION

General Comments

All reactions, unless otherwise noted, were performed under an argon atmosphere using standard Schlenk techniques. Glassware was oven dried overnight, assembled while hot and dried *in vacuo* before refilling with Ar. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from United Chemical Technologies and distilled from magnesium turnings before use. Tetravinylsilane (95% purity) was purchased from Gelest and used as received. Karstedt catalyst (Pt divinyltetramethyldisiloxane complex)[61-65] solutions were purchased from

United Chemical Technologies (cat. no. PC072; 2 - 3 wt% in xylenes, corresponding to ~0.1 M) or Gelest, Inc. (cat. no. SIP6831.0; 2.1 - 2.4 wt% Pt in xylenes, corresponding to ~0.1 M) and stored refrigerated in a desiccator; solutions from the two vendors were found to display similar activity. Chloroplatinic acid was obtained from Aldrich Chemical Co. as the hexahydrate and used as a 0.1 M solution in isopropanol. Tetrallylsilane and trimethyltin chloride were purchased from Aldrich and used as received. Bis(mesityl)fluoroborane was purchased from Aldrich and purified by sublimation. Magnesium turnings were activated by placing in a glass frit and successively rinsing with 5% HCl (aq), water and acetone, followed by drying *in vacuo*. (Chloromethyl)dimethylsilane,[66,67] allylmagnesium bromide,[68] trimethylsilylmethylmercuric chloride[69,70] and (chloro)(trimethylsilylmethyl)(cycloocta-1,4-diene)platinum(II)[71] were synthesized according to literature procedures.

Proton NMR spectra were obtained on a Varian XL-300 NMR spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from tetramethylsilane. Proton decoupled ^{13}C NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 75.4 MHz using $CDCl_3/CHCl_3$ as a reference at 77.0 ppm downfield from tetramethylsilane. ^{29}Si NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 59.59 MHz in $CDCl_3$ using tetramethylsilane (0.0 ppm) as the external standard. ^{119}Sn NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 111.9 MHz in $CDCl_3$ using tetramethylstannane (0.0 ppm) as the external standard. ^{195}Pt NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 64.4 MHz in $CDCl_3$ using a solution of K_2PtCl_4 in D_2O (-1631 ppm) as the external standard. Infrared spectra were obtained on a Perkin Elmer 1600 Series FTIR.

GPC molecular weight determinations were made using a Waters Millipore 150-C ALC/GPC chromatograph equipped with a three column setup (Waters Ultrastyragel 10^4, 10^3 Å; Waters μPorasil GPC 60 Å) using a refractive index detector and toluene as the eluent.

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark; Galbraith Laboratories, Inc., Knoxville, TN, and E+R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of Vinylsilane-Based Dendrimers

Preparation of $1G_{Vinyl}$*-8Cl According to the Method of Zhou and Roovers*[26] *(SWK VII/27c)*

Tetravinylsilane (2.68 g, 19.7 mmol) was combined with 9.0 mL of methyldichlorosilane (9.9 g, 86 mmol, 9% excess) and 40 mL of dry THF in a 100 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two glass stoppers. Three drops of Karstedt catalyst were added, and the reaction mixture was heated in an oil bath to 60 °C. After several minutes, a strong exotherm ensued which was controlled by briefly removing the heating bath. After the solution began to cool, the flask was again immersed in the 60 °C oil bath. After stirring for 18 h, an aliquot was transferred via cannula to an Ar-filled NMR tube equipped with a rubber septum. The sample was evacuated and dried for 15 min at room temperature and 0.01 torr before refilling with Ar and dissolving in dry $CDCl_3$. Analysis by ^1H NMR showed 11.7% α-addition as well as signals for poly(THF).

^1H NMR ($CDCl_3$): δ 0.65 - 0.90 (m, $SiC\underline{H}_2CH_2SiCl$, $SiC\underline{H}(CH_3)SiCl$), 0.77 (s, $SiCH_3Cl_2$) (overlapped, 5.15 H); 0.90 - 1.10 (m, 2.00 H, $SiCH_2C\underline{H}_2SiCl$); 1.22 (d, J

= 8 Hz, 0.40 H, SiCH(C<u>H</u>$_3$)SiCl); 1.6 (m, br, 0.55 H), 1.7 (m, 0.11 H), 1.83 (m, br, 0.24 H) (OCH$_2$C<u>H</u>$_2$C<u>H</u>$_2$CH$_2$)$_n$); 3.5 (m, br, 0.55 H), 3.53 (m, 0.13 H), 3.84 (m, br, 0.26 H) (OC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_2$)$_n$).

Typical Procedure for Preparation of Vinylmagnesium Bromide [72] *(SWK VII/48)*

A 500 mL three-necked, round-bottomed flask equipped with a dry ice condenser, two rubber septa and a large magnetic stir bar was charged with 6.57 g of Mg turnings (0.270 g atom); these were covered with a thin layer (*ca.* 30 mL) of dry THF. Vinyl bromide (36.7 g, 342 mmol, 27% excess) was condensed at -78 °C in an Ar-filled 100 mL flask equipped with a rubber septum. After the condensation was complete, this flask was removed from the dry ice/acetone cooling bath, and the vapors allowed to pass through a cannula into the THF which was covering the Mg turnings. After approximately 5 min, the Mg turnings were heated with a heat gun until a brown color began to develop in the THF solution. At this point, the reaction mixture was diluted with *ca.* 300 mL of dry THF and the vinyl bromide addition was continued at a rate sufficient to maintain a gentle reflux. After the addition was complete (approximately 2 h), the reaction mixture was stirred for an additional 4 h, resulting in complete consumption of the Mg turnings.

Reaction of ***1G$_{Vinyl}$-8Cl*** *Containing α-Addition Products with Vinylmagnesium Bromide (SWK VII/28)*

1G$_{Vinyl}$-8Cl (19.8 mmol) was prepared as above, except using 5 drops of chloroplatinic acid solution (0.1 M in isopropanol) in place of the Karstedt catalyst. An aliquot of this substance showed 15% α-addition when analyzed

by ^{1}H NMR. This substance, a white waxy solid, was dried in its reaction vessel *in vacuo* for 8 h to remove excess chlorosilane before redissolving in 15 mL of dry THF. This solution was carefully added via cannula to a 500 mL three-necked, round-bottomed flask which was equipped with a reflux condenser, two rubber septa and a magnetic stir bar and which contained a freshly prepared solution of 0.238 mol (50% excess) of vinylmagnesium bromide in 250 mL of THF (see procedure above). The reaction mixture became warm, and reflux began. The hydrosilylation reaction vessel was rinsed twice with 10 mL portions of dry THF, and these rinses were added to the 500 mL flask via cannula. The reaction mixture then was immersed in an oil bath and heated to reflux. After stirring for 15 h, the reaction mixture was cooled to room temperature and carefully poured into 200 mL of sat. NH_4Cl (aq) solution. The organic layer was separated, and the aqueous layer was washed twice with 50 mL portions of diethyl ether. The combined organic layers were washed once with 100 mL of sat. NaCl (aq), dried over anhydrous $MgSO_4$ and filtered into a tared flask. All volatiles were removed at reduced pressure, and the resulting yellow oil was dried for 16 h at 0.01 torr (mass 10.1 g) before being purified by column chromatography (4.5 cm diam. column; 55 g of silica gel; 0.8% ethyl acetate in hexane as eluent). The first fraction, a clear, colorless, viscous oil (3.97 g), contained <5% higher-molecular-weight impurities by GPC. Analysis of subsequent fractions by GPC showed increasing amounts of higher-molecular-weight products. Yield 3.97 g (38%). Analysis of the first fraction by ^{1}H NMR showed 11% α-addition.

^{1}H NMR ($CDCl_3$): δ 0.109 (s, $SiCH_2CH_2SiC\underline{H}_3$), 0.130 (s, $SiCH(CH_3)SiC\underline{H}_3$) (overlapped, 12 H), 0.435 (s, br, 11.7 H, $Si(C\underline{H}_2C\underline{H}_2Si)_4$), 0.473 (s, br, 5.2 H, $Si(C\underline{H}_2C\underline{H}_2Si)_3(CH(CH_3)Si)$), 0.999 (d, J = 7.7 Hz, 1.5 H, $SiCH(C\underline{H}_3)Si$), 5.691 (dd,

J_{gem} = 20 Hz, J_{cis} = 4.6 Hz, 8 H, SiCH=C$\underline{H}_2$ (*trans* to Si)), 5.97 - 6.09 (m; 16 H; SiC$\underline{H}$=CH_2, SiCH=C$\underline{H}_2$ (*cis* to Si)).

Improved Synthesis of ***1G$_{Vinyl}$-8Vinyl*** *(SWK VII/48)*

Tetravinylsilane (2.31 g, 16.9 mmol) was combined with 8.00 mL of methyldichlorosilane (8.84 g, 76.8 mmol, 14% excess), 0.30 mL of triphenylphosphine solution (0.1 M in benzene) and 0.02 mL of Karstedt catalyst (~0.1 M in xylenes) in an Ar-filled, 40 mL thick-walled glass ampoule equipped with a rubber septum and a magnetic stir bar. Dry benzene (4 mL) added via syringe was used to rinse all material into the bottom of the ampoule. After changing the septum under Ar flow, the ampoule was immersed in a -78 °C dry ice/isopropanol bath and evacuated through a needle inserted into the septum. When a suitable vacuum had been established, the ampoule was flame-sealed. After warming to room temperature, the ampoule was immersed in an oil bath and heated with stirring to 120 °C; after 3 h the reaction mixture was cooled to 70 °C. After stirring for 13 h, the ampoule was cooled to room temperature, resulting in the formation of large crystals. The ampoule was opened in a Vacuum Atmospheres glove box. An aliquot analyzed by ^{1}H NMR showed complete consumption of vinyl groups and no measurable α-addition.

The entire contents of the ampoule were transferred in the glove box to a 100 mL Schlenk flask and dried *in vacuo* for 4 h, leaving a white, crystalline solid which was redissolved in 30 mL of dry THF. This solution was carefully added via cannula to a 500 mL three-necked, round-bottomed flask which was equipped with a reflux condenser, two rubber septa and a magnetic stir bar and which contained a freshly prepared solution of 0.270 mol (100% excess) of vinylmagnesium bromide in 330 mL of THF (see procedure above for

preparation of vinylmagnesium bromide). The reaction mixture warmed itself to reflux. When it began to cool, it was immersed in an oil bath and heated to reflux. After stirring for 46 h, the reaction mixture was cooled to room temperature and carefully poured into 200 mL of sat. NH_4Cl (aq) solution. The organic layer was separated, and the aqueous layer was washed twice with 150 mL portions of diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered into a tared flask. All volatiles were removed at reduced pressure, and the resulting yellow oil was dried for 14 h at 0.005 torr (mass 9.14 g). This oil was purified by column chromatography (3.5 cm diam. column; 51 g of silica gel; hexane eluent), giving **1G$_{Vinyl}$-8Vinyl** as a clear, colorless, viscous oil containing 3.7% higher-molecular-weight impurities by GPC. Yield 6.90 g (77%). Analysis by ^1H NMR showed no detectable α-addition.

^1H NMR ($CDCl_3$): δ 0.109 (s, 12 H, $SiCH_3$), 0.435 (s, br, 16 H, $Si(C\underline{H}_2C\underline{H}_2Si)_4$), 5.691 (dd, J_{gem} = 20 Hz, J_{cis} = 4.6 Hz, 8 H, $SiCH=C\underline{H}_2$ (*trans* to Si)), 5.97 - 6.09 (m; 16 H; $SiC\underline{H}=CH_2$, $SiCH=C\underline{H}_2$ (*cis* to Si)).

GPC: M_w = 547, M_n = 524, D = 1.04; (Calcd M_n = 529).

Improved Synthesis of ***2G$_{Vinyl}$-16Vinyl*** *(SWK VII/73b)*

Following the above procedure for the improved synthesis of **1G$_{Vinyl}$-8Vinyl**, 0.94 g of **1G$_{Vinyl}$-8Vinyl** (1.78 mmol), 0.3 mL of triphenylphosphine solution (0.1 M in benzene), 1.80 mL of dichloromethylsilane (1.98 g, 17.2 mmol, 21% excess), 0.02 mL of Karstedt catalyst (~0.1 M in xylenes) and 4.0 mL of dry benzene were placed in a 40 mL ampoule containing a stir bar. The ampoule was flame-sealed under vacuum and then immersed in an oil bath and heated to 85 - 90 °C. After 20.6 h stirring, the reaction mixture was cooled

to room temperature and analyzed by ^{1}H NMR which showed complete reaction of vinyl groups and no α-addition.

Following the above procedure for the improved synthesis of **1G$_{Vinyl}$-8Vinyl**, the chlorosilane-terminated intermediate **2G$_{Vinyl}$-16Cl** was isolated as a slightly yellow, viscous oil and reacted with a solution of 58.0 mmol (100% excess) of vinylmagnesium bromide in 100 mL of THF. After stirring for 93 h at reflux, the reaction mixture was hydrolyzed with 200 mL of sat. NH_4Cl (aq) solution. The organic layer was separated, and the aqueous layer was washed twice with 50 mL portions of diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered into a tared flask. All volatiles were removed at reduced pressure, and the resulting yellow oil was dried for 24 h at 0.1 torr (mass 2.26 g). This oil was purified by column chromatography (3.5 cm diam. column; 40 g of silica gel; hexane followed by 4% ethyl acetate in hexane as eluents). The fractions collected with hexane eluent crystallized as colorless plates and contained no higher-molecular-weight impurities observable by GPC; analysis by ^{1}H NMR showed no detectable α-addition. Yield 0.790 g (34%), m.p. 35 - 36 °C.

^{1}H NMR ($CDCl_3$): δ -0.105 (s, 12 H, Si($C\underline{H}_3$)($CH_2C\underline{H}_2$)$_3$), 0.107 (s, 24 H, Si($C\underline{H}_3$)CH=$C\underline{H}_2$), 0.318 (s, br, 16 H, Si($C\underline{H}_2C\underline{H}_2$)$_4$), 0.439 (m, 32 H, Si$C\underline{H}_2C\underline{H}_2$SiCH=$C\underline{H}_2$), 5.691 (dd, J_{gem} = 20 Hz, J_{cis} = 4.5 Hz, 16 H, SiCH=$C\underline{H}_2$ (*trans* to Si)), 5.97 - 6.09 (m; 32 H; Si$C\underline{H}$=CH_2, SiCH=$C\underline{H}_2$ (*cis* to Si)).
GPC: M_w =1429, M_n = 1375, D = 1.04; (Calcd M_n = 1315).

Preparation of Allylsilane-Based Dendrimers

Preparation of ***1G$_{Allyl}$-12Allyl***[24,25,48] *(SWK VII/51b)*

Tetraallylsilane (2.44 g, 12.7 mmol) was combined with 10.2 mL of freshly distilled trichlorosilane (13.7 g, 101 mmol, 99% excess) and 15 mL of dry THF in a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa. Karstedt catalyst (80 μL) was added via syringe, resulting in the formation of bubbles and an exotherm which lasted approximately 8 min. When the reaction mixture began to cool, it was immersed in an oil bath and heated to 45 °C. After 50 min., the reaction mixture had become cloudy, so an additional 80 μL of catalyst was added. After an additional 3 h, an aliquot was removed via syringe and analyzed by ^{1}H NMR which showed 91% conversion of allyl groups. An additional 80 μL of catalyst was added, and the reaction mixture was stirred for 16 h at 50 °C. At this point, another aliquot was removed which showed complete conversion of allyl groups by ^{1}H NMR. The reaction mixture was cooled to room temperature and evacuated, drying 1.5 h at 0.01 torr.

Allylmagnesium bromide was prepared in a 1 L three-necked, round-bottomed flask equipped with a reflux condenser, a pressure-equalizing dropping funnel, a rubber septum and a magnetic stir bar by slowly adding (over a period of 24 h) 34.6 mL of allyl bromide (48.4 g, 400 mmol) dissolved in 125 mL of diethyl ether to 9.62 g of Mg turnings (0.396 g atom) suspended in 550 mL of diethyl ether which had been cooled to 0 °C in an ice bath. Titration of hydrolyzed aliquots of this solution vs. a standard 0.1 N HCl (aq) solution gave a concentration of 0.39 M, corresponding to *ca.* 0.26 mol of allylmagnesium bromide. The chlorosilane-terminated dendrimer intermediate was redissolved in 10 mL of dry THF and added via cannula to the allylmagnesium bromide reaction vessel followed by two 10 mL rinses of THF. With each addition, an exothermic reaction occurred. When the

addition was complete the reaction mixture was immersed in an oil bath and heated to reflux. After stirring for 3 d, the reaction mixture was cooled to room temperature and carefully poured into 200 mL of sat. NH_4Cl (aq) solution. The organic layer was separated, and the aqueous layer washed twice with 50 mL portions of diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered into a tared flask. All volatiles were removed at reduced pressure, and the resulting yellow oil was dried for 3 h at 0.01 torr (mass 26.48 g). Poly(THF) was removed from this oil by column chromatography, (4.5 cm diam. column; 60 g silica gel; hexane eluent), giving 10.26 g of a clear, colorless, viscous oil containing <5% higher-molecular-weight impurities by GPC. Pure dendrimer without any higher-molecular-weight contaminants was obtained by performing a second column (4.5 cm diam. column; 60 g of silica gel; hexane eluent). The clear, colorless, viscous oil obtained was dried for 2 h at room temperature and 0.001 torr. Yield 5.58 g (55%).

^{1}H NMR ($CDCl_3$): δ 0.53 (m, 8 H, $SiC\underline{H}_2CH_2CH_2SiCH_2CH{=}CH_2$); 0.63 (m, 8 H, $SiCH_2CH_2C\underline{H}_2SiCH_2CH{=}CH_2$); 1.33 (m, 8 H, $SiCH_2C\underline{H}_2CH_2SiCH_2CH{=}CH_2$); 1.56 (d, J = 7.8 Hz, 24 H, $C\underline{H}_2CH{=}CH_2$); 4.83 (s, 12 H), 4.88 (d, J = 7.8 Hz, 12 H) ($CH_2CH{=}C\underline{H}_2$); 5.75 (m, 12 H, $CH_2C\underline{H}{=}CH_2$).

^{13}C NMR ($CDCl_3$): δ 16.52, 17.50, 18.26 ($Si\underline{C}H_2\underline{C}H_2\underline{C}H_2Si$); 30.31 ($\underline{C}H_2CH{=}CH_2$); 113.53 ($CH_2CH{=}\underline{C}H_2$); 134.35 ($CH_2\underline{C}H{=}CH_2$).

GPC: M_w = 898, M_n = 856, D = 1.05; (Calcd M_n = 802).

Preparation of ***2G$_{Allyl}$-36Allyl***[24,25,48] *(SWK VII/71)*

1G$_{Allyl}$-12Allyl (1.81 g, 2.26 mmol) was combined with 5.4 mL of freshly distilled trichlorosilane (7.2 g, 54 mmol, 99% excess) and 45 mL of dry

THF in a 100 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa. Karstedt catalyst (0.75 mL) was added via syringe. The reaction mixture was immersed immediately in an oil bath and heated to 50 °C. After stirring for 5 h, an aliquot was removed via syringe and analyzed by ^{1}H NMR which showed complete conversion of allyl groups. The reaction mixture was cooled to room temperature and evacuated, drying 5 h at 0.01 torr. The chlorosilane-terminated dendrimer intermediate was redissolved in 10 mL of dry THF and added via cannula along with two 10 mL rinses of THF to a 1 L three-necked, round-bottomed flask which was equipped with a reflux condenser, two rubber septa and a magnetic stir bar and which contained an allylmagnesium bromide solution in diethyl ether (0.35 M, 775 mL total volume, 0.27 mol). The reaction mixture was immersed in an oil bath and heated to reflux. After stirring for 57 h, the reaction mixture was cooled to room temperature and carefully poured into 300 mL of sat. NH_4Cl (aq) solution. The organic layer was separated, and the aqueous layer was washed twice with 100 mL portions of diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered into a tared flask. All volatiles were removed at reduced pressure, and the resulting yellow oil was briefly dried *in vacuo* (mass 16.59 g). Poly(THF) was removed from this oil by column chromatography (4.5 cm diam. column; 60 g of silica gel; hexane eluent). Earlier fractions contained no higher-molecular-weight impurities by GPC, and later fractions contained only traces. The combined fractions were dried for 2 h at room temperature and 0.01 torr, giving a clear, colorless, viscous oil. Yield 3.77 g (64%).

^{1}H NMR ($CDCl_3$): δ 0.53 (m, br, 32 H, $SiC\underline{H_2}CH_2CH_2Si$ (two types)); 0.63 (m, br, 32 H, $SiCH_2CH_2C\underline{H_2}Si$ (two types)); 1.33 (br, 32 H, $SiCH_2C\underline{H_2}CH_2Si$ (two types));

1.56 (d, J = 7.8 Hz, 72 H, $C\underline{H}_2CH=CH_2$); 4.83 (s, 36 H), 4.88 (d, J = 7.8 Hz, 36 H) ($CH_2CH=C\underline{H}_2$); 5.75 (m, 36 H, $CH_2C\underline{H}=CH_2$).

Preparation of Chloromethyl-Functionalized Dendrimers

Preparation of ***1G$_{Vinyl}$-4CH$_2$Cl*** *(SWK V/19)*

Tetravinylsilane (4.0 g, 30 mmol) was combined with 13.8 g of (chloromethyl)dimethylsilane (127 mmol) and 75 mL of dry THF in a 200 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two glass stoppers. Three drops of Karstedt catalyst were added, and one of the glass stoppers was replaced with an internal thermometer. After stirring for approximately 1 min the reaction temperature rose to 75 °C; this exotherm persisted for approximately 5 min. After the solution began to cool, it was immersed in a 46 °C oil bath. After stirring for 3 h, the reaction mixture was cooled to room temperature, and all volatiles were removed at reduced pressure, leaving a slightly brown, semi-crystalline solid containing 4% α-addition by ^{1}H NMR. This was recrystallized from hot ethanol, giving **1G$_{Vinyl}$-4CH$_2$Cl** as colorless needles containing negligible amounts of α-addition by ^{1}H NMR. Yield (3 crops): 12.44 g (67%), m.p. 56-7°C. Anal. Calcd for $C_{20}H_{48}Cl_4Si_5$ (570.83 g/mol): C, 42.08; H, 8.48%. Found: C, 42.32; H, 8.40%.

^{1}H NMR ($CDCl_3$): δ 0.085 (s, 24 H, CH_3), 0.45 (s, br, 16 H, CH_2CH_2), 2.78 (s, 8 H, CH_2Cl).

^{13}C NMR ($CDCl_3$): δ -5.11 (CH_3), 2.31 ($Si\underline{C}H_2CH_2SiCH_2Cl$), 5.60 ($SiCH_2\underline{C}H_2SiCH_2Cl$), 29.89 ($CH_2Cl$).

^{29}Si NMR ($CDCl_3$): δ 5.11 (4 Si, $SiCH_2Cl$), 9.82 (1 Si, $Si(CH_2CH_2)_4$).

GPC: M_w = 509, M_n = 480, D = 1.06.

IR (NaCl disk): 2955 (s, ν_{as} $SiCH_3$), 2903 (s, ν_s $SiCH_3$), 2881 (s, ν_{as} aliphatic CH_2), 2785 (m, ν_s aliphatic CH_2), 1395 (s, δ_{as} CH), 1247 (s, δ_s $SiCH_3$), 1173 (m), 1129 (s), 1104 (m), 1054 (s), 842 (s, br, ρ $SiCH_3$).

Preparation of $2G_{Vinyl}$-$8CH_2Cl$ *(SWK VII/68)*

In a 100 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa were combined 50 mL of dry THF, 3.37 g of **1G$_{Vinyl}$-8Vi** (6.36 mmol) and approximately 2 g of a total of 7.26 g of (chloromethyl)dimethylsilane (66.8 mmol, 31% excess) which had been weighed into a syringe. Karstedt catalyst (40 μL) was added, and the reaction mixture effervesced. The reaction mixture was immersed in an oil bath and heated with stirring to 35 °C. After 10 min, an additional 20 μL of catalyst was added along with another 2 g of the silane. Approximately 1 min after this, a strong exotherm occurred which was accompanied by the development of a bright green color. Upon completion of the exotherm, the remainder of the silane was added, and the reaction mixture was heated to 55 °C. After 19 h, an aliquot was removed via syringe and examined by ^1H NMR which showed complete consumption of vinyl groups and 7% α-addition. The reaction mixture was cooled to room temperature, and all volatiles were removed at reduced pressure. The resulting tan solid was extracted with 75 mL of hot hexane and filtered through a pad of silica gel. Hexane was removed at reduced pressure, and the white, semi-crystalline residue was dried for 12 h at room temperature and 0.01 torr before recrystallizing from 100 mL of hot ethanol. Two crops of crystals (colorless needles), total mass 4.99 g, were collected which contained 3.5% α-addition by ^1H NMR. The mother liquor was evaporated and dried for 5 h at room temperature and 0.1 torr, giving 2.22 g of a colorless, viscous oil which contained 17% α-addition

by ^{1}H NMR. Yield: 4.99 g (52%), m.p. 83-5°C. Anal. Calcd for $C_{52}H_{124}Cl_8Si_{13}$ (1398.27 g/mol): C, 44.67; H, 8.94%. Found: C, 45.05; H, 8.83%.

^{1}H NMR ($CDCl_3$): δ -0.079 (s, 12 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$), 0.074 (s, 48 H, $Si(C\underline{H}_3)_2CH_2Cl$), 0.35 (s, br, 16 H, $Si(C\underline{H}_2C\underline{H}_2)_4$], 0.44 (m, 32 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2Cl$), 2.77 (s, 16 H, CH_2Cl).

^{13}C NMR ($CDCl_3$): δ -6.63 ($Si(\underline{C}H_3)(CH_2CH_2)_3$), -5.04 ($Si(\underline{C}H_3)_2CH_2Cl$), 2.55 ($Si(\underline{C}H_2CH_2)_4$), 4.21 ($Si\underline{C}H_2CH_2SiCH_2Cl$), 4.70 ($Si(CH_2\underline{C}H_2)_4$), 5.68 ($SiCH_2\underline{C}H_2SiCH_2Cl$), 29.93 ($CH_2Cl$).

^{29}Si NMR ($CDCl_3$): δ 4.89 (8 Si, $SiCH_2Cl$), 7.99 (4 Si, $Si(CH_3)(CH_2CH_2)_3$), 9.06 (1 Si, $Si(CH_2CH_2)_4$).

GPC: M_w = 1310, M_n = 1260, D = 1.04.

IR (NaCl disk): 2954 (s, ν_{as} $SiCH_3$), 2901 (s, ν_s $SiCH_3$), 2881 (s, ν_{as} aliphatic CH_2), 2787 (m, ν_s aliphatic CH_2), 1394 (s, δ_{as} CH), 1248 (s, δ_s $SiCH_3$), 1174 (m), 1130 (s), 1104 (m), 1057 (s), 845 (s, br, ρ $SiCH_3$).

Preparation of ***3G$_{Vinyl}$-16CH$_2$Cl*** *(SWK VIII/19)*

In a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa were combined 20 mL of dry THF, 0.512 g of **2G$_{Vinyl}$-16Vi** (0.389 mmol) and 1.01 g of (chloromethyl)dimethylsilane (9.28 mmol, 50% excess). Three drops of Karstedt catalyst were added; the reaction mixture effervesced and underwent a mild exotherm. After the completion of the exotherm, the reaction mixture was immersed in a 54 °C oil bath. After stirring for 22 h, the reaction mixture was cooled to room temperature. All volatiles were removed at reduced pressure, leaving a viscous, brown oil which was purified by flash chromatography (silica gel; 5% ethyl acetate in hexane). Removal of the

solvents at reduced pressure left a clear, colorless, viscous oil which was dried for 20 h at room temperature and 0.09 torr. ^{1}H NMR analysis of this oil showed 8.8% α-addition. Yield: 1.08 g (90%). Anal. Calcd for $C_{116}H_{276}Cl_{16}Si_{29}$ (3053.195 g/mol): C, 45.63; H, 9.11%. Found: C, 46.10; H, 9.09%.

^{1}H NMR ($CDCl_3$): δ -0.082 (s, 36 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$ (two types)), 0.078 (s, 96 H, $Si(C\underline{H}_3)_2CH_2Cl$), 0.36 (s, br, 48 H, $SiC\underline{H}_2C\underline{H}_2Si(CH_3)(CH_2CH_2)_2$ (two types)), 0.44 (m, 64 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2Cl$), 1.00 (d, J = 7.4 Hz, 4.2 H, $SiCH(C\underline{H}_3)Si$), 2.76 (s, 32 H, CH_2Cl).

^{13}C NMR ($CDCl_3$): δ -6.52 ($Si(\underline{C}H_3)(CH_2CH_2)_3$ (two types)), -5.03 ($Si(\underline{C}H_3)_2CH_2Cl$), 2.42 (br, $Si(\underline{C}H_2CH_2)_4$), 4.20 ($Si\underline{C}H_2CH_2SiCH_2Cl$), 4.37 ($Si(CH_3)\underline{C}H_2CH_2Si(CH_3)(CH_2CH_2)_2$), 4.68 ($Si(CH_3)CH_2\underline{C}H_2Si(CH_3)(CH_2CH_2)_2$), 4.84 ($Si(CH_2\underline{C}H_2)_4$), 5.69 ($SiCH_2\underline{C}H_2SiCH_2Cl$), 29.86 ($CH_2Cl$).

^{29}Si NMR ($CDCl_3$): δ 4.32 (16 Si, $SiCH_2Cl$); 7.25 ($\underline{Si}(CH_3)(CH_2CH_2Si(CH_3)(CH_2CH_2)_2)_2$), 7.44 ($\underline{Si}(CH_3)(CH_2CH_2SiCH_2Cl)_2$) (overlapped, 12 Si); 9.01 (1 Si, $Si(CH_2CH_2)_4$).

GPC: M_w = 2100, M_n = 1940, D = 1.08.

IR (NaCl disk): 2953 (s, ν_{as} $SiCH_3$), 2903 (s, ν_s $SiCH_3$), 2788 (m, ν_s aliphatic CH_2), 1404 (s, δ_{as} CH), 1248 (s, δ_s $SiCH_3$), 1174 (m), 1130 (s), 1104 (m), 1059 (s), 793 (s, br, ρ $SiCH_3$).

Preparation of ***1G$_{Allyl}$-4CH$_2$Cl*** *(SWK VII/46)*

In a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa were combined 1.47 g of tetraallylsilane (7.65 mmol), 20 mL of dry THF and *ca.* 1 g of a total 4.32 g of (chloromethyl)dimethylsilane (39.7 mmol, 30% excess) which had been weighed into a syringe. Karstedt catalyst (40 μL) was added via syringe; the

weighed into a syringe. Karstedt catalyst (40 μL) was added via syringe; the reaction mixture effervesced and underwent a mild exotherm. The remainder of the silane was added over the course of the next 20 min, during which time a deep green color developed in the reaction mixture. When the addition was complete, the reaction mixture was immersed in a 50 °C oil bath. After 49.5 h stirring, the reaction mixture (now a brown color) was cooled to room temperature, and all volatiles were removed at reduced pressure, leaving a brown oil which was dried for 2 h at room temperature and 0.01 torr. This oil was extracted with 70 mL of hexane and filtered through a pad of silica gel. Removal of the hexane at reduced pressure left a clear, colorless, viscous oil which was dried for 18 h at room temperature and 0.02 torr. Yield: 4.60 g (96%). Anal. Calcd for $C_{24}H_{56}Cl_4Si_5$ (626.948 g/mol): C, 45.98; H, 9.00%. Found: C, 45.69; H, 9.53%.

^{1}H NMR ($CDCl_3$): δ 0.079 (s, 24 H, CH_3), 0.553 (m, 8 H, $SiCH_2CH_2CH_2SiCH_2Cl$), 0.686 (m, 8 H, $SiCH_2CH_2CH_2SiCH_2Cl$), 1.330 (m, 8 H, $SiCH_2CH_2CH_2SiCH_2Cl$), 2.75 (s, 8 H, CH_2Cl).

^{13}C NMR ($CDCl_3$): δ -4.55 (CH_3); 17.19, 18.23, 18.50 ($SiCH_2CH_2CH_2SiCH_2Cl$); 30.31 (CH_2Cl).

^{29}Si NMR ($CDCl_3$): δ 0.19 (1 Si, $Si(CH_2CH_2CH_2)_4$), 2.38 (4 Si, $SiCH_2Cl$).

GPC: M_w = 564, M_n = 535, D = 1.05 (contains two lower molecular weight peaks of roughly one-third the intensity of the primary peak).

IR (NaCl disk): 2957 (s, ν_{as} $SiCH_3$), 2915 (s, ν_s $SiCH_3$), 2875 (s, ν_{as} aliphatic CH_2), 1395 (s, δ_{as} CH), 1249 (s, δ_s $SiCH_3$), 1145 (s), 944 (m), 911 (s), 849 (s, br, ρ $SiCH_3$).

Preparation of $2G_{Allyl}$-$12CH_2Cl$ (SWK VII/44)

In a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa were combined 15 mL of dry THF, 3.37 g of **$1G_{Allyl}$-12Allyl** (6.36 mmol) and approximately 2 g of a total of 4.35 g of (chloromethyl)dimethylsilane (40.0 mmol, 29% excess) which had been weighed into a syringe. Karstedt catalyst (40 μL) was added, and the reaction mixture effervesced. The remainder of the silane was added over the course of the next 5 min, during which time a yellow-green color developed in the reaction mixture. When the addition was complete, the reaction mixture was immersed in an oil bath and heated to 55 °C. After stirring for 18 h, the reaction mixture (now a brown color) was cooled to room temperature, and all volatiles were removed at reduced pressure, leaving a brown oil which was dried for 4 h at 35 °C and 0.01 torr. This oil was purified by column chromatography (3.5 cm diam. column; 30 g of silica gel; hexane followed by 3% ethyl acetate in hexane as eluents), giving a faintly yellow, clear, viscous oil which was dried for 12 h at room temperature and 0.02 torr. Yield: 5.10 g (94%). Anal. Calcd for $C_{84}H_{192}Cl_{12}Si_{17}$ (2105.338 g/mol): C, 47.92; H, 9.19%. Found: C, 47.59; H, 9.43%.

^{1}H NMR ($CDCl_3$): δ 0.079 (s, 72 H, CH_3), 0.55 (m, br; 40 H; $Si(C\underline{H}_2CH_2C\underline{H}_2)_4$, $SiCH_2CH_2C\underline{H}_2SiCH_2Cl$), 0.69 (m, br, 24 H, $SiCH_2CH_2C\underline{H}_2SiCH_2Cl$), 1.33 (br, 32 H, $SiCH_2C\underline{H}_2CH_2Si$ (two types)), 2.75 (s, 32 H, CH_2Cl).

^{13}C NMR ($CDCl_3$): δ -4.43 (CH_3); 17.32, 18.33, 18.62 ($SiC\underline{H}_2C\underline{H}_2C\underline{H}_2SiCH_2Cl$); 17.47, 17.77, 17.90 ($Si(C\underline{H}_2C\underline{H}_2C\underline{H}_2)_4$); 30.41 ($CH_2Cl$).

^{29}Si NMR ($CDCl_3$): δ -0.046 (1 Si, $Si(CH_2CH_2CH_2)_4$), 0.121 (4 Si, $\underline{Si}CH_2CH_2CH_2SiCH_2Cl$), 2.48 (12 Si, $SiCH_2Cl$).

GPC: M_w = 1730, M_n = 1680, D = 1.03.

IR (NaCl disk): 2956 (s, ν_{as} $SiCH_3$), 2913 (vs, ν_s $SiCH_3$), 2873 (m, ν_{as} aliphatic CH_2), 1394 (m, δ_{as} CH), 1248 (s, δ_s $SiCH_3$), 1143 (m), 910 (m), 834 (s, br, ρ $SiCH_3$).

Attempted Preparation of $3G_{Allyl}$*-36*CH_2Cl *(SWK VIII/1)*

In a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa were combined 15 mL of dry THF, 0.505 g of **$2G_{Allyl}$-36Allyl** (0.192 mmol) and 1.01 g of (chloromethyl)dimethylsilane (9.30 mmol, 35% excess). Karstedt catalyst (50 µL) was added; the reaction mixture underwent an exotherm and developed a green color. After several minutes, the reaction mixture was immersed in an oil bath which had been pre-heated to 50 °C. After stirring for 17 h, the reaction mixture (now a brown color) was cooled to room temperature, and all volatiles were removed at reduced pressure, leaving a brown oil which was briefly dried *in vacuo*. This oil was extracted with 35 mL of hot hexane and filtered through a pad of silica gel. A solution of 10% ethyl acetate in hexane was used to elute the product from the silica gel, giving a colorless, viscous oil which was dried for 24 h at room temperature and 0.1 torr. Yield: 1.10 g (88%). Analysis by ^1H NMR showed 10% unreacted allyl groups.

A portion of this product (0.939 g, 0.144 mmol) was redissolved in 20 mL of dry THF in a reaction vessel like that described above. (Chloromethyl)dimethylsilane (0.68 g, 6.3 mmol) was added, followed by 5 drops of Karstedt catalyst. The reaction mixture effervesced and became a deep green color. The reaction mixture was immersed in an oil bath and heated to 45 °C. After stirring for 22 h, the reaction mixture was cooled to room temperature, and the product purified as described above, giving a colorless, viscous oil which was dried for 16 h at room temperature and 0.03 torr. Yield: 0.931 g. Analysis by ^1H NMR showed 8% unreacted allyl groups.

This product was redissolved in *ca.* 3 mL of dry THF and transferred via cannula to an Ar-filled, 40 mL thick-walled glass ampoule containing a magnetic stir bar. (Chloromethyl)dimethylsilane (0.50 g, 4.6 mmol) and 50 μL of Karstedt catalyst were added via syringe. The ampoule was sealed as described in the procedure for the preparation of **$1G_{Vinyl}$-8Vinyl**, immersed in an oil bath and heated to 105 °C. A deep green color formed in the reaction mixture. After stirring for 8 h, the reaction mixture had become a brown color. After stirring an additional 12 h, the reaction was cooled to room temperature, and the product was purified as described above. Yield: 0.876 g (82% overall). Analysis by ^{1}H NMR showed 3.4% unreacted allyl groups.

^{1}H NMR ($CDCl_3$): δ 0.085 (s, 216 H, CH_3), 0.57 (m, br; 136 H; $Si(C\underline{H}_2CH_2C\underline{H}_2)_4$ (two types), $SiC\underline{H}_2CH_2CH_2SiCH_2Cl$), 0.69 (m, br, 72 H, $SiCH_2CH_2C\underline{H}_2SiCH_2Cl$), 1.35 (br, 104 H, $SiCH_2C\underline{H}_2CH_2Si$ (three types)), 1.81 (d, J= 8 Hz, 2.5 H, $SiC\underline{H}_2CH{=}CH_2$), 2.75 (s, 72 H, CH_2Cl).

Derivatization Reactions of First Generation Dendrimeric Grignard Reagent

Reaction of $1G_{Vinyl}$-$4CH_2Cl$ with Magnesium (SWK V/16C)

A 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, pressure-equalizing dropping funnel, magnetic stir bar and a rubber septum was charged with 0.49 g of Mg turnings (0.020 g atom, 20% excess). These were stirred vigorously for 2 h while heating under vacuum. After cooling the flask to room temperature, 10 mL of dry THF was added. **$1G_{Vinyl}$-$4CH_2Cl$** (2.40 g, 4.20 mmol) was introduced into the dropping funnel and dissolved in 10 mL of dry THF. The reaction mixture was immersed in an oil bath and heated to 35 °C. Ethylene dibromide (*ca.* 5 drops) was added to the unstirred solution in such a way as to let the drops slide down the inside

of the flask to the Mg turnings; small bubbles formed on the surface of the Mg turnings for approximately 5 min. The dendrimer solution was slowly added dropwise to the stirred Mg turnings over a period of 3 h. Upon completion of the addition, the reaction mixture was heated to reflux. After stirring for 16 h, the reaction mixture was cooled to room temperature. Nearly all the Mg turnings had been consumed. Analysis of a hydrolyzed aliquot by ^{1}H NMR showed complete consumption of chloromethyl groups.

Reaction of $\mathbf{1G_{Vinyl}\text{-}4CH_2MgCl}$ *with tert-Butyldimethylchlorosilane (SWK V/14)*

A solution of $\mathbf{1G_{Vinyl}\text{-}4CH_2MgCl}$ (2.08 mmol) in 40 mL of THF was prepared according to the above procedure in a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, pressure-equalizing dropping funnel, magnetic stir bar and a rubber septum. *tert*-Butyldimethylchlorosilane (1.47 g, 9.75 mmol, 17% excess) was introduced into the dropping funnel and dissolved in 5 mL of dry THF; this solution was added to the reaction vessel over a period of 10 min. After completion of the addition, the reaction mixture was heated to reflux. After stirring for 17 h, the reaction mixture was cooled to room temperature and carefully poured into 30 mL of sat. NH_4Cl (aq) solution. Hexane (20 mL) was added, and the organic layer was separated and washed twice with 30 mL portions of water and once with 30 mL of sat. NaCl (aq). After drying over anhydrous $MgSO_4$ and filtering into a tared flask, all volatiles were removed at reduced pressure, giving a white crystalline solid which was dried for 2 h *in vacuo* and recrystallized from hot ethanol. Analysis by ^{1}H NMR showed no reaction had occurred with the chlorosilane, and that instead the hydrolysis product $\mathbf{1G_{Vinyl}\text{-}12CH_3}$ was isolated. Yield (4 crops): 0.724 g (80%), m.p. 87.5 - 88 °C.

Anal. Calcd for $C_{20}H_{52}Si_5$ (433.060 g/mol): C, 55.47; H, 12.10%. Found: C, 55.03; H, 11.99%.

^{1}H NMR ($CDCl_3$): δ -0.047 (s, 36 H, $SiCH_3$), 0.34 (m, 16 H, CH_2CH_2).

^{13}C NMR ($CDCl_3$): δ -2.10 (CH_3), 2.76 ($Si\underline{C}H_2CH_2SiCH_3$), 8.78 ($SiCH_2\underline{C}H_2SiCH_3$).

^{29}Si NMR ($CDCl_3$): δ 2.49 (4 Si, $SiCH_3$), 8.82 (1 Si, $Si(CH_2CH_2)_4$).

Reaction of ***$1G_{Vinyl}$-$4CH_2MgCl$*** *with Vinyldimethylchlorosilane (SWK V/20B)*

Vinyldimethylchlorosilane (2.3 mL, 2.0 g, 17 mmol, 100% excess) was added to a 50 mL three-necked, round-bottomed flask which was equipped with a reflux condenser, magnetic stir bar and two rubber septa and which contained 2.1 mmol of **$1G_{Vinyl}$-$4CH_2MgCl$** dissolved in 10 mL of THF. After stirring for 5 d at room temperature, the reaction mixture was carefully poured into 30 mL of sat. NH_4Cl (aq) solution. Hexane (30 mL) was added, and the organic layer was separated and washed twice with 30 mL portions of water and once with 30 mL of sat. NaCl (aq). After drying over anhydrous $MgSO_4$ and filtering into a tared flask, all volatiles were removed at reduced pressure, giving a clear, light yellow oil which was dried for 14 h at 40 - 50 °C and 0.005 torr. Yield: 1.63 g (100%). Anal. Calcd for $C_{36}H_{84}Si_9$ (769.832 g/mol): C, 56.17; H, 11.00%. Found: C, 56.22; H, 11.01%.

^{1}H NMR ($CDCl_3$): δ -0.246 (s, 8 H, $SiCH_2Si$), 0.025 (s, 24 H, $Si(C\underline{H}_3)_2CH_2SiCH{=}CH_2$), 0.072 (s, 24 H, $Si(C\underline{H}_3)_2CH{=}CH_2$), 0.34 (m, 16 H, CH_2CH_2), 5.620 (dd, J_{cis} = 4.0 Hz, J_{gem} = 20.1 Hz; 4 H; $SiCH{=}C\underline{H}_2$ (*trans* to Si));

5.876 (dd, J_{cis} = 4.0 Hz, J_{trans} = 14.4 Hz; 2 H; SiC<u>H</u>=CH_2); 6.155 (dd, J_{trans} = 14.4 Hz, J_{gem} = 20.1 Hz; 2 H; SiCH=C<u>H</u>$_2$ (*cis* to Si)).

^{13}C NMR ($CDCl_3$): δ -1.07 (Si(<u>C</u>H_3)$_2$CH=CH_2), -0.30 (Si(<u>C</u>H_3)$_2$$CH_2$SiCH=$CH_2$), 0.64 (Si$CH_2$Si), 2.93 (Si<u>C</u>$H_2$$CH_2$SiCH$_2$Si), 10.11 (SiCH$_2$<u>C</u>H$_2$SiCH$_2$Si), 130.49 (SiCH=<u>C</u>H_2), 141.36 (Si<u>C</u>H=CH_2).

^{29}Si NMR ($CDCl_3$): δ -7.09 (4 Si, SiCH=CH_2), 2.95 (4 Si, <u>Si</u>(CH$_3$)$_2$$CH_2$SiCH=$CH_2$), 8.67 (1 Si, Si($CH_2CH_2$)$_4$).

Reaction of ***1G$_{Vinyl}$-4CH$_2$MgCl*** *with Trimethyltin Chloride (SWK V/21)*

Trimethyltin chloride (1.9 g, 9.5 mmol, 13% excess) was dissolved in 10 mL of dry THF in a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa. A solution of **1G$_{Vinyl}$-4CH$_2$MgCl** (2.1 mmol) in 20 mL of THF was slowly added via syringe over a period of 40 min. Upon completion of the addition, the reaction mixture was immersed in an oil bath and heated to reflux. After stirring for 24 h, the reaction mixture was cooled to room temperature and carefully poured into 30 mL of sat. NH_4Cl (aq) solution. Hexane (30 mL) was added, and the organic layer was separated and washed with 30 mL of water. After drying over anhydrous $MgSO_4$ and filtering into a tared flask, all volatiles were removed at reduced pressure, giving a cloudy, lt. yellow oil which was dried for 24 h at 0.005 torr. Yield: 2.09 g (92%). Anal. Calcd for $C_{32}H_{84}Si_5Sn_4$ (1084.206 g/mol): C, 35.45; H, 7.81%. Found: C, 36.31; H, 7.93%. Calcd for 0.96 $C_{32}H_{84}Si_5Sn_4$ + 0.04 $C_{20}H_{52}Si_5$: C, 36.25; H, 7.98%.

^{1}H NMR ($CDCl_3$): δ -0.275 (s, $^2J_{Sn-H}$ = 73 Hz, 8 H, $SiCH_2Sn$), -0.044 (s, 24 H, $SiCH_3$), 0.068 (s, $^2J_{Sn-H}$ = 53 Hz, 36 H, $SnCH_3$), 0.35 (m, 16 H, CH_2CH_2).

^{13}C NMR ($CDCl_3$): δ -7.68 ($J_{^{117}Sn\text{-}C}$ = 315 Hz, $J_{^{119}Sn\text{-}C}$ = 330 Hz, $SnCH_3$), -6.16 ($J_{^{117}Sn\text{-}C}$ = 241 Hz, $J_{^{119}Sn\text{-}C}$ = 252 Hz, $SiCH_2Sn$), -0.71 ($SiCH_3$), 3.22 ($Si\underline{C}H_2CH_2SiCH_2Sn$), 10.41 ($SiCH_2\underline{C}H_2SiCH_2Sn$).

^{29}Si NMR ($CDCl_3$): δ 4.80 (4 Si, $SiCH_2Sn$), 8.32 (1 Si, $Si(CH_2CH_2)_4$).

^{119}Sn NMR ($CDCl_3$): δ 7.70.

Reaction of ***$1G_{Vinyl}$-$4CH_2MgCl$*** *with (Chloro)(trimethylsilylmethyl)(cycloocta-1,4-diene)platinum(II) (SWK VII/11)*

A 100 mL Schlenk flask equipped with a magnetic stir bar and a rubber septum was charged with 2.10 g of (chloro)(trimethylsilylmethyl)(cycloocta-1,4-diene)platinum(II) (4.93 mmol). Diethyl ether (20 mL) was added, and the resulting suspension was cooled to -78 °C in a dry ice/acetone bath. A solution of 4.76 mmol of **$1G_{Vinyl}$-$4CH_2MgCl$** in 14 mL of dry THF was added dropwise via syringe to the stirred suspension over a period of 15 min. When the addition was complete, the solution was allowed to slowly warm to room temperature. After 39 h, an aliquot removed via syringe and examined by ^1H NMR showed complete reaction. The reaction mixture was cooled to -20 °C, and 10 mL of sat. NH_4Cl (aq) were added. After warming to room temperature, the organic layer was separated, and the aqueous layer was washed three times with 15 mL portions of diethyl ether. After drying over anhydrous $MgSO_4$ and filtering, solvents were removed at reduced pressure, leaving a clear, yellow, viscous oil which was dried for 15 h at room temperature and 0.55 torr (mass 2.39 g). A portion of this oil (0.52 g) was purified by column chromatography (50 g silica gel; 4% ethyl acetate in hexane as eluent), giving 0.226 g of a clear, colorless, viscous oil. Yield: 0.226 g (45%). Anal. Calcd for $C_{68}H_{140}Pt_4Si_9$ (1990.989 g/mol): C, 41.02; H, 7.09%. Found: C,

41.60; H, 7.52%. Calcd for 0.96 $C_{68}H_{140}Pt_4Si_9$ + 0.04 $C_{20}H_{52}Si_5$: C, 41.59; H, 7.29%

^{1}H NMR ($CDCl_3$): δ -0.323 (s, 36 H, $Si(CH_3)_3$); 0.364 (s, 24 H, $Si(C\underline{H}_3)_2CH_2Pt$); 0.92 (m, 16 H, CH_2CH_2); 1.165 (s, $^2J_{Pt-H}$ = 95 Hz), 1.194 (s, $^2J_{Pt-H}$ = 93 Hz) (24 H, $SiCH_2Pt$ (two types)); 1.75 (m, br, 16 H, COD CH_2); 2.00 (br, 16 H, COD CH_2); 4.57 (s, br, $^2J_{Pt-H}$ = 40 Hz, 16 H, COD CH).

^{13}C NMR ($CDCl_3$): δ 1.42 ($Si(CH_3)_3$); 3.82 ($Si(\underline{C}H_3)_2CH_2Pt$); 4.85 ($Si\underline{C}H_2CH_2SiCH_2Pt$); 12.36 ($^1J_{Pt-C}$ = 709 Hz), 14.00 ($^1J_{Pt-C}$ = 711 Hz) ($SiCH_2Pt$ (two types)); 12.57 ($SiCH_2\underline{C}H_2SiCH_2Pt$); 30.08 (COD CH_2); 97.27 ($^1J_{Pt-C}$ = 66 Hz), 97.32 ($^1J_{Pt-C}$ = 63 Hz) (COD CH).

^{29}Si NMR ($CDCl_3$): δ 0.59 (4 Si, $^2J_{Pt-Si}$ = 32 Hz, $Si(CH_3)_3$), 4.37 (4 Si, $^2J_{Pt-Si}$ = 32 Hz, $Si(CH_3)_2CH_2Pt$), 8.88 (1 Si, $Si(CH_2CH_2)_4$).

^{195}Pt NMR ($CDCl_3$): δ -3489.

*Reaction of **$1G_{Vinyl}$-$4CH_2MgCl$** with Bis(mesityl)fluoroborane (SWK VII/19B)*

A solution of **$1G_{Vinyl}$-$4CH_2MgCl$** (4.2 mmol) in 21 mL of THF was prepared according to the above procedure was added to a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, pressure-equalizing dropping funnel, magnetic stir bar and a rubber septum which contained 4.869 g of bis(mesityl)fluoroborane (18.2 mmol, 8% excess) dissolved in 15 mL of dry diethyl ether. The reaction mixture was stirred for 2 d at room temperature, followed by 7 d at reflux. After cooling to room temperature, THF was removed at reduced pressure, and the resulting residue was extracted with 30 mL of diethyl ether and 30 mL of water. The organic layer was separated, and the aqueous layer was washed with 30 mL of diethyl ether. The combined organic fractions were dried over anhydrous

$MgSO_4$ and filtered into a tared flask. Solvents were removed at reduced pressure, leaving a slightly yellow, viscous oil which was dried for 48 h at room temperature and 0.15 torr (mass 6.588 g). Analysis by ^1H NMR showed conversion to 87% $SiCH_2BMes_2$ groups and 13% $SiMe_3$ groups; in addition, the hydrolyzed excess Mes_2BF was present as Mes_2BOH. A portion of this oil (0.529 g) was purified by column chromatography (3.5 cm diam. column; 50 g of silica gel; 1% ethyl acetate in hexane as eluent), which removed the Mes_2BOH and changed the ratio of $SiCH_2BMes_2$ to $SiMe_3$ groups to 90 : 10. The resulting clear, colorless oil was dried for 15.5 h at room temperature and 0.1 torr (mass 0.318 g).

^1H NMR ($CDCl_3$): δ -0.12 (s, 22 H, $Si(C\underline{H}_3)_2CH_2B$), -0.045 (s, 3.5 H, $Si(CH_3)_3$), 0.2 (br, 16 H, CH_2CH_2), 1.64 (s, 8 H, $SiCH_2B$), 2.21 (s; 47 H; o-$C\underline{H}_3$, $SiCH_2BMes_2$), 2.25 (s; 24 H; p-$C\underline{H}_3$, $SiCH_2BMes_2$), 6.75 (s; 16 H; m-$\underline{H}$, $SiCH_2BMes_2$).

Reaction of ***$1G_{Vinyl}$-$4CH_2MgCl$*** *with Trimethylsilylmethylmercuric Chloride (SWK VII/13)*

A suspension of 1.75 g of trimethylsilylmethylmercuric chloride (5.41 mmol) in 15 mL of dry diethyl ether was cooled to -10 °C in a 100 mL Schlenk flask equipped with a magnetic stir bar and a rubber septum. A solution of 1.35 mmol of **$1G_{Vinyl}$-$4CH_2MgCl$** in 15.9 mL of THF was added via syringe. After stirring for 20 min, the reaction mixture was allowed to warm to room temperature. After stirring for an additional 72 h, the reaction mixture was hydrolyzed with 15 mL of sat. NH_4Cl (aq). The organic layer was separated, and the aqueous layer was washed twice with 20 mL portions of diethyl ether. The combined organic fractions were washed with 15 mL of water, dried over anhydrous $MgSO_4$ and filtered into a tared flask. Solvents were removed at

reduced pressure, leaving a colorless oil which was dried for 15 h at room temperature and 0.55 torr (mass 2.031 g). Analysis by ^{1}H NMR showed conversion to 75% $SiCH_2HgCH_2SiMe_3$ groups and 25% $SiMe_3$ groups. Attempts to purify this product by column chromatography were unsuccessful.

^{1}H NMR ($CDCl_3$): δ -0.048 (s, 6.5 H, $CH_2CH_2Si(C\underline{H}_3)_3$), -0.033 (s, 12.5 H, $Si(C\underline{H}_3)_2CH_2Hg$), -0.004 (s; 22 H; $Si(CH_3)_2C\underline{H}_2Hg$, $HgCH_2Si(C\underline{H}_3)_3$) 0.032 (s, 5.3 H, $HgCH_2Si(CH_3)_3$), 0.084 (s, 4.2 H, $(C\underline{H}_3)_3SiCH_2HgCl$), 0.37 (m, 16 H, CH_2CH_2), 1.02 (s, 0.9 H, $(CH_3)_3SiC\underline{H}_2HgCl$).

Reactions of Nucleophilic Reagents with Chloromethyl-Terminated Dendrimers

Reaction of ***1G$_{Vinyl}$-4CH$_2$Cl*** *with Sodium Iodide (SWK V/23)*

In a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa were combined 25 mL of acetone, 0.50 g of **1G$_{Vinyl}$-4CH$_2$Cl** (0.87 mmol) and 5.5 g of NaI (42 mmol, 1100% excess). The reaction vessel was covered in Al foil, immersed in an oil bath and heated to reflux. After stirring for 4 d, the reaction mixture was cooled to room temperature and poured into 75 mL of hexane. The organic layer was separated and washed twice with 20 mL portions of water. The aqueous layers were combined and extracted with 15 mL of hexane. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. Removal of solvents at reduced pressure and drying the resulting oil 10 h at 0.01 torr left **1G$_{Vinyl}$-4CH$_2$I** as an analytically pure, white, crystalline solid (0.74). **1G$_{Vinyl}$-4CH$_2$I** formed colorless plates when recrystallized from diethyl

ether/acetone. Yield: 0.74 g (91%), m.p. 51.5 - 52.5°C. Anal. Calcd for $C_{20}H_{48}I_4Si_5$ (936.647 g/mol): C, 25.65; H, 5.17%. Found: C, 25.88; H, 5.21%.

^{1}H NMR ($CDCl_3$): δ 0.109 (s, 24 H, $SiCH_3$), 0.46 (m, 16 H, CH_2CH_2), 2.00 (s, 8 H, CH_2I).

^{13}C NMR ($CDCl_3$): δ -13.52 (CH_2I), -3.62 ($SiCH_3$), 2.46 ($Si\underline{C}H_2CH_2SiCH_2I$), 6.99 ($SiCH_2\underline{C}H_2SiCH_2I$).

^{29}Si NMR ($CDCl_3$): δ 5.70 (4 Si, $SiCH_3$), 9.19 (1 Si, $Si(CH_2CH_2)_4$).

Reaction of $2G_{Vinyl}$-$8CH_2Cl$ with Sodium Iodide (SWK VIII/14)

In a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two rubber septa were combined 25 mL of acetone, 0.431 g of **$2G_{Vinyl}$-$8CH_2Cl$** (0.308 mmol) and 3.68 g of NaI (24.6 mmol, 898% excess). The reaction vessel was covered in Al foil, immersed in an oil bath and heated to reflux. After stirring for 11 h, the reaction mixture was cooled to room temperature and poured into 75 mL of pentane. The organic layer was separated and washed twice with 15 mL portions of water. The aqueous layers were combined and extracted with 25 mL of pentane. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. Removal of solvents at reduced pressure and drying the resulting oil 66.5 h at room temperature and 0.003 torr left **$2G_{Vinyl}$-$8CH_2I$** as an analytically pure, white, crystalline solid. Yield: 0.575 g (88%), m.p. 43 - 44 °C. Anal. Calcd for $C_{52}H_{124}I_8Si_{13}$ (2129.904 g/mol): C, 29.32; H, 5.87%. Found: C, 29.60; H, 5.63%.

^{1}H NMR ($CDCl_3$): δ -0.067 (s, 12 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$), 0.110 (s, 48 H, $Si(C\underline{H}_3)_2CH_2I$), 0.38 (s, br, 16 H, $Si(C\underline{H}_2C\underline{H}_2)_4$], 0.47 (m, 32 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2I$), 2.00 (s, 16 H, CH_2I).

^{13}C NMR ($CDCl_3$): δ -13.32 (CH_2I), -6.28 ($Si(\underline{C}H_3)(CH_2CH_2)_3$), -3.40 ($Si(\underline{C}H_3)_2CH_2I$), 2.90 ($Si(\underline{C}H_2CH_2)_4$), 4.50 ($Si\underline{C}H_2CH_2SiCH_2I$), 5.02 ($Si(CH_2\underline{C}H_2)_4$), 6.99 ($SiCH_2\underline{C}H_2SiCH_2I$).

^{29}Si NMR ($CDCl_3$): δ 5.72 (8 Si, $SiCH_2I$), 7.70 (4 Si, $Si(CH_3)(CH_2CH_2)_3$), 8.82 (1 Si, $Si(CH_2CH_2)_4$).

REFERENCES

1. Tomalia, D. A.; Durst, H. D. "Genealogically Directed Synthesis: Starburst™/Cascade Dendrimers and Hyperbranched Structures," In *Topics in Current Chemistry;* Weber, E., Ed.; Springer-Verlag: Berlin, 1993; Vol. 165, pp 193-313.
2. Ardoin, N.; Astruc, D. "Molecular Trees: From Synthesis Towards Applications," *Bull. Soc. Chim. Fr.* **1995**, *132*, 875-909.
3. Newkome, G. R.; Moorefield, C. N. "Dendrimers," In *Comprehensive Supramolecular Chemistry;* Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F. and Lehn, J.-M., Eds.; Pergamon: Tarrytown, NY, 1996; Vol. 10, pp 777-832.
4. Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives;* VCH: Weinheim, Germany, 1996, p 261.
5. Barth, R. F.; Adams, D. M.; Soloway, A. H.; Alam, F.; Darby, M. V. "Boronated Starburst Dendrimer-Monoclonal Antibody Immunoconjugates: Evaluation as a Potential Delivery System for Neutron Capture Therapy," *Bioconjugate Chem.* **1994**, *5*, 58-66.
6. Russell, D. D.; Bearss, J. G.; Hewlett-Packard Co., USA: European Patent Appl. 726502, 1996; Chem. Abstr. **125**: 261188a (1996).

7. Watson, A. D.: U.S. Patent Appl. 772,349, 1991; Chem. Abstr. **119**: 220702w (1991).

8. Kawaguchi, T.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. "Double Exponential Dendrimer Growth," *J. Am. Chem. Soc.* **1995**, *117*, 2159-65.

9. The author is grateful to Glenn P. Tesler, U. of California, San Diego for assistance in deriving this formula. A special case of this formula, applicable to PAMAM dendrimers, may be found in ref. 1.

10. Buhleier, E.; Wehner, W.; Vögtle, F. "'Cascade'- and 'Nonskid-Chain-Like' Syntheses of Molecular Cavity Topologies," *Synthesis* **1978**, 155-8.

11. Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. "A New Class of Polymers: Starburst-Dendritic Macromolecules," *Polym. J.* **1985**, *17*, 117-32.

12. Tomalia, D. A.; Naylor, A. M.; Goddard III, W. A. "Starburst Dendrimers: Molecular-Level Control of Size, Shape, Surface Chemistry, Topology, and Flexibility from Atoms to Macroscopic Matter," *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138-75.

13. Aldrich Chemical. Co., Milwaukee, WI.

14. Hawker, C. J.; Wooley, K. L. "The Convergent-Growth Approach to Dendritic Macromolecules," In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press, Inc.: Greenwich, CT, 1995; Vol. 2, pp 1-40.

15. Moorefield, C. N.; Newkome, G. R. "A Review of Dendritic Macromolecules," In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press, Inc.: Greenwich, CT, 1994; Vol. 1, pp 1-68.

16. Eaborn, C. *Organosilicon Compounds*; Butterworths: London, 1960.

17. Pawlenko, S. *Organosilicon Chemistry;* Walter de Gruyter: New York, 1986.

18. Mathias, L. J.; Carothers, T. W. "Silicon-Based Stars, Dendrimers, and Hyperbranched Polymers," In *Advances in Dendritic Macromolecules;* Newkome, G. R., Ed.; JAI Press, Inc.: Greenwich, CT, 1995; Vol. 2, pp 101-21.

19. Marciniec, B. *Comprehensive Handbook on Hydrosilylation;* Pergamon: Oxford, 1992.

20. Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. "General Strategy for the Systematic Synthesis of Oligosiloxanes. Silicone Dendrimers," *J. Am. Chem. Soc.* **1990**, *112*, 7077-9.

21. Morikawa, A.; Kakimoto, M.-a.; Imai, Y. "Synthesis and Characterization of New Polysiloxane Starburst Polymers," *Macromolecules* **1991**, *24*, 3469-74.

22. Mathias, L. J.; Carothers, T. W. "Hyperbranched Poly(siloxysilanes)," *J. Am. Chem. Soc.* **1991**, *113*, 4043-4.

23. Muzafarov, A. M.; Gorbatsevich, O. B.; Rebrov, E. A.; Ignat'eva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. "Organosilicon Dendrimers: Volume-Growing Polyallylcarbosilanes," *Vysokomol. Soedin.* **1993**, *35*, 1867-72.

24. van der Made, A.; van Leeuwen, P. W. N. M. "Silane Dendrimers," *J. Chem. Soc. Chem. Comm.* **1992**, 1400-1.

25. van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brandes, R. A. C. "Dendrimeric Silanes," *Adv. Mater.* **1993**, *5*, 466-8.

26. Zhou, L.-L.; Roovers, J. "Synthesis of Novel Carbosilane Dendritic Macromolecules," *Macromolecules* **1993**, *26*, 963-8.

27. Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. "Synthesis of an Organosilicon Dendrimer Containing 324 Si-H Bonds," *Organometallics* **1994**, *13*, 2682.

28. Lambert, J. B.; Pflug, J. L.; Stern, C. L. "Synthesis and Structure of a Dendritic Polysilane," *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 98-9.

29. Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. "Polysilane Dendrimers," *J. Am. Chem. Soc.* **1995**, *117*, 4195-6.

30. Lambert, J. B.; Pflug, J. L.; Denari, J. M. "First-Generation Dendritic Polysilanes," *Organometallics* **1996**, *15*, 615-25.

31. Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. "Polysilane Dendrimer. Synthesis and Characterization of $[2,2\text{-}(Me_3Si)_2Si_3Me_5]_3SiMe$," *Chem. Lett.* **1995**, 293-4.

32. Kochs, P. "Poly(organosilanes), Poly(carbosilanes), Poly(organosilazanes)," In *Silicon in Polymer Synthesis;* Kricheldorf, H. R., Ed.; Springer-Verlag: Berlin, 1996, pp 223-87.

33. Issberner, J.; Moors, R.; Vögtle, F. "Dendrimers: From Generations and Functional Groups to Functions," *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413-20.

34. Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. "Encapsulation of Guest Molecules into a Dendritic Box," *Science* **1994**, *266*, 1226-9.

35. Jansen, J. F. G. A.; Janssen, R. A. J.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. "Triplet Radical Pairs of 3-Carboxyproxyl Encapsulated in a Dendritic Box," *Adv. Mater.* **1995**, *7*, 561-4.

36. Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. "The Dendritic Box: Shape-Selective Liberation of Encapsulated Guests," *J. Am. Chem. Soc.* **1995**, *117*, 4417-8.

37. Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F. "Organometallic Dendritic Macromolecules: Organosilicon and Organometallic Entities as Cores or Building Blocks," In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press, Inc.: Greenwich, CT, 1996; Vol. 3, pp 151-201.

38. Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. "Organometallic Silicon Dendrimers," *J. Chem. Soc. Chem. Comm.* **1994**, 2575-6.

39. Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. "Electrodes Modified with Electroactive Films of Organometallic Dendrimers," *Chem. Mater.* **1995**, *7*, 1440-2.

40. Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. "Homogeneous Catalysts Based on Silane Dendrimers Functionalized with Arylnickel(II) Complexes," *Nature* **1994**, *372*, 659-63.

41. Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. "Preparation of Carbosilane Dendrimers with Peripheral Acetylenedicobalt Hexacarbonyl Substituents," *Organometallics* **1995**, *14*, 5362-6.

42. Cuadrado, I.; Morán, M.; Moya, A.; Casado, C. M.; Barranco, M.; Alonso, B. "Organometallic Silicon-Based Dendrimers with Peripheral Si-Cyclopentadienyl, Si-Co and Si-Fe s-Bonds," *Inorg. Chim. Act.* **1996**, *251*, 5-7.

43. Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. "Regular Star Polymers with 64 and 128 Arms. Models for Polymeric Micelles," *Macromolecules* **1993**, *26*, 4324-31.

44. Krasovskii, V. G.; Sadovskii, N. A.; Gorbatsevich, O. B.; Muzafarov, A. M.; Myakushev, V. D.; Il'ina, M. N.; Dubovik, I. I.; Strelkova, T. V.;

Papkov, V. S. "Fluorescently Labeled Polyallylcarbosilane Dendrimers," *Vysokomol. Soedin.* **1994**, *36*, 714-20.

45. Miedaner, A.; Curtis, C. J.; Barkley, R. M.; DuBois, D. L. "Electrochemical Reduction of CO_2 Catalyzed by Small Organophosphine Dendrimers Containing Palladium," *Inorg. Chem.* **1994**, *33*, 5482-90.

46. Lobete, F.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J. "Silicon-Based Organometallic Dendritic Macromolecules Containing {η^6-(Organosilyl)arene}chromium Tricarbonyl Moieties," *J. Organomet. Chem.* **1996**, *509*, 109-13.

47. Seyferth, D.; Wyrwa, R.: U.S. Patent Appl., 1996.

48. Lorenz, K.; Mülhaupt, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. J. "Carbosilane-Based Dendritic Polyols," *Macromolecules* **1995**, *28*, 6657-61.

49. Lorenz, K.; Hölter, D.; Stühn, B.; Mülhaupt, R.; Frey, H. "A Mesogen-Functionalized Carbosilane Dendrimer: A Dendritic Liquid Crystalline Polymer," *Adv. Mater.* **1996**, *8*, 414-6.

50. Coen, M. C.; Lorenz, K.; Kressler, J.; Frey, H.; Mülhaupt, R. "Mono- and Multilayers of Mesogen-Substituted Carbosilane Dendrimers on Mica," *Macromolecules* **1996**, *29*, 8069-76.

51. Ponomarenko, S. A.; Rebrov, E. A.; Bobrovsky, A. Y.; Boiko, N. I.; Muzafarov, A. M.; Shibaev, V. P. "Liquid Crystalline Carbosilane Dendrimers: First Generation," *Liq. Cryst.* **1996**, *21*, 1-12.

52. Ref. 16, pp 393-5.

53. Puddephatt, R. J. "Synthesis of Transition Metal Alkyl and Aryl Complexes," In *Chemistry of the Metal-Carbon Bond*; Hartley, F. R. and Patai, S., Eds.; John Wiley & Sons: New York, 1982, pp 249-50.

54. Rose, J. B. "Cyclic Oxygen Compounds other than Epoxides," In *The Chemistry of Cationic Polymerization*; Plesch, P. H., Ed.; Pergamon: New York, 1963, pp 441-3.

55. Musolf, M. C.; Speier, J. L. "The Addition of Silicon Hydrides to Olefinic Double Bonds. X. Addition to Phenylalkenes. The Nuclear Magnetic Resonance Proton Spectra of (Phenylalkyl)silanes," *J. Org. Chem.* **1964**, *29*, 2519-24.

56. Čapka, M.; Svoboda, P.; Hetflejš, J. "Catalysis by Metal Complexes. XII. Selective Preparation of 1- and 2-trichlorosilyl-1-phenylethane by Hydrosilylation," *Coll. Czech. Chem. Comm.* **1973**, *38*, 3830-3.

57. Williams, E. A.; Cargioli, J. D. "Silicon-29 NMR Spectroscopy," In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1979; Vol. 9, pp 221-318.

58. Ankianiec, B. C.; Christou, V.; Hardy, D. T.; Thomson, S. K.; Young, G. B. "Mechanisms of Thermolytic Rearrangement of cis-Bis(silylmethyl)platinum(II) Complexes: β-Carbon Transfer Predominates over Hydrogen Transfer," *J. Am. Chem. Soc.* **1994**, *116*, 9963-78.

59. Jensen, F. R.; Bedard, R. L. "Cleavage of Tetrahydrofuran by Triphenylmethylmagnesium Bromide," *J. Org. Chem.* **1959**, *24*, 874-5.

60. Finkelstein, H. *Ber.* **1910**, *43*, 1528.

61. Lewis, L. N.; Colborn, R. E.; Grade, H.; Bryant, G. L., Jr.; Sumpter, C. A.; Scott, R. A. "Mechanism of Formation of Platinum(0) Complexes Containing Silicon-Vinyl Ligands," *Organometallics* **1995**, *14*, 2202-13.

62. Lappert, M. F.; Scott, F. P. A. "The Reaction Pathway from Speier's to Karstedt's Hydrosilylation Catalyst," *J. Organomet. Chem.* **1995**, *492*, C11-3.

63. Willing, D. N.: U.S. Patent 3,419,593, 1968.

64. Karstedt, B. D.: U.S. Patent 3,419,593, 1973.

65. Lewis, L. N.; Lewis, N.; Uriarte, R. J. "Hydrosilylation. A 'Homogeneous' Reaction Really Catalyzed by Colloids," In *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R. and Slocum, D. W., Eds.; American Chemical Society: Washington, D.C., 1992; Vol. 230, pp 541-9.

66. Hopper, S. P.; Tremelling, M. J.; Ginsberg, R. J.; Mendelowitz, P. C. "Heterogeneous Reactions. III. Evidence for an Alkoxide Induced 1,2-Hydride Shift from Silicon to Carbon under Heterogeneous Gas/Solid Phase Reaction," *J. Organomet. Chem.* **1977**, *134*, 173-80.

67. Tacke, R.; Becker, B.; Lange, H. "(Thioacetoxy-S-methyl)diorganylsilane und (Mercaptomethyl)diorganylsilane: Synthese und Eigenschaften," *J. Organomet. Chem.* **1990**, *388*, 57-62.

68. Grummitt, O.; Budewitz, E. P.; Chudd, C. C. "1,4-Pentadiene," In *Organic Syntheses, Coll. Vol. 4*; Rabjohn, N., Ed.; John Wiley and Sons: New York, 1963, pp 746-52.

69. Marvel, C. S.; Gauerke, C. G.; Hill, E. L. "The Identification of Primary Alkyl Bromides and Iodides," *J. Am. Chem. Soc.* **1925**, *47*, 3009-11.

70. Sommer, L. H.; Whitmore, F. C. "Organo-silicon Compounds. III. α- and β-Chloroalkyl Silanes and the Unusual Reactivity of the Latter," *J. Am. Chem. Soc.* **1946**, *68*, 485-7.

71. Thomson, S. K.; Young, G. B. "Synthesis and Spectroscopic Characteristics of Trimethylsilylmethylplatinum(II) Complexes with η^2 Alkene, Nitrogen and Phosphorus and Sulphur Donor Ligands," *Polyhedron* **1989**, *8*, 1953-64.

72. Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis;* Academic Press: New York, 1995, p 33.

CHAPTER FOUR

Synthesis and Characterization of Amphiphilic Carbosilane Dendrimers

INTRODUCTION

Amphiphilic molecules, those possessing both hydrophobic and hydrophilic moieties, are ubiquitous in the world around us. Their tendency to associate into structures of higher order—micelles, monolayers, vesicles and bilayers—forms the basis not only for many industrial applications, but also for essential biological features of life.[1] The complex structures of globular proteins, biological membranes and organelles derive in large part from the subtle interplay between conflicting hydrophobic and hydrophilic forces. These same forces produce micellar aggregates of synthetic surfactants, which modern man has harnessed for use in such applications as detergency, cosmetics, pharmaceuticals, emulsion polymerizations, surfactant-based separations, micellar catalysis and environmental processes.[2,3]

The self-assembly of surfactants into micelles has been actively studied since the beginning of this century, commencing with the pioneering work of McBain, Debye, Hartley, Langmuir and others.[2] Over the years, a composite picture has emerged of the structures of micelles as well as the thermodynamics and kinetics of their formation. Micelles form spontaneously in aqueous solutions of amphiphilic molecules whose concentrations exceed a certain value known as the critical micelle concentration (CMC). The CMC is particular to each amphiphile and varies with temperature, pressure and the presence of polar and nonpolar additives.[4]

Micelles are dynamic structures, forming and disintegrating at the rate of thousands of times per second; individual surfactant molecules enter and leave the micellar aggregates on the order of millions of times per second.[4] As might be expected, the sizes and shapes of micelles are not fixed, but vary according to such parameters as temperature, pressure and surfactant

concentration. At concentrations slightly above the CMC, amphiphiles assemble into roughly spherical aggregates with their polar head groups pointed outwards toward the bulk solution and their hydrophobic tails intertwined to form a viscous semi-liquid core (Figure 1). The average number of amphiphilic molecules in each micelle is referred to as the aggregation number (N). At high concentrations of amphiphile, N increases, and the micelles elongate to form ellipsoidal or cylindrical structures. The shapes of micelles and their aggregation numbers are also perturbed by changes in temperature, pressure and the addition of other polar or nonpolar solutes.

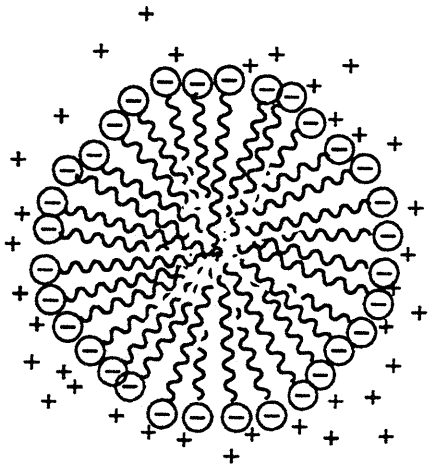


Figure 1. Typical Structure for a Micelle.

Because of the dynamic nature of micelles, their structures have never been observed directly, and instead have had to be inferred from a multitude of indirect measurements.[4] Recently, dendrimers bearing amphiphilic groups on their terminal branches have been proposed as model systems to mimic both the structure and the physical properties of micelles. Like micelles, amphiphilic dendrimers possess a globular structure, with a

relatively nonpolar core consisting of the dendrimer backbone and a hydrophilic surface arising from the polar head groups attached at the ends of the branches (Figure 2). Unlike micelles, however, dendrimers are discrete molecular systems with fixed, precisely defined molecular weights; their structures, therefore, are expected to be more uniform than those of micelles, even under changing conditions of temperature, pressure and concentration.

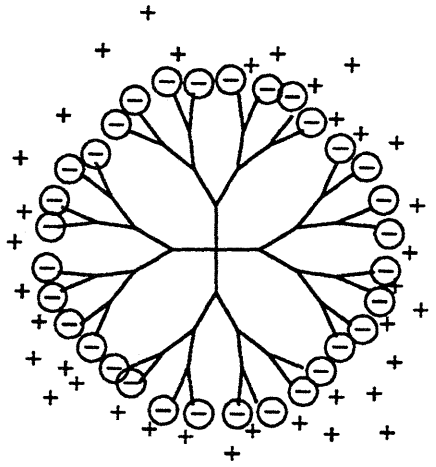


Figure 2. Amphiphilic Dendrimer.

Over the last decade, several groups have reported syntheses of amphiphilic dendrimers based on a variety of different backbone constructions. Many of these dendrimers have exhibited solution properties typically associated with micelles, e.g., the solubilization of organic compounds into water,[5] interactions with spectroscopic probe molecules,[4] and catalysis.[3] The first reports, published by George Newkome and coworkers in 1985 and 1986,[6,7] described the syntheses of dendritic "arborols" constructed from ether and amide linkages and bearing terminal alcohol

groups. These compounds, despite their high molecular weights (> 1600 Daltons), were completely soluble in water.

Later studies by Newkome and coworkers employed a similar dendrimer backbone system based on amide linkages with three different types of polar head groups: carboxylic acids, alcohols and primary amines; the structure of a representative second generation, carboxylic acid-terminated dendrimer is shown in Figure 3.[8-11] The amine- and acid-terminated dendrimers exhibited "smart" behavior, swelling or shrinking in response to changes in the solution's pH.[8,9] The acid-terminated dendrimers (in the form of their carboxylate salts) showed the same behavior as micelles when used in micellar electrokinetic capillary chromatography (MECC) experiments, separating uncharged organic molecules based on hydrophobic interactions.[10] They also made useful model compounds to test theoretical predictions about the permeation of multiply charged colloids into like-charged cavities.[11]

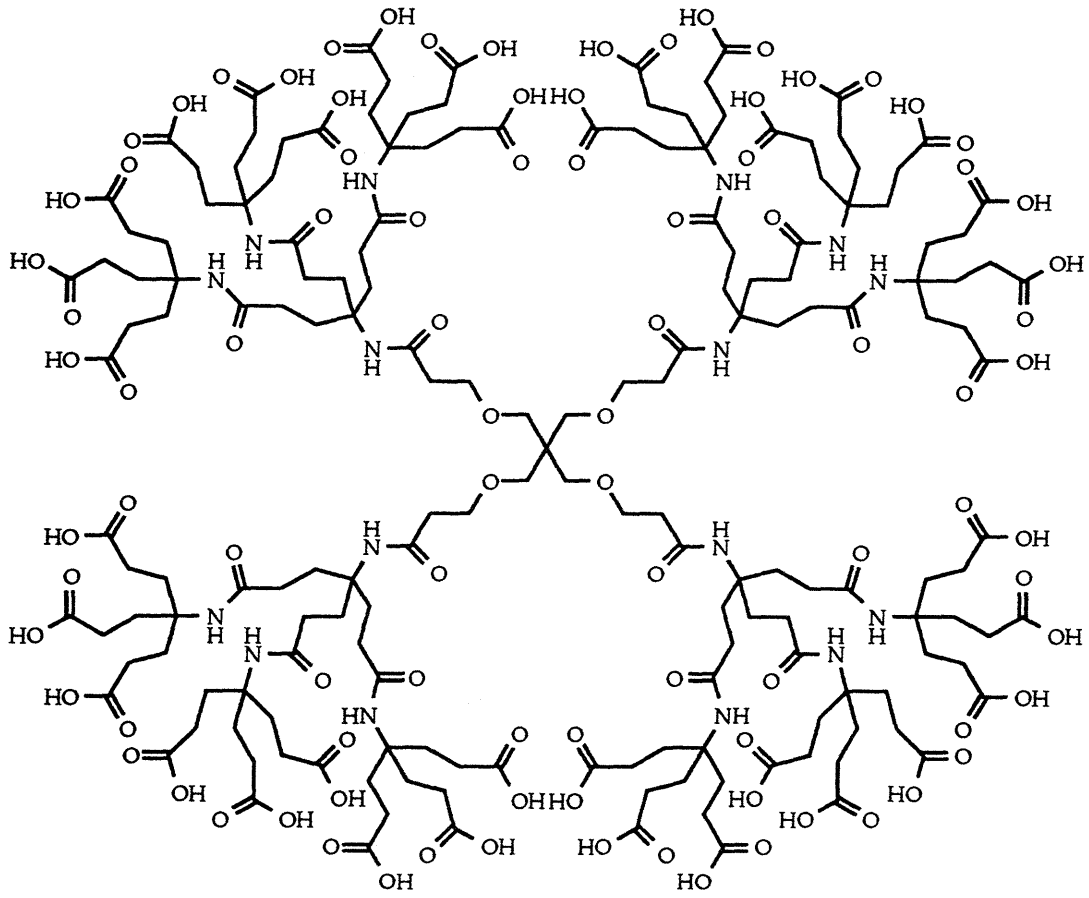


Figure 3. Carboxylic Acid-Terminated Amphiphilic Dendrimer (see ref.).

Newkome and coworkers are also credited with providing the only reported examples of water-soluble amphiphilic dendrimers constructed from completely hydrophobic backbones (Figure 4).[12] Of all the amphiphilic dendrimers reported to date, these most closely resemble the polarities of actual micelles. Unfortunately, their syntheses were quite tedious (preparation of the core molecule alone required 8 steps and proceeded in 24% overall yield). Like micelles, the second generation dendrimer (Figure 4) interacted with spectroscopic probe molecules to give marked changes in their absorbance and emission spectra.[13] It also enhanced the solubility of naphthalene in water. These dendrimers could also be prepared with sulfate

endgroups, and could be functionalized at interior alkyne sites to give water-soluble derivatives bearing dodeca-*o*-carborane clusters.[14]

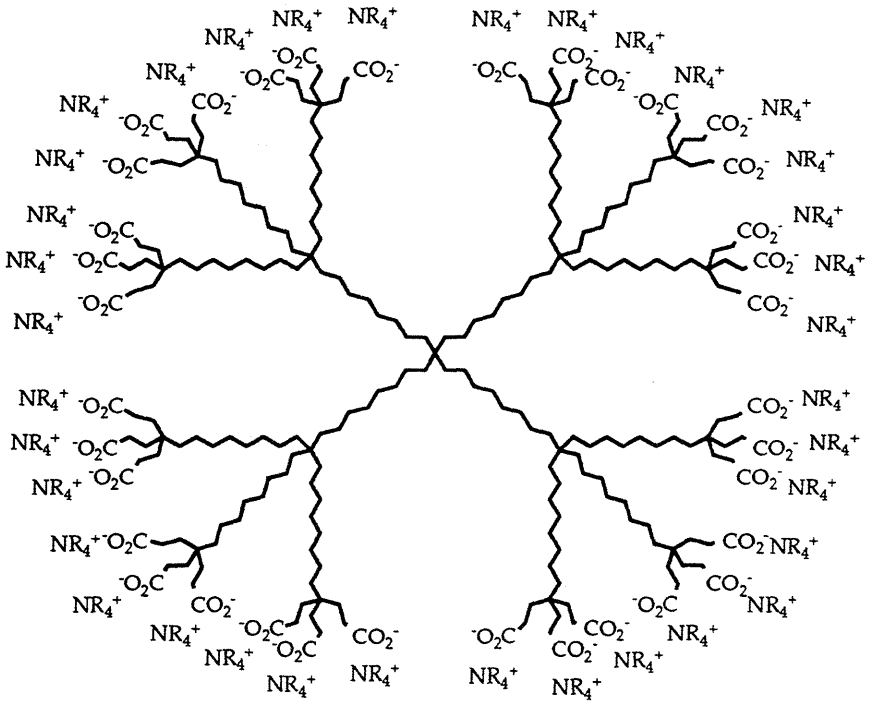


Figure 4. Amphiphilic Dendrimer with Completely Hydrophobic Backbone.

Water-soluble derivatives of Tomalia's poly(amidoamine) (PAMAM) dendrimers[15] have been formed by alkaline hydrolysis of terminal ester groups of "half generation" dendrimers[16] or by protonation of terminal amine groups of "full generation" dendrimers.[17,18] Like Newkome's arborols, these amphiphilic dendrimers contain polar groups (amides and tertiary amines) in their backbone structures and so do not completely mimic the structures of traditional micelles. Consequently, studies employing fluorescent and radical probes have shown that hydrophobic interactions with these dendrimers are considerably weaker than those observed in traditional micellar systems.[19-21] Like micelles, however, these dendrimers do bear highly charged surfaces which can function as restricted reaction

spaces for bringing together charged reactants, thereby enhancing the rates of their reactions.[22-25]

Fréchet and coworkers have prepared water-soluble dendrimers by attaching polar head groups to dendritic polyesters[26] and polyethers.[27,28] Carboxylate-terminated polyether dendrimers were shown to solubilize a number of polycyclic aromatic compounds over a wide range of dendrimer concentrations.[27] In a separate study, a water-soluble polyether dendrimer bearing attached poly(ethyleneoxide) (PEO) segments showed evidence for the incorporation of the fluorescence probe molecule pyrene into its hydrophobic interior.[28]

Numerous other water-soluble dendrimer and hyperbranched polymer systems have appeared in the literature over the last several years. In 1990, Kim and Webster reported the preparation of a water-soluble "unimolecular micelle" based on an irregular hyperbranched polyphenylene; this polymer was able to solubilize nonpolar organic compounds such as naphthalene into water.[29] Two groups have synthesized and studied the properties of amphiphilic diblock copolymers of dendrimers: the first example involved attaching hydrophilic PEO oligomers to the cores of hydrophobic poly(lysine) dendrimers;[30] the second system involved building poly(propylene imine) dendrimers from a polystyrene chain terminated in an amino group.[31,32] In 1994, Lee et. al. described the synthesis of a water-soluble polyether dendrimer bearing 36 quaternary ammonium iodide moieties; this dendritic polycation catalyzed the rates of two aqueous reactions involving organic anions,[33] thereby demonstrating behavior similar to that observed for micellar catalysts.[3]

Two recent publications have outlined the construction of water-soluble dendrimer frameworks with transition metal porphyrin complexes as

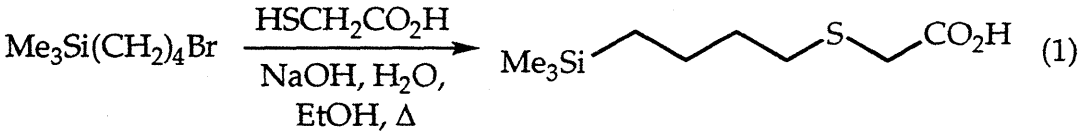
cores; these systems displayed interesting electrochemistry. A water-soluble poly(aryl ether) dendrimer with a zinc porphyrin complex at the core exhibited long-range photoinduced electron transfer through the dendrimer backbone.[34] The poly(amide) dendritic framework surrounding an iron porphyrin complex shifted its $Fe^{III/II}$ reduction potential significantly towards positive values, similar to effect of the protein sheath of the metalloenzyme cytochrome c.[35]

Research on water-soluble dendrimers to this point has shown great promise for making supramolecular structures whose properties resemble those of amphiphilic aggregates such as micelles and proteins. However, all but one of these dendrimer systems were based on polar backbone structures, which do not allow for the same degree of hydrophobic interactions present in micelles. The one system which did incorporate hydrophobic backbone structures (Figure 4) suffered from tedious reaction sequences and poor yields.

Carbosilane dendrimers are hydrophobic structures which can be synthesized in high yields from readily available starting materials.[36-39] However, the only attempt made so far to fit these dendrimers with terminal amphiphilic groups met with limited success. The alcohol-terminated carbosilane dendrimers prepared by Lorenz, et. al. were insoluble in water; they also contained significant amounts of missing branches arising from incomplete reactions during the backbone construction sequence.[40]

In the previous chapter, the synthesis of carbosilane dendrimers bearing terminal chloromethyl substituents was described. The clean reactions of these dendrimers with the iodide nucleophile suggested that further examples of this reaction type might also be successful. In 1953, Perklev reported the functionalization of a (bromoalkyl)silane with a mercapto-substituted carboxylic acid (eq. 1).[41] Following this example,

chloromethyl-substituted carbosilane dendrimers were reacted with several mercapto-substituted amphiphilic compounds. These derivatizations proceeded quantitatively to give, in high isolated yields, a series of water-soluble dendrimers terminated with both cationic and anionic amphiphilic groups. These new amphiphilic dendrimers were characterized by spectroscopic and mass spectrometric techniques. Their similarities to micelles were explored through studying their interactions with lipophilic compounds in aqueous solution.

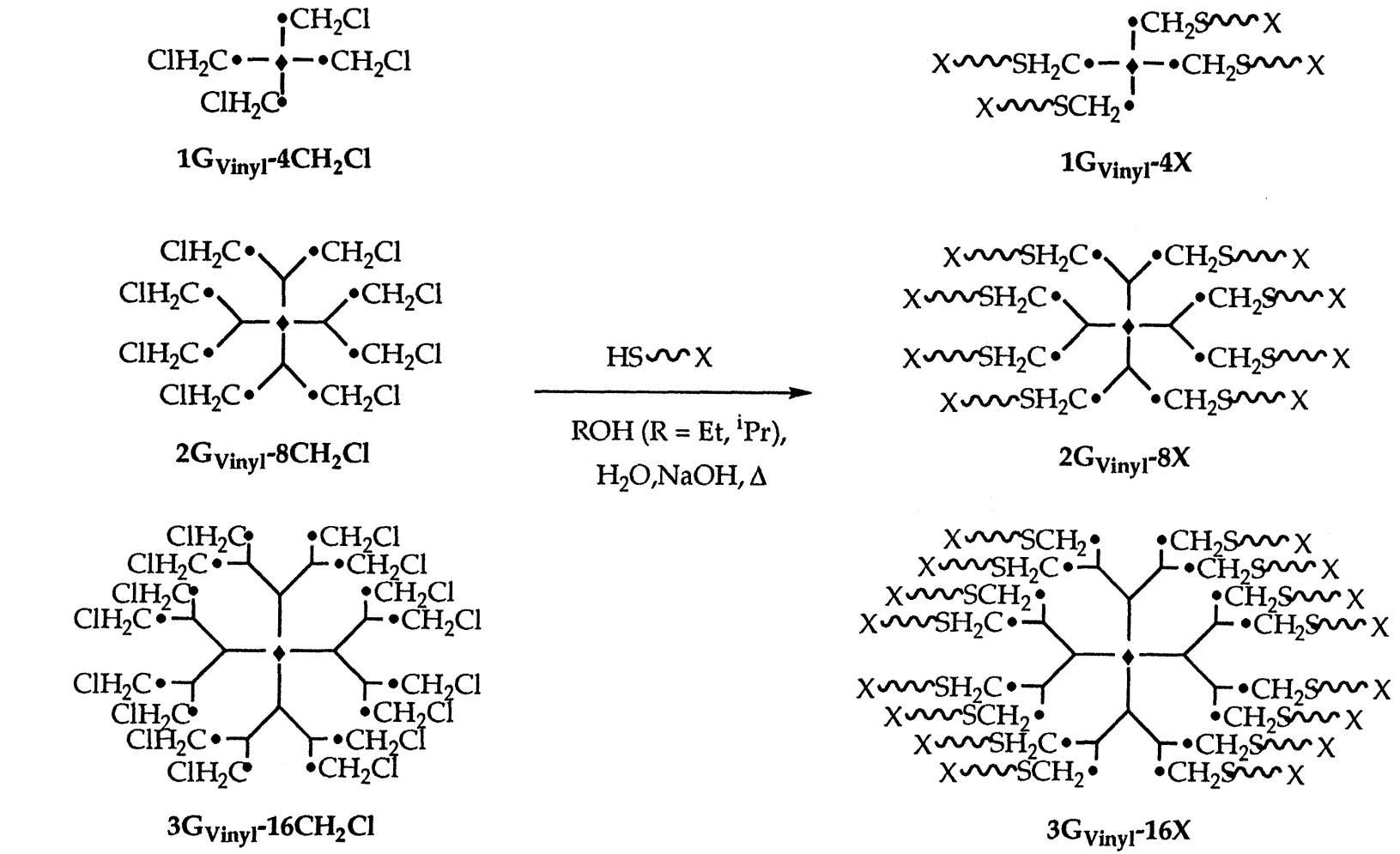


(1)

RESULTS AND DISCUSSION

Synthesis and Characterization

As illustrated in Scheme 1, amphiphilic groups were attached to the terminal branches of carbosilane dendrimers via thioether linkages. The syntheses involved deprotonating amphiphile-substituted mercaptans with NaOH and reacting the resulting thiolates with chloromethyl-terminated dendrimers **1G$_{Vinyl}$-4CH$_2$Cl**, **2G$_{Vinyl}$-8CH$_2$Cl** and **3G$_{Vinyl}$-16CH$_2$Cl** in alcohol/water solvent mixtures (ethanol was used for **1G$_{Vinyl}$-4CH$_2$Cl**, and isopropanol for **2G$_{Vinyl}$-8CH$_2$Cl** and **3G$_{Vinyl}$-16CH$_2$Cl**). Reaction mixtures were initially biphasic, but clarified over time with heating; extra water or alcohol was added as needed to assist in the dissolution of all reagents. In most cases, quantitative substitution of all chloromethyl groups occurred within several hours. In those cases where some chloromethyl groups remained unreacted at the termination of the reaction, complete substitution



♦ Si Y SiMe • $SiMe_2$ —— CH_2CH_2

HS~X = $HS(CH_2)_2NMe_2HCl$, $HS(CH_2)_2OH$
$HS(CH_2)_3SO_3Na$

Scheme 1. Synthesis of Amphiphile-Terminated Dendrimers.

was effected by reapplication of the reaction procedure. Products and yields of these reactions are given in Table 1.

Table 1. Attachment of Amphiphilic Groups to Chloromethyl-Terminated Dendrimers.

Chloromethyl-Terminated Dendrimer	Mercapto-Substituted Amphiphile	Product	Yield
$1G_{Vinyl}$-$4CH_2Cl$	$HSCH_2CH_2OH$	**$1G_{Vinyl}$-4OH**	98
$2G_{Vinyl}$-$8CH_2Cl$	$HSCH_2CH_2OH$	**$2G_{Vinyl}$-8OH**	99
$1G_{Vinyl}$-$4CH_2Cl$	$HSCH_2CH_2NMe_2HCl$	**$1G_{Vinyl}$-$4NMe_2$**	100
$2G_{Vinyl}$-$8CH_2Cl$	$HSCH_2CH_2NMe_2HCl$	**$2G_{Vinyl}$-$8NMe_2$**	92
$3G_{Vinyl}$-$16CH_2Cl$	$HSCH_2CH_2NMe_2HCl$	**$3G_{Vinyl}$-$16NMe_2$**	92
$1G_{Vinyl}$-$4CH_2Cl$	$HSCH_2CH_2CH_2SO_3Na$	**$1G_{Vinyl}$-$4SO_3Na$**	80
$2G_{Vinyl}$-$8CH_2Cl$	$HSCH_2CH_2CH_2SO_3Na$	**$2G_{Vinyl}$-$8SO_3Na$**	66
$3G_{Vinyl}$-$16CH_2Cl$	$HSCH_2CH_2CH_2SO_3Na$	**$3G_{Vinyl}$-$16SO_3Na$**	75

All of the substitutions listed in Table 1 proceeded without any observable side-reactions. Purification of the dendrimeric products required only the removal of solvents, excess mercaptans, excess NaOH and NaCl by-product. For reactions involving 2-mercaptoethanol and 2-dimethylaminoethanethiol hydrochloride, the products were soluble in organic solvents and insoluble in water, and were thus easily separated from inorganic contaminants by extraction. Since the excess mercaptans in these cases were volatile, they were removed by heating the crude products under vacuum, giving the desired products in analytically pure form in high yields. The first generation, alcohol-terminated dendrimer **$1G_{Vinyl}$-4OH** was a crystalline solid. Its second generation analog **$2G_{Vinyl}$-8OH** was a viscous oil,

as were the dimethylamino-terminated dendrimers **$1G_{Vinyl}$-$4NMe_2$**, **$2G_{Vinyl}$-$8NMe_2$** and **$3G_{Vinyl}$-$16NMe_2$**.

Dendrimeric products bearing terminal sodium sulfonate groups were completely soluble in water and essentially insoluble in all organic solvents, including alcohols. The non-volatile mercaptan used to synthesize these products was also poorly soluble in organic solvents. The first generation dendrimer **$1G_{Vinyl}$-$4SO_3Na$** precipitated from the reaction mixture upon cooling to room temperature, leaving excess mercaptan behind in solution. For syntheses of **$2G_{Vinyl}$-$8SO_3Na$** and **$3G_{Vinyl}$-$16SO_3Na$**, lower excesses of the mercaptan were used, since its removal from the products required multiple extractions with isopropanol.

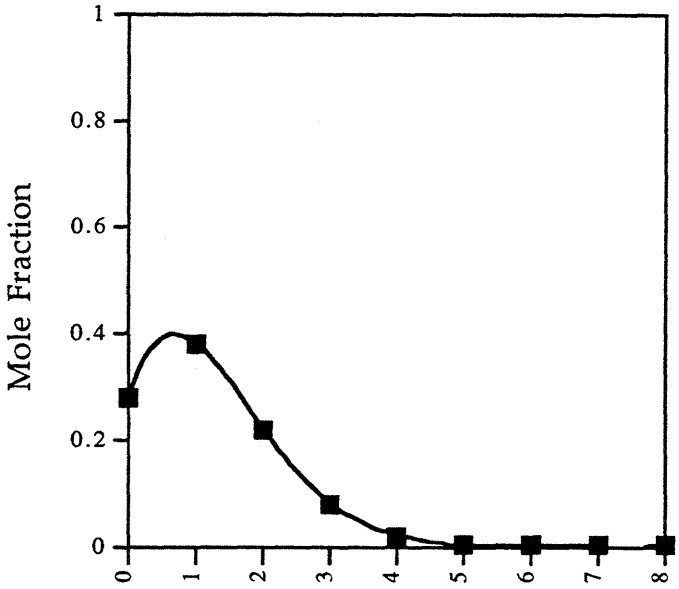
Removal of NaCl from the water-soluble, sodium sulfonate-terminated dendrimers was accomplished by acidifying aqueous solutions of the crude products to neutral pH and dialyzing in cellulose ester membranes with low molecular weight cutoff values (100 - 500 Daltons). Results of combustion analyses of samples of **$1G_{Vinyl}$-$4SO_3Na$** and **$3G_{Vinyl}$-$16SO_3Na$** which had been purified in this manner indicated nearly complete removal of sodium chloride. Results for **$2G_{Vinyl}$-$8SO_3Na$** purified under similar conditions, however, indicated the presence of 5% (w/w) residual NaCl.

The chloromethyl-terminated dendrimers employed as synthons for the amphiphilic derivatives were essentially free from missing branches and higher molecular weight condensation products. However, since the present studies preceded the discovery of the method described in Chapter 3 for suppressing α-addition reactions in the production of vinyl-terminated dendrimers **$1G_{Vinyl}$-8Vinyl** and **$2G_{Vinyl}$-16Vinyl**, samples of **$2G_{Vinyl}$-$8CH_2Cl$** and **$3G_{Vinyl}$-$16CH_2Cl$** used as starting points for the syntheses of the amphiphilic derivatives contained α-addition isomers in the inner branches

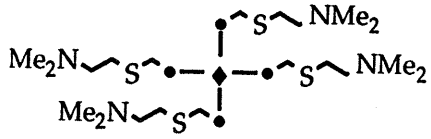
(approximately 10% for each hydrosilylation step). After the development of the new method for synthesizing **1G$_{Vinyl}$-8Vinyl** and **2G$_{Vinyl}$-16Vinyl**, time constraints only allowed for the re-synthesis of the second generation amphiphilic dendrimers from starting materials containing no α-addition isomers.

The distribution of α-addition isomers in the third generation amphiphilic dendrimers can be calculated by two sequential applications of eq. 1 from Chapter 3, assuming 10% α-addition occurs in both of the hydrosilylation steps in the synthesis of **2G$_{Vinyl}$-16Vinyl**. The results of this calculation, shown in Figure 5, indicate that the majority (72%) of the third generation, chloromethyl- and amphiphile-terminated dendrimers will have at least one of their twelve inner branches shortened by one carbon due to α-addition. These defects do not affect the mass of the dendrimers or the number of branches. Since they are buried in the cores of the dendrimers, they were not detectable by any spectroscopic means (*vide infra*).

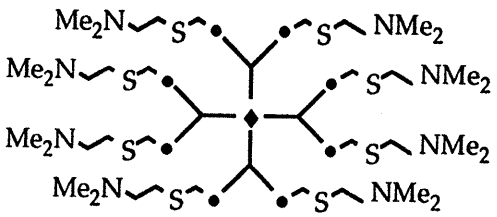
Figure 5. Calculated Distribution of α-Addition Isomers in Inner Branches of Third Generation Dendrimers



Further reactions involving the dimethylamino-terminated dendrimers **1G$_{Vinyl}$-4NMe$_2$**, **2G$_{Vinyl}$-8NMe$_2$** and **3G$_{Vinyl}$-16NMe$_2$** converted them into water-soluble derivatives. Protonating their terminal dimethylamino groups with HCl (aq) gave the water-soluble hydrochloride adducts **1G$_{Vinyl}$-4NMe$_2$HCl**, **2G$_{Vinyl}$-8NMe$_2$HCl** and **3G$_{Vinyl}$-16NMe$_2$HCl**. The first generation hydrochloride adduct was a crystalline solid; higher generations were amorphous solids. Reactions of the dimethylamino-terminated dendrimers with excess MeI[42] provided the quaternary ammonium salts in high yields as analytically pure white powders (Scheme 2). Metathesizing the iodide counterions of these compounds for chloride ions using AgCl[43] greatly enhanced their solubilities in water. The masses of the hygroscopic solids obtained from the metathesis reactions suggested that



$1G_{Vinyl}$-$4NMe_2$



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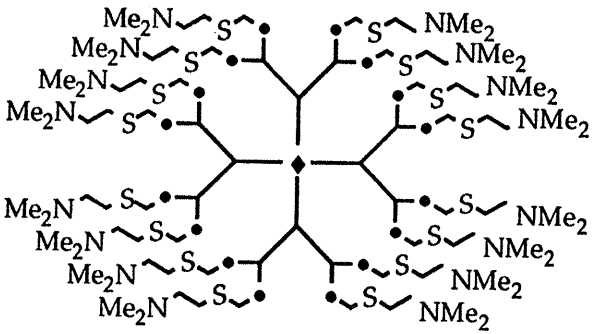
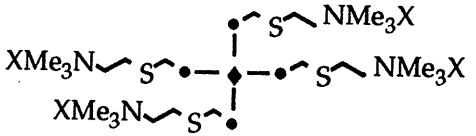


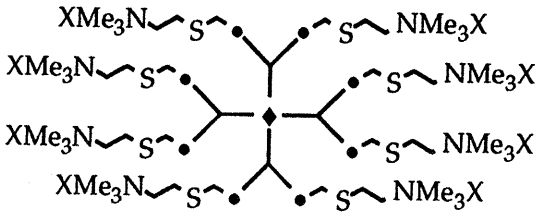
$3G_{Vinyl}$-$16NMe_2$

1. MeI

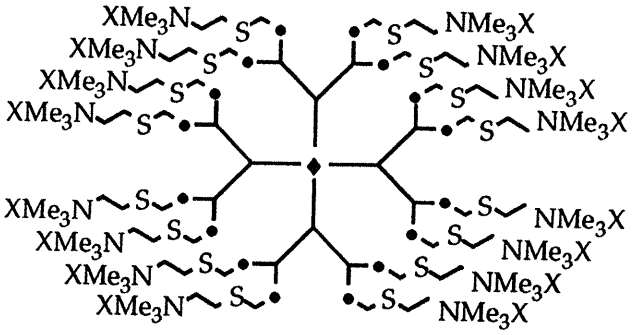
2. AgCl



$1G_{Vinyl}$-$4NMe_3X$



$2G_{Vinyl}$-$8NMe_3X$



$3G_{Vinyl}$-$16NMe_3X$

X = 1. I; 2. Cl

♦ Si Y SiMe • $SiMe_2$ —— CH_2CH_2

Scheme 2. Synthesis of Dendrimers Terminated with Quaternary Ammonium Salts.

complete exchange of counterions had occurred; this was corroborated by the results of combustion analyses.

All of the dendrimeric products synthesized in this study were characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The majority of these compounds were also characterized by MALDI-TOF mass spectrometry. The results of these studies confirmed the identities of these compounds and the regularity of their structures.

NMR Spectroscopy

The ^{1}H, ^{13}C and ^{29}Si NMR spectra of the amphiphile-terminated dendrimers in most cases were completely consistent with their proposed structures (exceptions are discussed below). Dendrimers which were readily soluble in organic solvents (i.e., the chloromethyl-, alcohol-, and dimethylamino-terminated dendrimers) exhibited sharp signals in their NMR spectra; those which were soluble in water generally displayed broader signals. The broadening of the ^{1}H NMR resonances of $\mathbf{2G_{Vinyl}\text{-}8NMe_2}$ upon its conversion to water-soluble derivatives is shown in Figure 6. Increased linewidths most likely reflect dipolar broadening effects arising from the expected decrease in mobility of these predominantly hydrophobic dendrimers in water.[44] NMR relaxation studies conducted on PAMAM dendrimers have also shown decreased mobilities of inner carbon atoms.[16] The ^{1}H NMR resonances of the quaternary ammonium iodide compounds, which were poorly soluble in water, dramatically broadened when the spectra were measured in D_2O rather than CD_3OD (Figure 7). Linewidths did not change appreciably with generation, as shown by the ^{1}H NMR spectra of sodium sulfonate-terminated dendrimers in Figure 8.

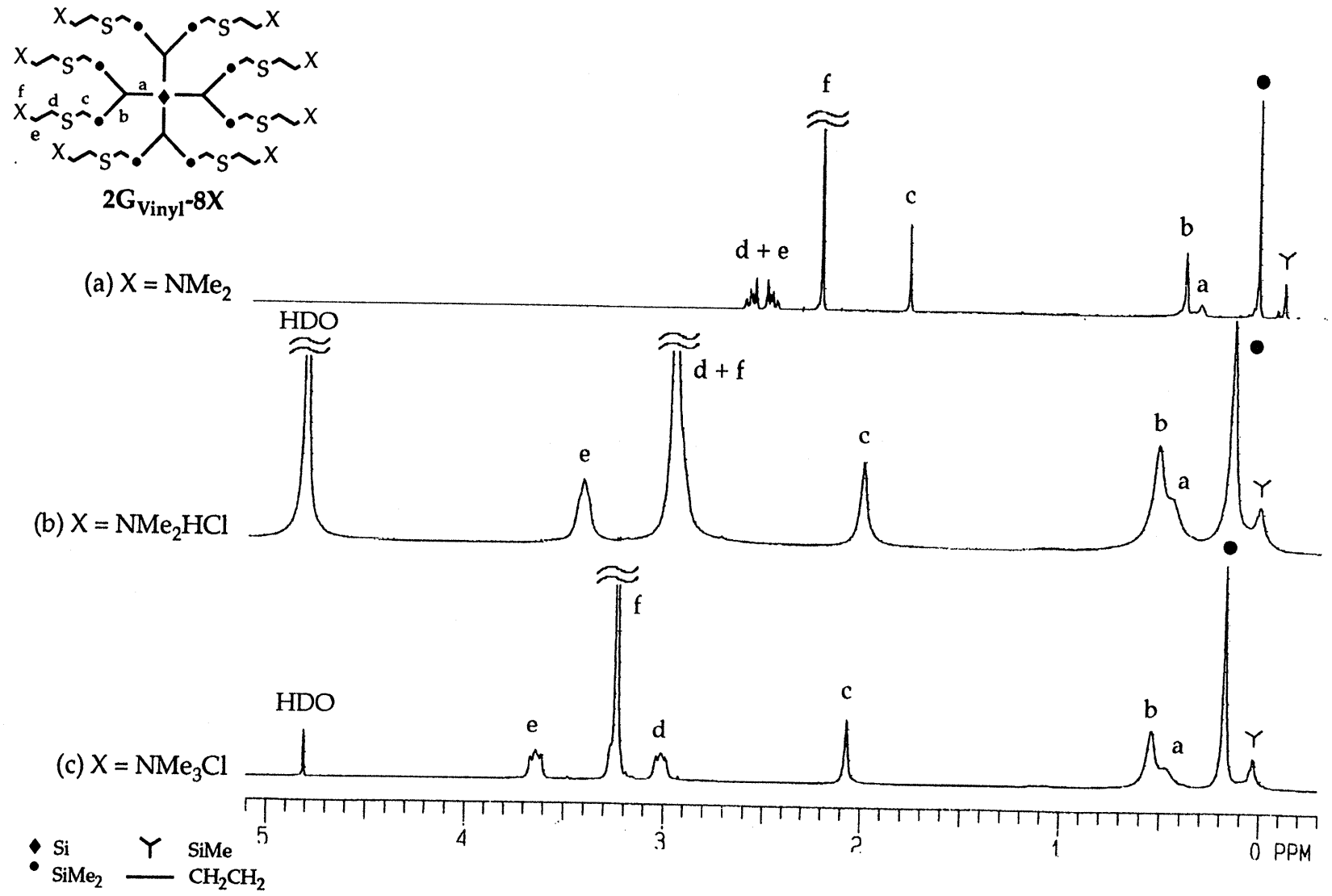


Figure 6. ^{1}H NMR Spectra of (a) **2G$_{Vinyl}$-8NMe$_2$** in $CDCl_3$, and (b) **2G$_{Vinyl}$-8NMe$_2$HCl** and (c) **2G$_{Vinyl}$-8NMe$_3$Cl** in D_2O.

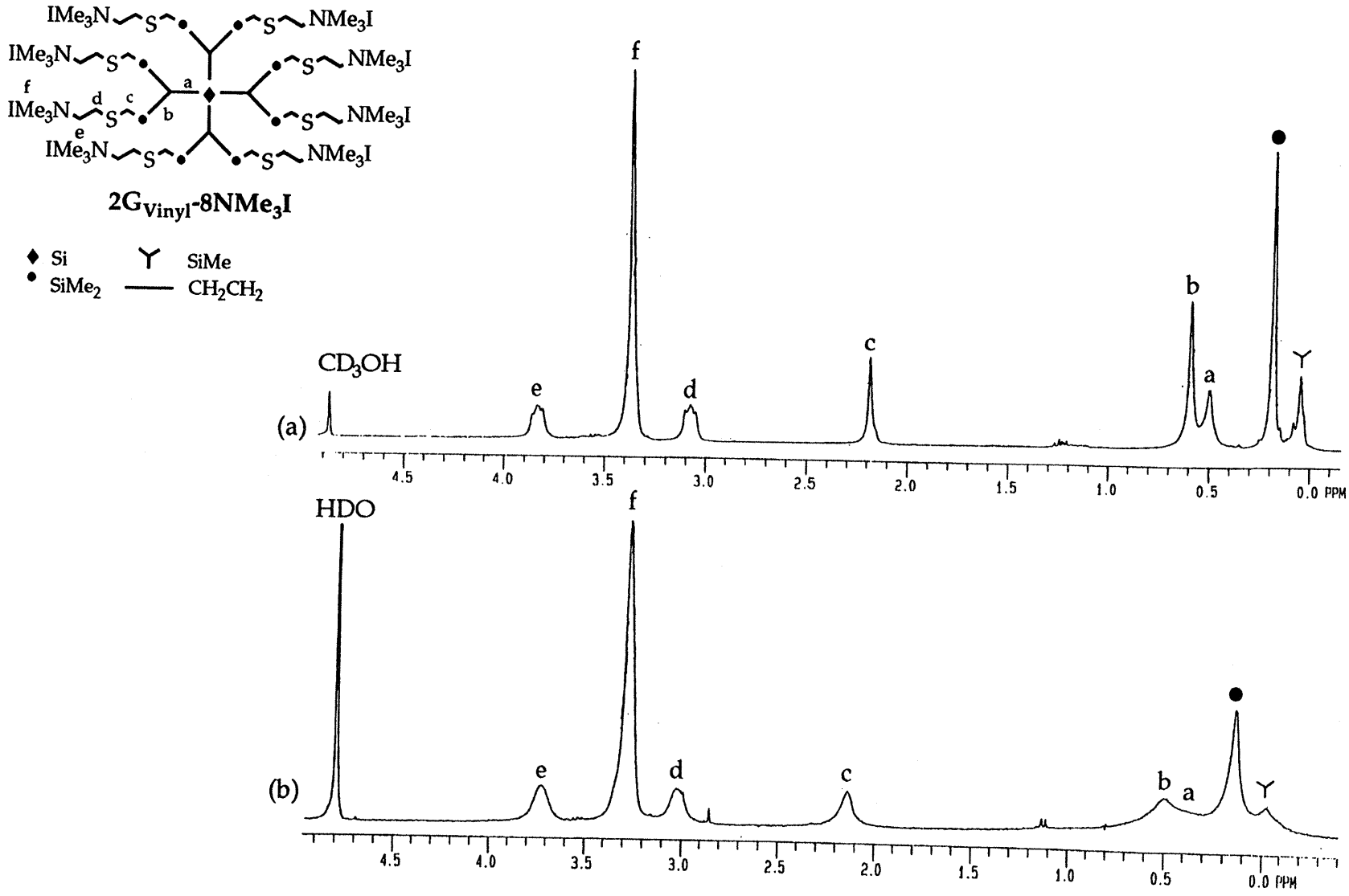


Figure 7. ^{1}H NMR Spectra of **2G$_{Vinyl}$-8NMe$_3$I** in (a) CD_3OD and (b) D_2O.

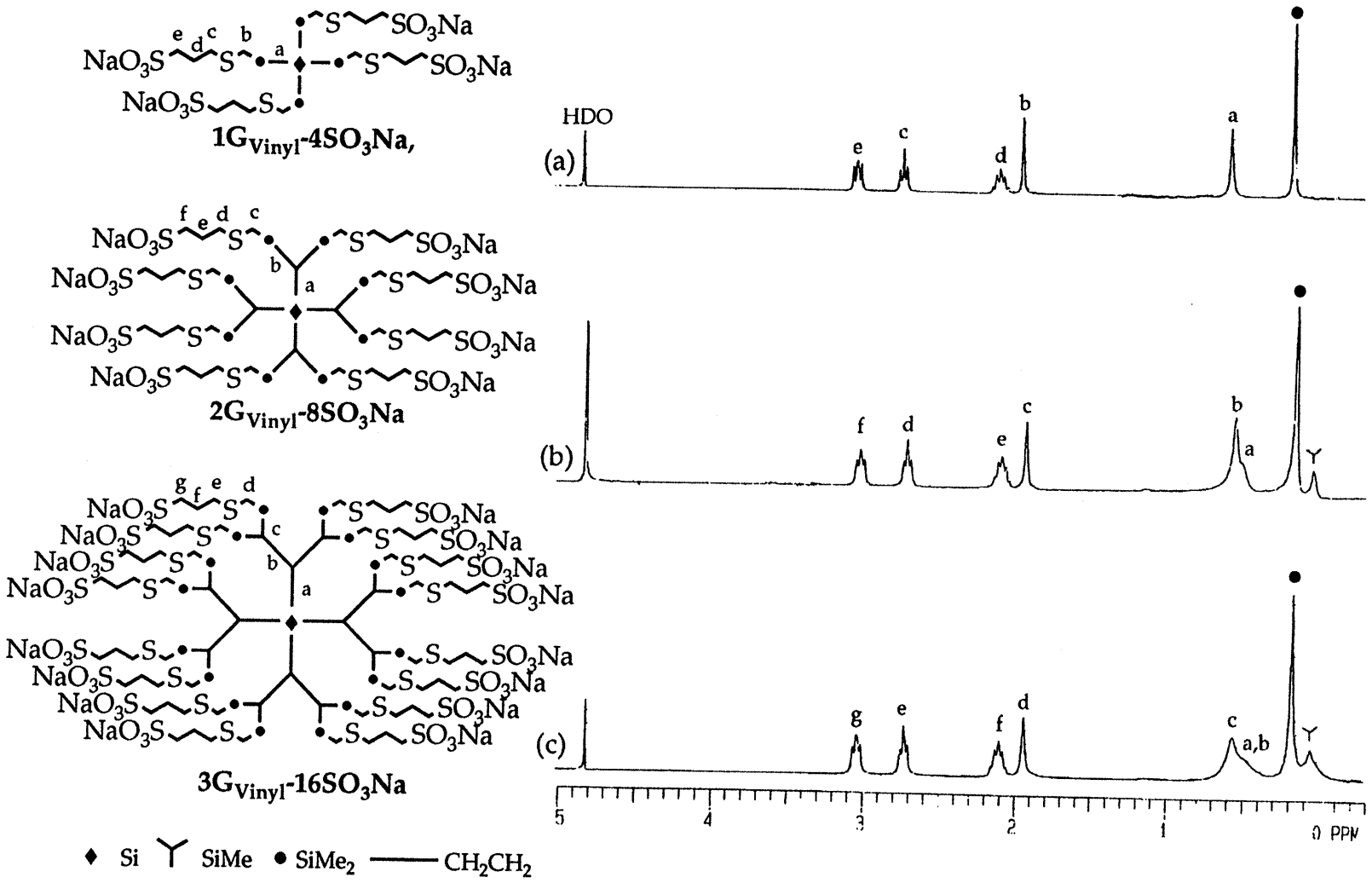


Figure 8. ^{1}H NMR Spectra of (a) **1G$_{Vinyl}$-4SO$_3$Na**, (b) **2G$_{Vinyl}$-8SO$_3$Na** and (c) **3G$_{Vinyl}$-16SO$_3$Na** in D_2O.

In addition to displaying broad linewidths, the ^{1}H NMR spectra of the water-soluble dendrimeric ammonium salts exhibited shoulders on the signals associated with the terminal amphiphilic branches; in some cases, shoulders also were observed in the ^{13}C NMR spectra. Given the high purities of these compounds indicated by elemental analysis and MALDI-TOF mass spectrometry (*vide infra*), these extra signals are attributed to the effects of aggregation. Consistent with this explanation, the intensities of shoulders on the NMe and $SiCH_2S$ resonances in the ^{1}H NMR spectrum of **1G$_{Vinyl}$-4NMe$_3$I** varied with the dendrimer's concentration in CD_3OD (Figure 9).

MALDI-TOF Mass Spectrometry

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has emerged as an invaluable tool for confirming the identities and molecular weight distributions of dendrimers.[40,45-51] Using this technique, molecular ions of dendrimers with masses up to 40 kDa have been measured with high degrees of accuracy.[46] So far, there has been only one reported example of the use of MALDI-TOF-MS to characterized carbosilane dendrimers.[40] Analyses of the dendrimers synthesized in the present study as well as several several examples synthesized in Chapter 3 were performed by Dr. Zhuchun Wu and Professor Klaus Biemann of the Department of Chemistry at M.I.T. These studies represented the first attempts at mass-spectrometric characterization of dendrimers functionalized with chloromethyl, iodomethyl, sodium sulfonate and trimethylammonium halide groups. The results of these measurements are compiled in Table 2.

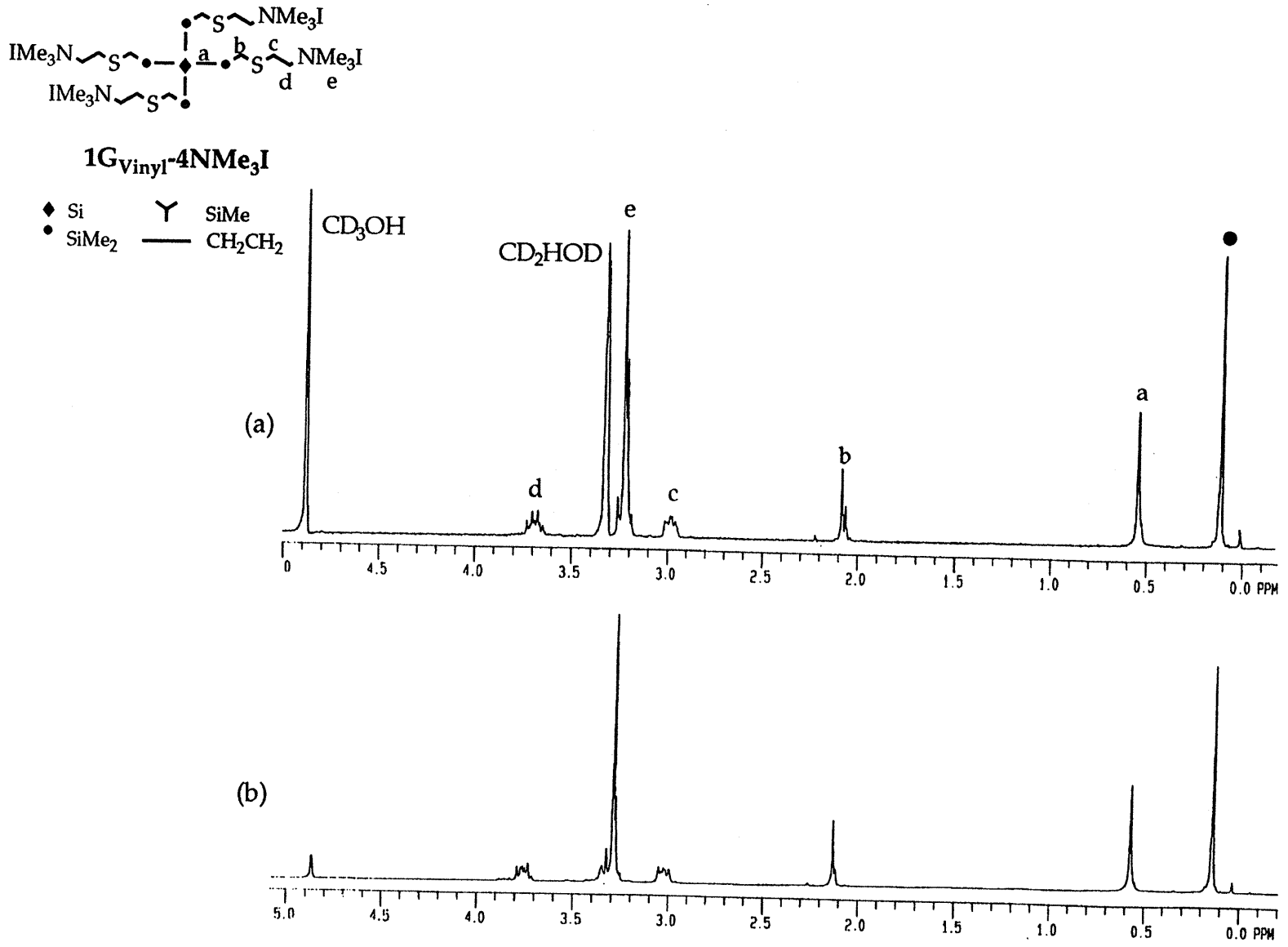


Figure 9. ^{1}H NMR Spectra of **1G$_{Vinyl}$-4NMe$_3$I** in (a) dilute and (b) concentrated CD_3OD.

Table 2. Results of MALDI-TOF Mass Spectrometry of Dendrimers.

Compound	Matrix[a] /Solvent	Molecular Ion Observed	Calculated Mass[b]	Measured Mass[b]
$1G_{Vinyl}$-$4CH_2Cl$	CSA, Ag(tfa), ethanol	$[M + Ag]^+$	675.04[c]	674.72[c]
$2G_{Vinyl}$-$8CH_2Cl$	CSA, Ag(acac), isopropanol	$[M + Ag]^+$	1506.14 1499.326[c]	1506.03 1499.23[c]
$3G_{Vinyl}$-$16CH_2Cl$	CSA, Ag(acac), acetone	$[M + Ag]^+$	3161.06	3159.86
$1G_{Vinyl}$-$4CH_2I$	CSA, Ag(tfa), acetone	$[M + Ag]^+$	1042.78[c]	1042.86[c]
$2G_{Vinyl}$-$8CH_2I$	CSA, Ag(tfa), ethanol	$[M + Ag]^+$	2234.81[c]	2234.44[c]
$1G_{Vinyl}$-4OH	DHB, Na(cit), isopropanol	$[M + Na]^+$	759.27[c]	759.24[c]
$2G_{Vinyl}$-8OH	DHB, Na(cit), isopropanol	$[M + Na]^+$	1751.71[c]	1752.06[c]
$1G_{Vinyl}$-$4NMe_2$	CSA, ethanol	$[M + H]^+$	845.48	845.41
$2G_{Vinyl}$-$8NMe_2$	CSA, ethanol	$[M + H]^+$	1949.20 1946.10[c]	1948.97 1946.21[c]
$3G_{Vinyl}$-$16NMe_2$	DNB, water	$[M + H]^+$	4154.00	4152.28
$1G_{Vinyl}$-$4SO_3Na$	DHB, water	$[M + 3\ H]^-$	1047.19[c]	1047.57[c]
$2G_{Vinyl}$-$8SO_3Na$	DHB, water	$[M + 7\ H]^-$	2355.26	2353.6
$3G_{Vinyl}$-$16SO_3Na$	DHB, NH_4(cit) water	$[M + 15\ H]^-$	4968.2	4967.0
$1G_{Vinyl}$-$4NMe_3I$	DHB, water	$[M + 3\ DHB^-]^+$	1365.27	1365.56
$1G_{Vinyl}$-$4NMe_3I$	CSA, water	$[M + 3\ CSA^-]^+$	1420.61	1421.31
$2G_{Vinyl}$-$8NMe_3I$	DHB, water	$[M + 7\ DHB^-]^+$	3140.27	3142.50
$2G_{Vinyl}$-$8NMe_3I$	CSA, water	$[M + 7\ CSA^-]^+$	3269.39	3272.92
$1G_{Vinyl}$-$4NMe_3Cl$	DHB, water	$[M + 3\ DHB^-]^+$	1365.27	1365.42
$2G_{Vinyl}$-$8NMe_3Cl$	DHB, water	$[M + 7\ DHB^-]^+$	3140.27	3142.62

[a]CSA = 5-chlorosalicylic acid; tfa = trifluoroacetate; acac = acetylacetonate; cit = citrate; DHB = 3,5-dihydroxybenzoic acid.

[b]Masses given are weighted isotopic averages, unless otherwise indicated.

[c]Monoisotopic mass.

For all compounds except **$3G_{Vinyl}$-16NMe_3X** (X = Cl, I), molecular ions were observed whose masses correlated well with calculated values. Representative spectra are shown in Figures 10 - 13. In some cases, mass spectra with isotopic resolution were obtained (Figures 10a, 10b, 11a, 11b and 12a); comparison of the experimentally determined isotopic distribution patterns with those calculated from known natural abundances provided confirmation of the proposed structures. For spectra of lower resolution, molecular ions appeared as single peaks at an *m/z* value corresponding to the weighted isotopic average. Spectra of first and second generation dendrimers exhibited narrow signals and a relatively low abundance of peaks arising from fragmentation. Those of third generation dendrimers contained broad signals and significant fragmentation in addition to sharp peaks for the molecular ions.

Dendrimers terminated with chloromethyl, iodomethyl, and alcohol groups gave molecular ions corresponding to their respective monoadducts with a matrix cation (either Ag^+ or Na^+). MALDI-TOF spectra of the chloromethyl-terminated dendrimers (Figure 10) were of particular interest, since they served as starting points for the syntheses of all the water-soluble derivatives. Spectra of the first and second generation compounds contained essentially no lower molecular weight peaks (Figure 10a,b). The spectrum of **$3G_{Vinyl}$-16CH_2Cl** (Figure 10c), however, exhibited a broad expanse of lower molecular weight peaks which extended approximately 350 mass units below the sharp molecular ion peak. In addition, a sharp, intense peak was observed at *m/z* = 1746.8 mass units. The random distribution of these peaks argues for their arising from fragmentation processes rather than lower molecular weight impurities, since the presence of missing branches in dendrimers produces a pattern of regularly spaced lower molecular weight

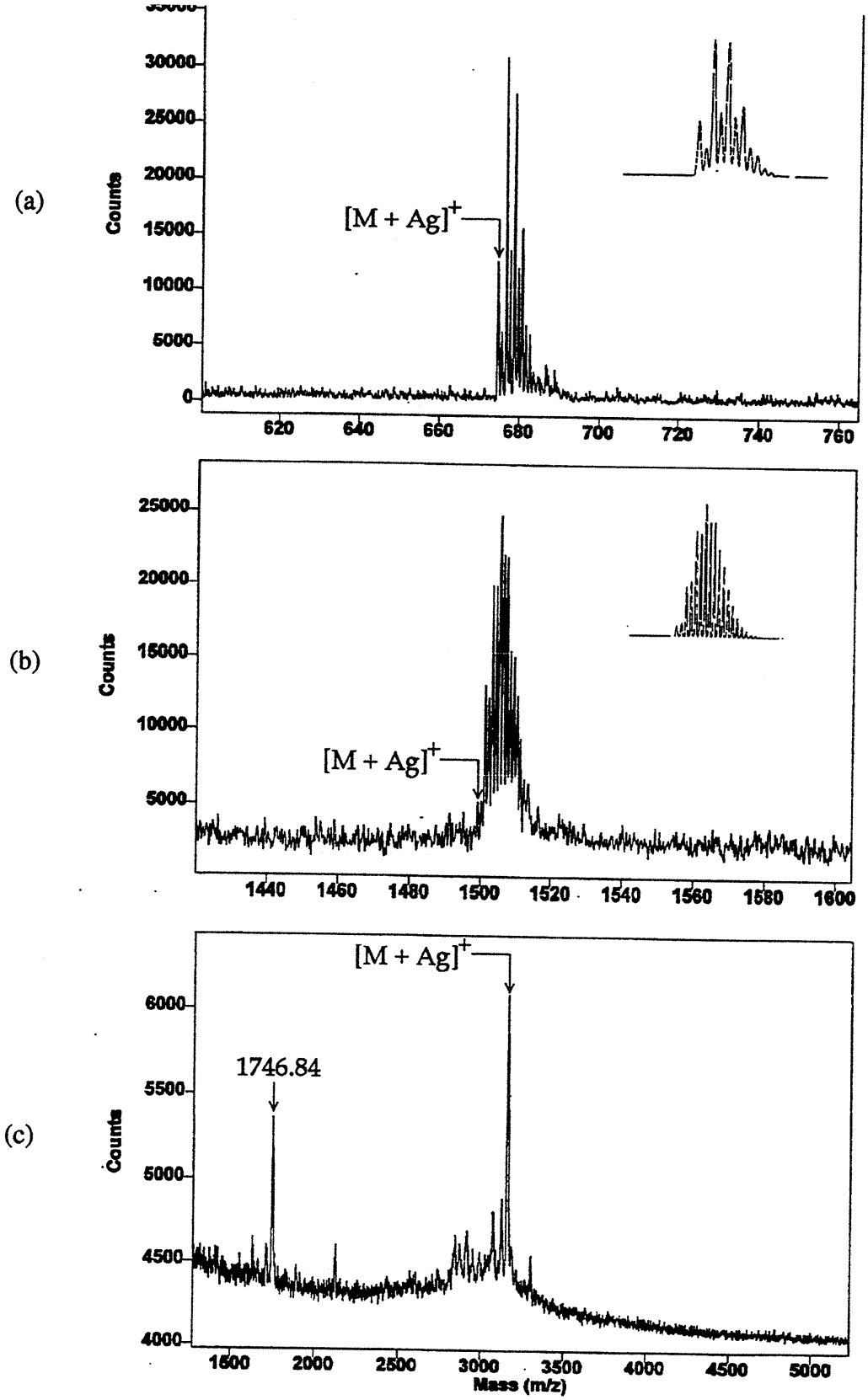


Figure 10. MALDI-TOF Mass Spectra of (a) $1G_{Vinyl}$-$4CH_2Cl$, (b) $2G_{Vinyl}$-$8CH_2Cl$ and (c) $3G_{Vinyl}$-$16CH_2Cl$. (Calculated isotopic distributions are shown as insets.)

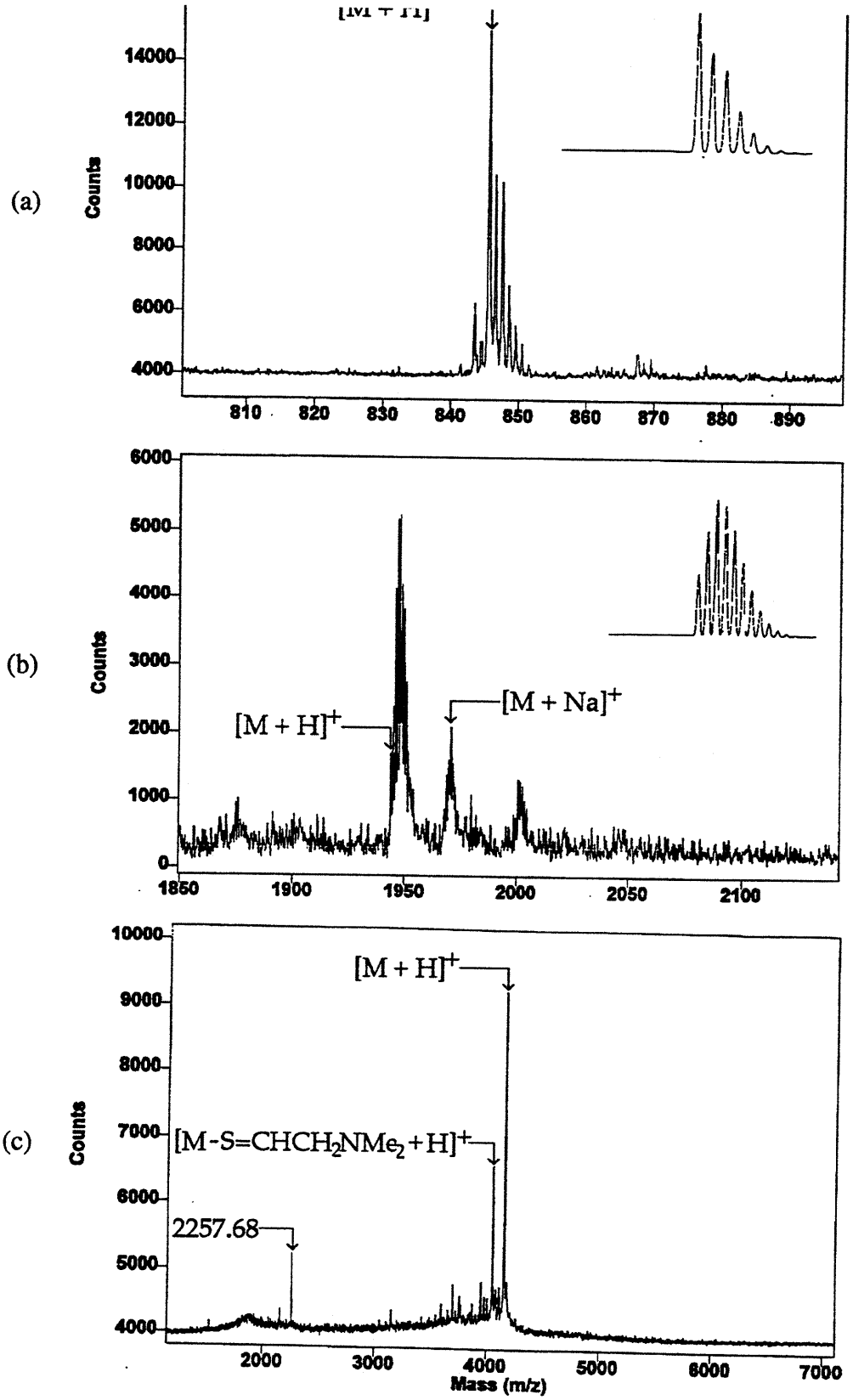


Figure 11. MALDI-TOF Mass Spectra of (a) $\mathbf{1G_{Vinyl}\text{-}4NMe_2}$, (b) $\mathbf{2G_{Vinyl}\text{-}8NMe_2}$ and (c) $\mathbf{3G_{Vinyl}\text{-}16NMe_2}$. (Calculated isotopic distributions are shown as insets.)

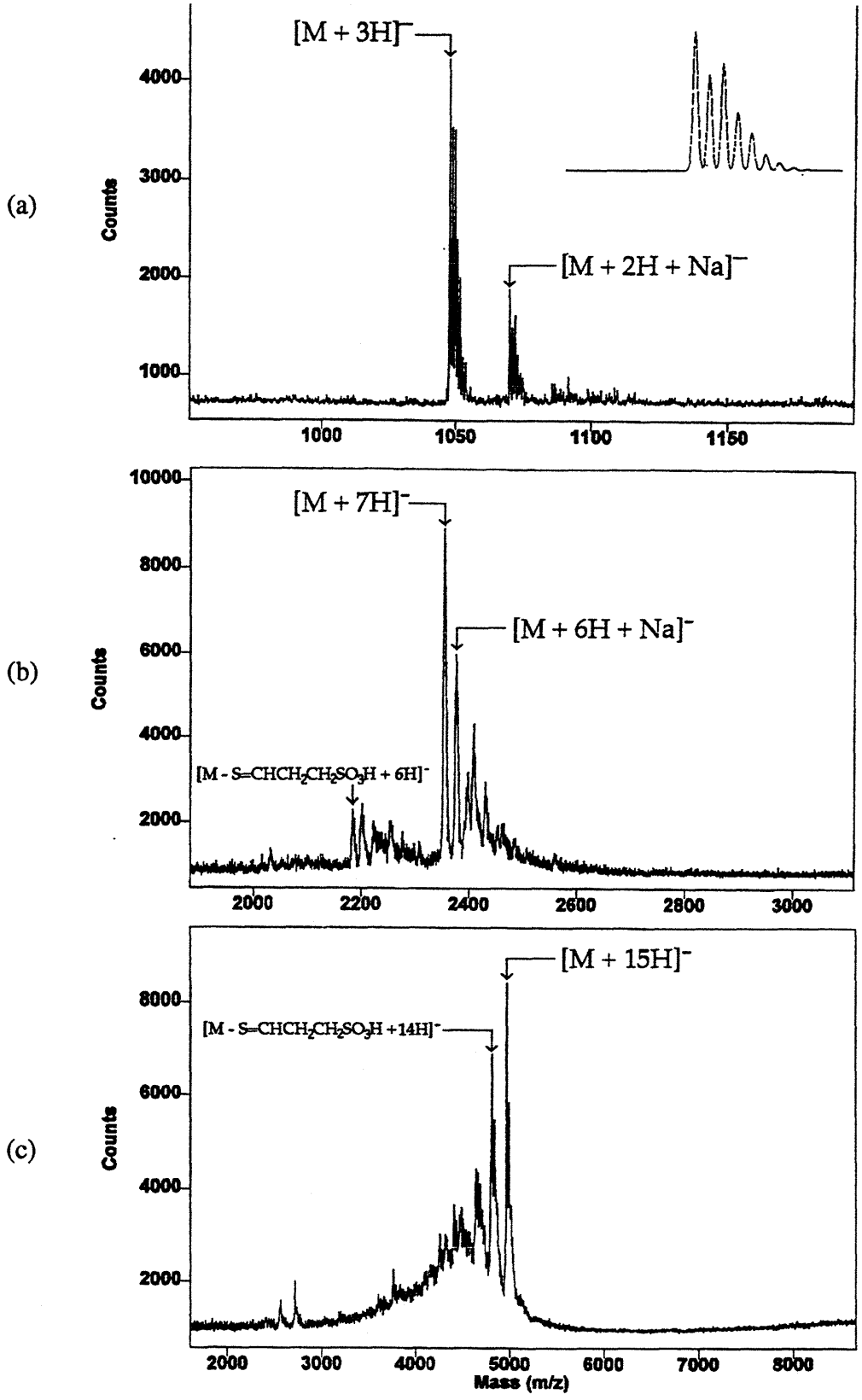


Figure 12. MALDI-TOF Mass Spectra of (a) $\mathbf{1G_{Vinyl}\text{-}4SO_3Na}$, (b) $\mathbf{2G_{Vinyl}\text{-}8SO_3Na}$ and (c) $\mathbf{3G_{Vinyl}\text{-}16SO_3Na}$. (The calculated isotopic distribution for $\mathbf{1G_{Vinyl}\text{-}4SO_3Na}$ is shown as an inset.)

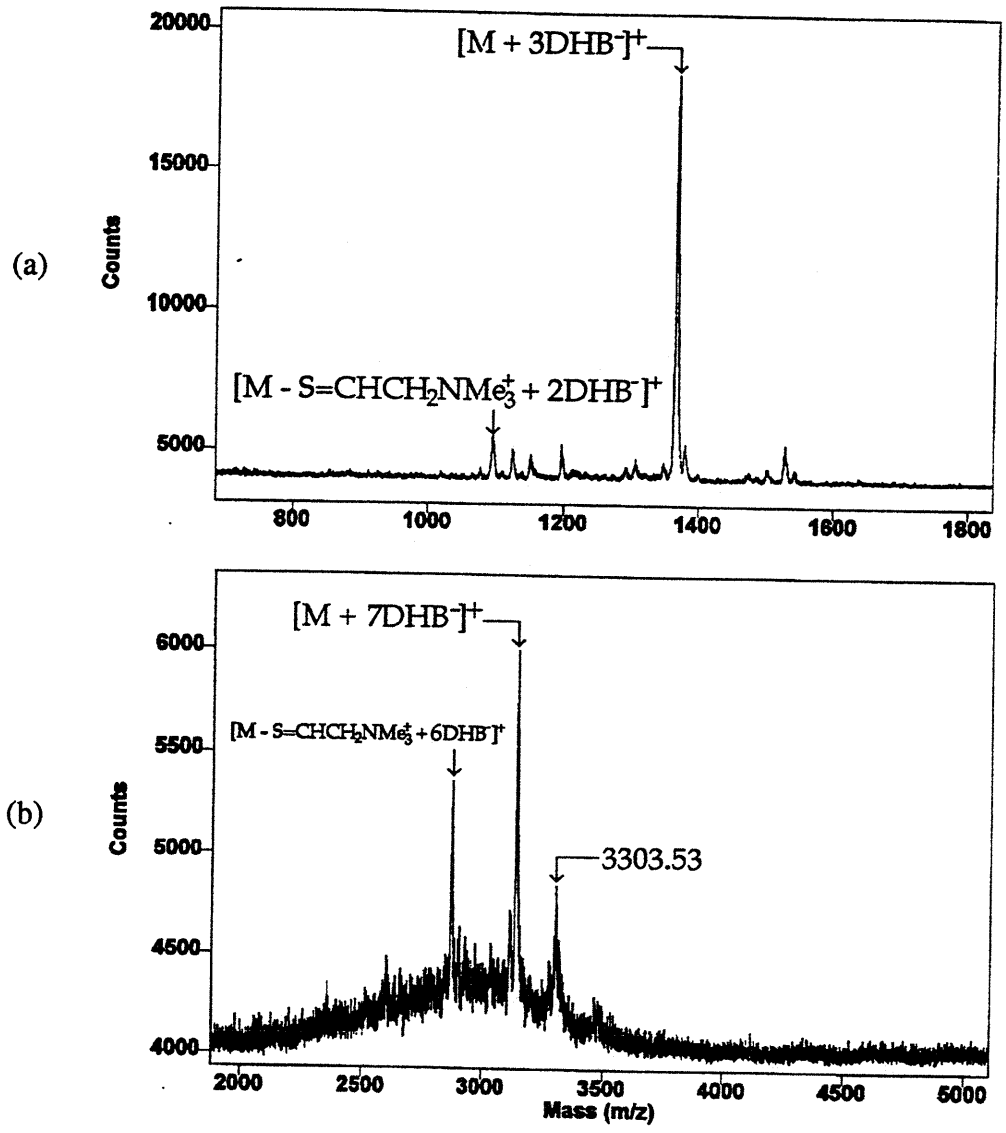


Figure 13. MALDI-TOF Mass Spectra of (a) $\mathbf{1G_{Vinyl}\text{-}4NMe_3I}$, and (b) $\mathbf{2G_{Vinyl}\text{-}8NMe_3I}$ in 2.5-Dihydroxybenzoic Acid Matrix.

peaks whose intensities roughly corresponded to distributions predicted by eq. 1 of Chapter 3.[40]

The mass spectra of **$1G_{Vinyl}$-4NMe_2**, **$2G_{Vinyl}$-8NMe_2** and **$3G_{Vinyl}$-16NMe_2** displayed molecular ions arising from the protonation of one of the dimethylamino groups (Figure 11). These spectra also exhibited alkali metal ion adducts and a prominent fragment ion resulting from the elimination of a $S{=}CHCH_2NMe_2$ group (Figure 11c). Successful analyses of sodium sulfonate-terminated dendrimers required that they be converted, using an ion exchange resin, to their respective ammonium salts. Under irradiation, these salts dissociated into the free sulfonic acids, which gave molecular ions corresponding to deprotonation of one of the SO_3H groups (Figure 12). Complex cationization patterns appeared at higher *m/z* values. The most prominent fragment ions corresponded to the loss of $S{=}CHCH_2CH_2SO_3H$ groups.

The trimethylammonium halide-terminated dendrimers displayed the most interesting behavior under the conditions of the MALDI-TOF-MS experiments. The chloride and iodide salts gave nearly identical spectra with molecular ions corresponding to the tetra- or octa-cation complexed with three or seven deprotonated matrix molecules, respectively (Figure 13). Changing the matrix resulted in a corresponding change in the mass of the molecular ion (Table 2). Fragmentation of these species involved the loss of one $S{=}CHCH_2NMe_3^+$ group along with its corresponding matrix anion. These complexes appeared not to be very stable–only broad, unresolved signals were observed in attempts to acquire a spectrum of **$3G_{Vinyl}$-16NMe_3I** using the same conditions as those used for the first and second generation dendrimers.

These studies confirmed the structural regularity of the dendrimers synthesized in this study and in Chapter 3. None of the features evident in the spectra of any of these derivatives suggested the presence of missing branches, incomplete substitutions or higher molecular weight condensation products. In addition, these studies led to the discovery of a novel complex formation between the multiply charged trimethylammonium-terminated dendrimers and anions derived from the matrix.

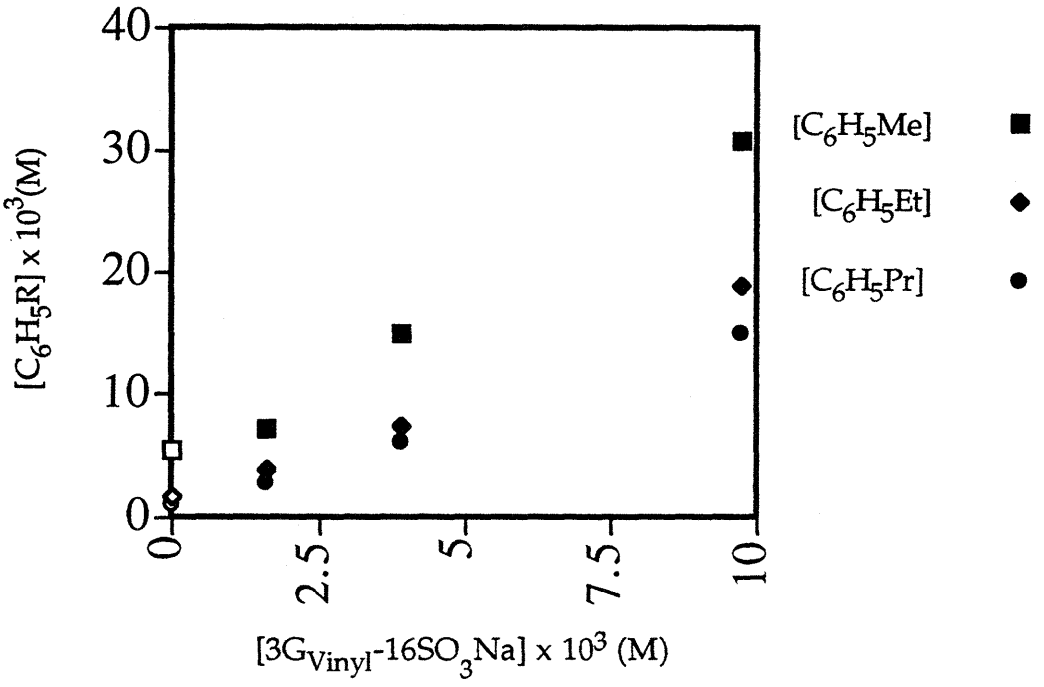
Solubilization Studies

Various groups have reported the enhancement of the water solubility of lipophilic compounds in the presence of amphiphilic dendrimers.[13,27,29,30] This type of behavior is one of the signature properties of micelles, and is utilized in a variety of applications ranging from soaps and detergents[52] to micelle-based chromatographic separations.[53] Recently, Hawker, et. al. reported that poly(aryl ether) dendrimers bearing terminal carboxylate groups were able to significantly enhance the solubility of pyrene and other polycyclic aromatic compounds into water.[27] The extent of solubilization varied linearly with the concentration of dendrimer, which is the same behavior that is observed for surfactant solutions above the CMC.[5] The ability of these dendrimers to solubilize such highly hydrophobic compounds was attributed in part to π-π interactions between the solubilizates and the aromatic rings of the dendrimer framework.

Aqueous solutions of **3G$_{Vinyl}$-16SO$_3$Na** showed no appreciable solubilization of naphthalene or anthracene (as measured by UV-Vis spectroscopy) under conditions similar to those reported in the study discussed above. The extent of solubilization of hydrophobic compounds in micellar solutions typically increases with the inherent aqueous solubility of

the organic solubilizate.[5] Thus, three compounds–toluene, ethylbenzene and propylbenzene–with aqueous solubilities (5.4×10^{-3}, 1.65×10^{-3} and 9.98×10^{-4} M, respectively[54]) greater than those of napthalene (2.2×10^{-4} M[55]) and anthracene (2.2×10^{-7} M[55]) were chosen to test the solubilizing ability of **$3G_{Vinyl}$-$16SO_3Na$**. Since the UV absorbance peaks of these compounds were obscured by dendrimer absorbances, their concentrations in aqueous (D_2O) solutions of **$3G_{Vinyl}$-$16SO_3Na$** were measured by comparing the integrated areas of the solubilizate peaks to those of the dendrimer (whose concentration was known) in the ^1H NMR spectra. Figure 14 shows the results of these studies for three different concentrations of **$3G_{Vinyl}$-$16SO_3Na$**. The concentrations of all three organic compounds increased linearly with the concentration of dendrimer, as expected. Extrapolation of these results to zero dendrimer concentration gave values for the inherent solubilities of the three organic compounds C_6H_5R in D_2O (3.0×10^{-3}, 4.7×10^{-4} and 2.2×10^{-4} for R = CH_3, CH_3CH_2 and $CH_3CH_2CH_2$, respectively) which were in qualitative agreement with the literature values for aqueous solubility.[54] The solubility enhancement corresponded to roughly 2 to 3 alkylbenzene molecules solubilized per dendrimer molecule. This may be compared to the results of Hawker, et. al. in which 0.45 molecules of pyrene were solubilized per amphiphilic poly(aryl ether) dendrimer molecule.[27]

Figure 14. Solubilization of Alkyl-Substituted Benzene Derivatives by Third Generation, Sodium Sulfonate-Terminated Dendrimer. (Closed symbols represent experimental data; open symbols represent literature solubility values.)



CONCLUSIONS

A new method was developed for the attachment of amphiphilic groups to the terminal branches of hydrophobic dendrimers to give molecules whose structures mimicked those of micelles. This method employed nucleophilic reactions of variously substituted thiolate anions with carbosilane dendrimers bearing chloromethyl groups on their terminal branches. In this manner, dendrimers with four, eight and sixteen terminal alcohol, dimethylamino, trimethylammonium halide and sodium sulfonate groups were prepared in high yields. Despite their high masses and

predominantly hydrophobic compositions, the poly(sulfonate) and -(ammonium) salts exhibited high solubilities in water.

Characterization of these highly functionalized dendrimers by multinuclear NMR and MALDI-TOF mass spectrometry revealed the high regularity of their structures. All compounds, except the third generation trimethylammonium salts, exhibited the expected molecular ions in their MALDI-TOF mass spectra. The first and second generation trimethylammonium halide-terminated dendrimers, bearing four and eight fixed positive charges, respectively, displayed heretofore unknown ionization behavior under MALDI conditions: each species formed multiple complexes with anions derived from the matrix. The third generation, sulfonate-terminated dendrimer demonstrated micelle-like properties in its ability to solubilize alkylbenzene derivatives into water.

EXPERIMENTAL

General Comments

All reactions, unless otherwise noted, were performed under an argon atmosphere using standard Schlenk techniques. 2-Mercaptoethanol, 2-dimethylaminoethanethiol hydrochloride and the sodium salt of 3-mercapto-1-propanesulfonic acid were purchased from Aldrich Chemical Co. and used as received. The preparation of the chloromethyl-terminated dendrimers **1G$_{Vinyl}$-4CH$_2$Cl** and **2G$_{Vinyl}$-8CH$_2$Cl** was described in Chapter 3. The third generation dendrimer **3G$_{Vinyl}$-16CH$_2$Cl** was also prepared according to the procedures outlined in Chapter 3, but from a sample of **2G$_{Vinyl}$-16Vinyl** that contained approximately 10% α-addition isomers in both the first and second hydrosilylation steps (see Results and Discussion section). Dialyses of sodium sulfonate-terminated dendrimers were carried out in Spectra/Por

DispoDialyzer Cellulose Ester membranes with molecular weight cutoff (MWCO) values of 100 and 500 Daltons, purchased from Spectrum.

Proton NMR spectra were obtained on a Varian XL-300 NMR spectrometer using the residual proton resonances of the deuterated solvents as internal references ($CHCl_3$ at 7.24 ppm, CD_2HOD at 3.31 ppm and HDO at 4.81 ppm downfield from tetramethylsilane). Proton decoupled ^{13}C NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 75.4 MHz. Spectra taken in $CDCl_3$ or CD_3OD solvents used solvent peaks as internal references (at 77.0 ppm and 49.15 ppm, respectively, downfield from tetramethylsilane). Those taken in D_2O solvent used tetramethylsilane (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 using tetramethylsilane (0.0 ppm) as the external standard. Infrared spectra were obtained on a Perkin Elmer 1600 Series FTIR. Absorption spectra were obtained on a Hewlett Packard HP 8453 UV-Visible Spectrophotometer using 1 cm quartz cuvettes.

MALDI-TOF mass spectrometric data were measured by Dr. Zhuchun Wu and Professor Klaus Biemann of the Department of Chemistry, M.I.T., using a Voyager-Elite Biospectrometry Workstation MALDI-TOF mass spectrometer purchased from PerSeptive Biosystems, Inc. and equipped with a nitrogen laser (337 nm). The mass spectrometer was operated at 20 kV accelerating voltage. Ions generated by laser desorption were extracted from the ion source using delayed extraction (DE). Signals from over 100 laser shots were recorded on a dual multichannel plate detector, digitized and averaged by a Tektronix TS520 digitizing oscilloscope. Spectra were recorded either in linear or reflection mode. The instrument was calibrated using standard peptides, such as insulin and angiotensin.

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark; Galbraith Laboratories, Inc., Knoxville, TN, and E+R Microanalytical Laboratory, Inc., Corona, NY.

Synthesis of Amphiphile-Functionalized Dendrimers

General Procedure for the Attachment of Amphiphilic Groups

The chloromethyl-terminated dendrimer (1 molar equiv.) was dissolved with heating in 15 - 30 mL of isopropanol (ethanol was used for **1G$_{Vinyl}$-4CH$_2$Cl**). The appropriate mercapto-substituted amphiphile (0 - 13% molar excess over the number of equiv. of chloromethyl groups; 22 - 26% molar excess for 2-mercaptoethanol) was combined under Ar with NaOH pellets (0.06 - 0.10 g per mmol of mercapto-substituted amphiphile; 0.14 - 0.17 g per mmol of 2-dimethylaminoethanethiol hydrochloride) and 1 - 8 mL of distilled water in a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two glass stoppers. After the amphiphile had dissolved, the dendrimer solution was added, forming a suspension of white solids. This mixture was heated with stirring to 80 - 100 °C. Extra water or alcohol was added as needed to assist in the dissolution of the reactants. After 6 - 17 h, the reaction was cooled to room temperature. Products were isolated as described below in the individual examples.

Preparation of ***1G$_{Vinyl}$-4OH*** *(SWK VII/66)*

Following the general procedure, **1G$_{Vinyl}$-4CH$_2$Cl** (0.746 g, 1.31 mmol) was combined with 0.62 g of NaOH pellets and 0.50 g (6.4 mmol) of 2-mercaptoethanol in *ca.* 25 mL of ethanol and 3 mL of distilled water. This mixture was heated to 80 °C for 6 h. After cooling to room temperature and acidifying to pH = 2 with conc. HCl (aq), all volatiles were removed at reduced

pressure. The residue was extracted with 30 mL of diethyl ether and 30 mL of distilled water. The organic layer was separated, and the aqueous layer was washed with 30 mL of diethyl ether. The combined organic phases were dried over anhydrous $MgSO_4$ and filtered. Diethyl ether was removed at reduced pressure, and the residue was dried for 20.5 h at room temperature and 0.1 torr, giving pure **$1G_{Vinyl}$-4OH** as a slightly yellow, crystalline solid. Yield: 0.943 g (98%), m.p. 39 - 40 °C. Anal. Calcd for $C_{28}H_{68}O_4S_4Si_5$ (737.513 g/mol): C, 45.60; H, 9.29%. Found: C, 45.44; H, 9.21%.

^{1}H NMR ($CDCl_3$): δ 0.063 (s, 24 H, CH_3), 0.43 (s, 16 H, $SiCH_2CH_2Si$), 1.77 (s, 8 H, $SiCH_2S$), 2.47 (br s, 4 H, OH), 2.69 (t, J = 5.9 Hz, 8 H, $SC\underline{H}_2CH_2OH$), 3.72 (t, J = 5.9 Hz, 8 H, $SCH_2C\underline{H}_2OH$).
^{13}C NMR ($CDCl_3$): δ -4.00 (CH_3), , 2.38 ($Si\underline{C}H_2CH_2SiCH_2S$), 6.82 ($SiCH_2\underline{C}H_2SiCH_2S$), 15.82 ($SiCH_2S$), 39.01 ($S\underline{C}H_2CH_2OH$), 59.20 ($SCH_2\underline{C}H_2OH$).
^{29}Si NMR ($CDCl_3$): δ 3.39 (4 Si, $SiCH_2S$), 9.30 (1 Si, $Si(CH_2CH_2)_4$).
IR (NaCl disk): 3356 (br s, ν OH), 2952 (s, ν_{as} $SiCH_3$), 2905 (s, ν_s $SiCH_3$), 2879 (s, ν_s aliphatic CH_2), 1404 (m, δ_{as} CH), 1247 (s, δ_s $SiCH_3$), 1131 (s), 1046 (s), 1009 (m), 845 (vs, ρ $SiCH_3$), 787 (s).

Preparation of $2G_{Vinyl}$-8OH (SWK VII/75)

Following the general procedure, **$2G_{Vinyl}$-8CH_2Cl** (0.995 g, 0.712 mmol) was combined with 0.72 g of NaOH pellets and 0.56 g (7.2 mmol) of 2-mercaptoethanol in *ca.* 15 mL of isopropanol and 3 mL of distilled water. This mixture was heated to 80 °C for 17 h. After cooling to room temperature, the product was purified as in the above procedure for the synthesis of **$1G_{Vinyl}$-4OH**. After an additional washing with 50 mL cold (-20 °C) pentane, the product was dried for 24 h at room temperature and 0.002 torr, giving

pure **2G$_{Vinyl}$-8OH** as a slightly yellow, viscous oil. The ^{1}H NMR spectra of this and other second and third generation dendrimers displayed a small doublet (J = 8 Hz) at approximately 1 ppm which was assigned to the methyl group of α-addition isomers (SiCH(CH$_3$)Si) present (in amounts less than 3.5 mol%) in the outer branches of the chloromethyl-terminated dendrimers. Yield: 1.221 g (99%). Anal. Calcd for $C_{68}H_{164}O_8S_8Si_{13}$ (1731.637 g/mol): C, 47.17; H, 9.55%. Found: C, 47.38; H, 9.23%.

^{1}H NMR ($CDCl_3$): δ -0.099 (s, 12 H, Si(C$\underline{H}_3$)(CH$_2$CH$_2$)$_3$); 0.038 (s, 48 H, Si(C$\underline{H}_3$)$_2$CH$_2$S); 0.33 (br s, 16 H, Si(C$\underline{H}_2$C$\underline{H}_2$)$_4$); 0.40 (br s, 32 H, SiC$\underline{H}_2$C$\underline{H}_2$SiCH$_2$S); 1.75 (s, 16 H, SiCH$_2$S); 2.6 (br, OH), 2.66 (t, J = 5.9 Hz, SC$\underline{H}_2$CH$_2$OH) (overlapped, 24 H); 3.69 (t, J = 5.9 Hz, 16 H, SCH$_2$C$\underline{H}_2$OH).
^{13}C NMR ($CDCl_3$): δ -6.60 (Si($\underline{C}$H$_3$)(CH$_2$CH$_2$)$_3$), -3.91 (Si($\underline{C}$H$_3$)$_2$CH$_2$S), 2.46 (Si($\underline{C}$H$_2$CH$_2$)$_4$), 4.27 (Si$\underline{C}$H$_2$CH$_2$SiCH$_2$S), 4.70 (Si(CH$_2$$\underline{C}H_2$)$_4$), 6.97 (SiCH$_2$$\underline{C}H_2$SiCH$_2$S), 15.78 (SiCH$_2$S), 39.06 (S$\underline{C}H_2CH_2$OH), 59.15 (SCH$_2$$\underline{C}H_2$OH).
^{29}Si NMR ($CDCl_3$): δ 3.36 (8 Si, SiCH$_2$S), 7.64 (Si(CH$_3$)(CH$_2$CH$_2$)$_3$), 8.87 (1 Si, Si(CH$_2$CH$_2$)$_4$).
IR (NaCl disk): 3355 (br m, ν OH), 2952 (s, ν_{as} SiCH$_3$), 2904 (s, ν_s SiCH$_3$), 2879 (s, ν_s aliphatic CH$_2$), 1404 (m, δ_{as} CH), 1248 (s, δ_s SiCH$_3$), 1130 (s), 1048 (s), 1011 (s), 838 (vs, ρ SiCH$_3$).

*Preparation of **1G$_{Vinyl}$-4NMe$_2$** (SWK V/72)*

Following the general procedure, **1G$_{Vinyl}$-4CH$_2$Cl** (0.51 g, 0.88 mmol) was combined with 0.54 g of NaOH pellets and 0.55 g (95% purity, 3.7 mmol) of 2-dimethylaminoethanethiol hydrochloride in *ca.* 25 mL of ethanol and 5 mL of distilled water. This mixture was heated to 80 °C for 9.5 h. After cooling to room temperature, the solvents were removed at reduced pressure.

The residue was extracted with 30 mL of diethyl ether and 10 mL of distilled water. The organic layer was separated and washed with twice with 10 mL portions of distilled water. The combined organic phases were dried over anhydrous $MgSO_4$ and filtered. Diethyl ether was removed at reduced pressure, and the residue was dried for 18.5 h at room temperature and 0.01 torr, giving pure **$1G_{Vinyl}$-4NMe_2** as a slightly yellow, viscous oil. Yield: 0.76 g (100%). Anal. Calcd for $C_{36}H_{88}N_4S_4Si_5$ (845.79 g/mol): C, 51.12; H, 10.49%. Found: C, 51.18; H, 10.97%.

^{1}H NMR ($CDCl_3$): δ 0.047 (s, 24 H, $SiCH_3$), 0.41 (s, 16 H, $SiCH_2CH_2Si$), 1.80 (s, 8 H, $SiCH_2S$), 2.23 (s, 24 H, NCH_3), 2.54 (m, 16 H, $SC\underline{H_2}C\underline{H_2}N$).
^{13}C NMR ($CDCl_3$): δ -3.89 ($SiCH_3$), , 2.51 ($Si\underline{C}H_2CH_2Si$), 7.04 ($SiCH_2\underline{C}H_2Si$), 17.13 ($SiCH_2S$), 34.28 ($S\underline{C}H_2CH_2N$), 45.45 (NCH_3), 58.99 ($SCH_2\underline{C}H_2N$).
^{29}Si NMR ($CDCl_3$): δ 3.21 (4 Si, $SiCH_2S$), 9.21 (1 Si, $Si(CH_2CH_2)_4$).
IR (NaCl disk): 2951 (s, ν_{as} $SiCH_3$), 2905 (s, ν_s $SiCH_3$), 2815 (s, ν_{as} NCH_3), 2766 (s, ν_s NCH_3), 1458 (s, δ_{as} CH_3), 1402 (m, δ_{as} CH), 1297 (m), 1247 (vs, δ_s $SiCH_3$), 1209 (w), 1166 (m, ν NC), 1130 (vs), 1054 (s), 1042 (s), 1013 (m), 852 (vs, ρ $SiCH_3$).

Preparation of $2G_{Vinyl}$-8NMe_2 (SWK VIII/10)

Following the general procedure, **$2G_{Vinyl}$-8CH_2Cl** (0.500 g, 0.358 mmol) was combined with 0.53 g of NaOH pellets and 0.451 g (95% purity, 3.02 mmol) of 2-dimethylaminoethanethiol hydrochloride in *ca.* 30 mL of isopropanol and 8 mL of distilled water. This mixture was heated to 85 °C for 11 h. After cooling to room temperature, the product was purified as in the above procedure for the synthesis of **$1G_{Vinyl}$-4NMe_2**. Analysis of this product by ^{1}H NMR indicated that approximately 10% of the chloromethyl groups remained unreacted. This product was again reacted with 0.094 g of NaOH pellets and

0.122 g (95% purity, 0.817 mmol) of dimethylaminoethanethiol hydrochloride in 1 mL of distilled water and 20 mL of isopropanol under the same reaction conditions as above. The new product was isolated as above and dried for 14 h at 85 °C and 0.005 torr, giving pure **$2G_{Vinyl}$-8NMe_2** as a clear, slightly yellow, viscous oil. Yield: 0.645 g (92%). Anal. Calcd for $C_{84}H_{204}N_8S_8Si_{13}$ (1948.189 g/mol): C, 51.79; H, 10.55%. Found: C, 51.36; H, 10.36%.

^{1}H NMR ($CDCl_3$): δ -0.089 (s, 12 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$), 0.043 (s, 48 H, $Si(C\underline{H}_3)_2CH_2S$), 0.32 (s, 16 H, $Si(C\underline{H}_2C\underline{H}_2)_4$), 0.41 (s, 32 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2S$), 1.79 (s, 16 H, $SiCH_2S$), 2.23 (s, 48 H, NCH_3), 2.54 (m, 32 H, $SC\underline{H}_2C\underline{H}_2N$).
^{13}C NMR ($CDCl_3$): δ -6.60 ($Si(\underline{C}H_3)(CH_2CH_2)_3$), -3.88 ($Si(\underline{C}H_3)_2CH_2S$), 2.50 ($Si(\underline{C}H_2CH_2)_4$), 4.29 ($Si\underline{C}H_2CH_2SiCH_2S$), 4.77 ($Si(CH_2\underline{C}H_2)_4$), 7.09 ($SiCH_2\underline{C}H_2SiCH_2S$), 17.10 ($SiCH_2S$), 34.17 ($S\underline{C}H_2CH_2N$), 45.37 ($NCH_3$), 58.94 ($SCH_2\underline{C}H_2N$).
^{29}Si NMR ($CDCl_3$): δ 3.20 (8 Si, $SiCH_2S$), 7.67 (4 Si, $Si(CH_3)(CH_2CH_2)_3$), 8.96 (1 Si, $Si(CH_2CH_2)_4$).
IR (NaCl disk): 2950 (s, ν_{as} $SiCH_3$), 2903 (s, ν_s $SiCH_3$), 2815 (s, ν_{as} NCH_3), 2766 (s, ν_s NCH_3), 1457 (s, δ_{as} CH_3), 1403 (m, δ_{as} CH), 1297 (w), 1247 (s, δ_s $SiCH_3$), 1130 (s), 1054 (s), 1012 (w), 843 (s, ρ $SiCH_3$).

Preparation of $3G_{Vinyl}$-16NMe_2 (SWK VI/48)

Following the general procedure, **$3G_{Vinyl}$-16CH_2Cl** (0.254 g, 0.0831 mmol) was combined with 0.22 g of NaOH pellets and 0.21 g (95% purity, 1.5 mmol) of 2-dimethylaminoethanethiol hydrochloride in *ca.* 25 mL of isopropanol and 1 mL of distilled water. This mixture was heated to reflux for 8.75 h. After cooling to room temperature, the product was purified as in the above procedure for the synthesis of **$1G_{Vinyl}$-4NMe_2** and dried for 18 h at

70 °C and 0.002 torr, giving pure **$3G_{Vinyl}$-16NMe$_2$** as a clear, slightly yellow, viscous oil. Yield: 0.318 g (92%). Anal. Calcd for $C_{180}H_{436}N_{16}S16_8Si_{29}$ (4152.989 g/mol): C, 52.06; H, 10.58%. Found: C, 52.49; H, 10.54%.

^{1}H NMR ($CDCl_3$): δ -0.098 (s, 36 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$ (two types)), 0.045 (s, 96 H, $Si(C\underline{H}_3)_2CH_2S$), 0.34 (br s, 48 H, $SiC\underline{H}_2C\underline{H}_2Si(CH_3)(CH_2CH_2)_2$ (two types)), 0.41 (br s, 64 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2S$), 1.79 (s, 32 H, $SiCH_2S$), 2.24 (s, 96 H, NCH_3), 2.55 (m, 64 H, $SC\underline{H}_2C\underline{H}_2N$).

^{13}C NMR ($CDCl_3$): δ -6.44 ($Si(\underline{C}H_3)(CH_2CH_2)_3$ (two types)), -3.85 ($Si(\underline{C}H_3)_2CH_2S$), 2.50 (br, $Si(\underline{C}H_2CH_2)_4$), 4.31 ($Si\underline{C}H_2CH_2SiCH_2S$), 4.78 ($Si(CH_2\underline{C}H_2)_4$, $Si(CH_3)\underline{C}H_2\underline{C}H_2Si(CH_3)CH_2CH_2SiCH_2S$), 7.04 ($SiCH_2\underline{C}H_2SiCH_2S$), 17.10 ($SiCH_2S$), 34.20 ($S\underline{C}H_2CH_2N$), 45.37 ($NCH_3$), 58.93 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR ($CDCl_3$): δ 3.18 (16 Si, $SiCH_2S$), 7.67 (12 Si, $Si(CH_3)(CH_2CH_2)_3$ (two types)), 9.26 (1 Si, $Si(CH_2CH_2)_4$).

IR (NaCl disk): 2950 (s, ν_{as} $SiCH_3$), 2903 (s, ν_s $SiCH_3$), 2815 (s, ν_{as} NCH_3), 2766 (s, ν_s NCH_3), 1457 (s, δ_{as} CH_3), 1404 (m, δ_{as} CH), 1297 (w), 1247 (s, δ_s $SiCH_3$), 1130 (s), 1055 (s), 1013 (w), 850 (s, ρ $SiCH_3$).

*Preparation of **$1G_{Vinyl}$-4SO$_3$Na** (SWK V/33)*

Following the general procedure, **$1G_{Vinyl}$-4CH$_2$Cl** (0.50 g, 0.87 mmol) was combined with 0.28 g of NaOH pellets and 0.70 g (90% purity, 3.7 mmol) of sodium 3-mercaptopropanesulfonate in *ca.* 25 mL of ethanol and 8 mL of distilled water. This mixture was heated to 80 °C for 6 h and then warmed to reflux for an additional 10 h. Upon cooling to room temperature, a white solid precipitated which was collected by suction filtration and dried at room temperature and 0.01 torr for 10 h (mass 0.98 g). A solution of 0.203 g of this

solid dissolved in *ca.* 4 mL of deionized water was acidified to pH = 6 - 7 with 1 M HCl (aq) and placed into a dialysis membrane (MWCO = 500) which was immersed in 65 mL of stirred deionized water for 9.5 h. Evaporation of the contents of the dialysis membrane and drying 48 h at room temperature and 0.005 torr left **1G$_{Vinyl}$-4SO$_3$Na** as a white, hygroscopic solid (mass 0.165 g). Yield: 80%. Anal. Calcd for $C_{32}H_{72}O_{12}S_8Na_4Si_5$ (1137.783 g/mol): C, 33.78; H, 6.38%. Found: C, 32.43; H, 6.80%. Anal. Calcd for $C_{32}H_{72}O_{12}S_8Si_5 \cdot 3H_2O$: C, 32.25; H, 6.60%.

^{1}H NMR (D_2O): δ 0.15 (s, 24 H, CH_3), 0.56 (s, 16 H, $SiCH_2CH_2Si$), 1.93 (s, 8 H, $SiCH_2S$), 2.06 (m, 8 H, $SCH_2C\underline{H}_2CH_2SO_3Na$), 2.71 (t, J = 7.7 Hz, 8 H, $.SCH_2CH_2C\underline{H}_2SO_3Na$), 2.99 (m, 8 H, $SC\underline{H}_2CH_2CH_2SO_3Na$).
^{13}C NMR (D_2O): δ -3.78 (CH_3), 2.45 ($Si\underline{C}H_2CH_2Si$), 6.78 ($SiCH_2\underline{C}H_2Si$), 15.98 ($SiCH_2S$), 23.79 ($SCH_2\underline{C}H_2CH_2SO_3Na$), 34.53 ($S\underline{C}H_2CH_2CH_2SO_3Na$), 50.14 ($SCH_2CH_2\underline{C}H_2SO_3Na$).
^{29}Si NMR (D_2O): δ 3.17 (4 Si, $SiCH_2S$), 9.69 (1 Si, $Si(CH_2CH_2)_4$).
IR (KBr pellet): 3437 (s, br, H_2O), 2954 (s, ν_{as} $SiCH_3$), 2905 (s, ν_s $SiCH_3$), 2878 (s, ν_{as} aliphatic CH_2), 1640 (w, br), 1456 (w), 1410 (w, δ_{as} CH), 1245 (s, δ_s $SiCH_3$), 1194 (vs, ν_{as} SO_3), 1129 (s), 1058 (s, ν_s SO_3), 842 (s, ρ $SiCH_3$), 779 (m), 734 (s), 612 (m), 532 (m).

Preparation of 2G$_{Vinyl}$-8SO$_3$Na (SWK VIII/11)

Following the general procedure, **2G$_{Vinyl}$-8CH$_2$Cl** (0.594 g, 0.425 mmol) was combined with 0.22 g of NaOH pellets and 0.630 g (90% purity, 3.54 mmol) of sodium 3-mercaptopropanesulfonate in *ca.* 25 mL of isopropanol and 3 mL of distilled water. This mixture was heated to 95 °C for 15 h. After cooling the solution to room temperature, all volatiles were removed under reduced

pressure, leaving a white powder which was stirred 15 h at 60 °C with 25 mL of isopropanol. The white solid was collected by centrifugation, washed once more with 20 mL of isopropanol and dried briefly *in vacuo*. Deionized water (*ca.* 6 mL) was added, and the suspension was acidified to pH = 6 with 1 M HCl (aq). Solids were removed by centrifugation, and the supernate was placed into a dialysis membrane (MWCO = 100) which was immersed in 80 mL of deionized water. After stirring for 13 h, the solution in which the dialysis membrane was immersed was replaced with 80 mL of deionized water. After stirring for an additional 9.75 h the contents of the dialysis tubing were collected and evaporated at reduced pressure to give **$2G_{Vinyl}$-$8SO_3Na$** as a hygroscopic, white solid which was dried at 70 °C and 0.05 torr for 19 h. Yield: 0.715 g (66%). Anal. Calcd for $C_{76}H_{172}Na_8O_{24}S_{16}Si_{13}$ (2532.177 g/mol): C, 36.05; H, 6.85%. Found: C, 33.72; H, 6.35; Total Halogen (Calcd as Cl), 3.23%. Anal. Calcd for $C_{76}H_{172}Na_8O_{24}S_{16}Si_{13}$ + 2.43 NaCl: C, 34.13; H, 6.49; Cl, 3.23.

^{1}H NMR (D_2O): δ 0.012 (s, 12 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$), 0.13 (s, 48 H, $Si(C\underline{H}_3)_2CH_2S$), 0.49 (s, 16 H, $Si(C\underline{H}_2C\underline{H}_2)_4$), 0.53 (s, 32 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2S$), 1.90 (s, 16 H, $SiCH_2S$), 2.06 (m, 16 H, $SCH_2C\underline{H}_2CH_2SO_3Na$), 2.68 (t, J^1 = 7.7 Hz, 8 H, $SCH_2CH_2C\underline{H}_2SO_3Na$), 2.99 (m, 8 H, $SC\underline{H}_2CH_2CH_2SO_3Na$).

^{13}C NMR (D_2O): δ -5.93 ($Si(\underline{C}H_3)(CH_2CH_2)_3$), -3.73 ($Si(\underline{C}H_3)_2CH_2S$), 2.90 (br, $Si(\underline{C}H_2CH_2)_4$), 4.39 ($Si\underline{C}H_2CH_2SiCH_2S$), 4.71 ($Si(CH_2\underline{C}H_2)_4$), 7.06 ($SiCH_2\underline{C}H_2SiCH_2S$), 16.09 ($SiCH_2S$), 23.85 ($SCH_2\underline{C}H_2CH_2SO_3Na$), 34.59 ($S\underline{C}H_2CH_2CH_2SO_3Na$), 50.09 ($SCH_2CH_2\underline{C}H_2SO_3Na$).

^{29}Si NMR (D_2O): δ 2.84 (8 Si, $SiCH_2S$), 7.29 (4 Si, $Si(CH_3)(CH_2CH_2)_3$), 8.88 (1 Si, $Si(CH_2CH_2)_4$).

IR (KBr pellet): 3456 (s, br, H_2O), 2951 (m, ν_{as} $SiCH_3$), 2904 (m, ν_s $SiCH_3$), 2879 (m, ν_{as} aliphatic CH_2), 1650 (m, br), 1452 (s, br), 1248 (s, δ_s $SiCH_3$), 1191 (vs, ν_{as} SO_3), 1130 (s), 1057 (s, ν_s SO_3), 843 (s, ρ $SiCH_3$).

Preparation of $3G_{Vinyl}$-$16SO_3Na$ *(SWK VI/49)*

Following the general procedure, **$3G_{Vinyl}$-$16CH_2Cl$** (0.252 g, 0.082 mmol) was combined with 0.1 g of NaOH pellets and 0.260 g (90% purity, 1.31 mmol) of sodium 3-mercaptopropanesulfonate in *ca.* 20 mL of isopropanol and 3 mL of distilled water. This mixture was heated to reflux for 4 h. After cooling the solution to room temperature, all volatiles were removed under reduced pressure, leaving a white powder Distilled water (*ca.* 10 mL) was added, and the resulting suspension was filtered. After reducing the volume to approximately 5 mL, the solution was acidified to pH = 6 with 1 M HCl(aq) and placed into a dialysis membrane (MWCO = 500) which was immersed in 65 mL of deionized water. After 8 h, the solution in which the dialysis membrane was immersed was replaced with 65 mL of deionized water. After an additional 12.5 h the contents of the dialysis tubing were evaporated at reduced pressure and dried at 48 °C and 0.03 torr for 19.75 h, yielding **$3G_{Vinyl}$-$16SO_3Na$** as a hygroscopic, white solid. Yield: 0.328 g (75%). Anal. Calcd for $C_{164}H_{372}Na_{16}O_{48}S_{32}Si_{29}$ (5320.965 g/mol): C, 37.02; H, 7.05%. Found: C, 36.44; H, 7.18%. Anal. Calcd for $C_{164}H_{372}Na_{16}O_{48}S_{32}Si_{29}\cdot 6H_2O$: C, 36.28; H, 7.13%.

^{1}H NMR (D_2O): δ 0.047 (br s, $Si(C\underline{H}_3)(CH_2CH_2)_3$ (two types)), 0.17 (br s, $Si(C\underline{H}_3)_2CH_2S$) (overlapped, 132 H); 0.55 (br, 112 H, $SiCH_2CH_2Si$); 1.93 (s, 32 H, $SiCH_2S$), 2.09 (pent, J = 7.3 Hz, 32 H, $SCH_2C\underline{H}_2CH_2SO_3Na$), 2.72 (t, J = 6.5 Hz, 32 H, $SC\underline{H}_2CH_2CH_2SO_3Na$), 3.03 (t, J = 7.6 Hz, 32 H, $SCH_2CH_2C\underline{H}_2SO_3Na$).

^{13}C NMR (D_2O): δ -5.88 ($Si(\underline{C}H_3)(CH_2CH_2)_3$ (two types)), -3.71 ($Si(\underline{C}H_3)_2CH_2S$), 4.38 (br, $Si\underline{C}H_2CH_2SiCH_2S$, $Si(CH_3)\underline{C}H_2CH_2Si(CH_3)CH_2CH_2SiCH_2S$), 5.2 ($SiCH_2\underline{C}H_2Si(CH_3)(CH_2CH_2)_2$ (two types)), 7.00 ($SiCH_2\underline{C}H_2SiCH_2S$), 16.05 ($SiCH_2S$), 23.87 ($SCH_2\underline{C}H_2CH_2SO_3Na$), 34.61 ($S\underline{C}H_2CH_2CH_2SO_3Na$), 50.17 ($SCH_2CH_2\underline{C}H_2SO_3Na$).

^{29}Si NMR (D_2O): δ 3.14 (16 Si, $SiCH_2S$); 7.44 ($SiCH_2CH_2\underline{Si}CH_3)_4$), 7.66 ($\underline{Si}(CH_3)CH_2CH_2SiCH_2S$), 8.23 ($Si(CH_2CH_2)_4$) (overlapped, 13 Si).

IR (KBr pellet): 3456 (s, br, H_2O), 2951 (s, ν_{as} $SiCH_3$), 2904 (s, ν_s $SiCH_3$), 2879 (m, ν_{as} aliphatic CH_2), 1636 (m, br), 1406 (br m, δ_{as} CH), 1248 (s, δ_s $SiCH_3$), 1194 (s, br, ν_{as} SO_3), 1131 (s), 1055 (s, ν_s SO_3), 795 (br s, ρ $SiCH_3$), 610 (m), 530 (m).

Preparation of ***1G$_{Vinyl}$-4NMe$_2$HCl*** *(SWK VI/18A)*

A solution of 0.205 g (0.242 mmol) of **1G$_{Vinyl}$-4NMe$_2$** in 60 mL of diethyl ether was shaken vigorously with *ca.* 50 mL of 1 M HCl (aq) in a separatory funnel. The aqueous layer was separated, and the water was removed under reduced pressure, leaving **1G$_{Vinyl}$-4NMe$_2$HCl** as a white crystalline solid which was dried at room temperature and 0.01 torr for 63.5 h. Yield: 0.238 g (99%). A concentrated aqueous solution yielded long, white needles, m.p. 237-8°C (dec.). $C_{36}H_{96}Cl_4N_4S_4Si_5$ (991.633 g/mol).

^{1}H NMR (D_2O): δ -0.094 (s, 24 H, $SiCH_3$), 0.529 (s, 16 H, $SiCH_2CH_2Si$), 1.967 (s, 8 H, $SiCH_2S$), 2.924 (s, m; 32 H; NCH_3, $SC\underline{H}_2CH_2N$), 3.402 (t, J = 7.3 Hz, 8 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (D_2O): δ -4.00 ($SiCH_3$), 2.33 ($Si\underline{C}H_2CH_2Si$), 6.60 ($SiCH_2\underline{C}H_2Si$), 15.76 ($SiCH_2S$), 29.49 ($S\underline{C}H_2CH_2N$), 42.88 (NCH_3), 56.05 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (D_2O): δ 3.34 (4 Si, $SiCH_2S$), 9.57 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of $2G_{Vinyl}$-$8NMe_2HCl$ *(SWK VI/32)*

The above procedure for the preparation of **$1G_{Vinyl}$-$4NMe_2HCl$** was followed, using 0.222 g (0.159 mmol) of **$2G_{Vinyl}$-$8NMe_2$** and 10 mL of 1 M HCl (aq). The product, a white tacky solid, was dried at room temperature and 0.01 torr for 18 h. Yield: 0.266 g (75%). $C_{84}H_{212}Cl_8N_8S_8Si_{13}$ (2239.876 g/mol).

^{1}H NMR (D_2O): δ 0.02 (br s, 12 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$), 0.16 (br s, 48 H, $Si(C\underline{H}_3)_2CH_2S$), 0.47 (br s, 16 H, $Si(C\underline{H}_2C\underline{H}_2)_4$), 0.52 (br s, 32 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2S$), 2.00 (br s, 16 H, $SiCH_2S$), 2.96 (br; 64 H; $SC\underline{H}_2CH_2N$, NCH_3), 3.42 (br m, 16 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (D_2O): δ -5.85 ($Si(\underline{C}H_3)(CH_2CH_2)_3$); -3.62, -3.58 ($Si(\underline{C}H_3)_2CH_2S$); 2.35 (br, $Si(\underline{C}H_2CH_2)_4$); 4.38 (br, $Si\underline{C}H_2CH_2SiCH_2S$); 4.75 (br, $Si(CH_2\underline{C}H_2)_4$); 6.94 ($SiCH_2\underline{C}H_2SiCH_2S$); 16.03 ($SiCH_2S$), 29.61 ($S\underline{C}H_2CH_2N$); 43.00 ($NCH_3$); 56.22 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (D_2O): δ 3.06 (8 Si, $SiCH_2S$), 7.31 (4 Si, $Si(CH_3)(CH_2CH_2)_3$), 8.66 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of $3G_{Vinyl}$-$16NMe_2HCl$ *(SWK VI/61)*

The above procedure for the preparation of **$1G_{Vinyl}$-$4NMe_2HCl$** was followed, using 0.144 g (0.035 mmol) of **$3G_{Vinyl}$-$16NMe_2$** and 20 mL of 1 M HCl (aq). The product, a white tacky solid, was dried at 50°C and 0.005 torr for 18 h. Yield: 0.162 g (99%). $C_{180}H_{452}Cl_{16}N_{16}S_{16}Si_{29}$ (4736.363 g/mol).

^{1}H NMR (D_2O): δ 0.016 (br, 36 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$ (two types)); 0.16 (br s, 96 H, $Si(C\underline{H}_3)_2CH_2S$); 0.45 (br, $SiC\underline{H}_2C\underline{H}_2Si(CH_3)(CH_2CH_2)_2$ (two types)), 0.53 (br, $SiC\underline{H}_2C\underline{H}_2SiCH_2S$) (overlapped, 112 H); 2.02 (br s, 32 H, $SiCH_2S$); 2.98 (br; 128 H; $SC\underline{H}_2CH_2N$, NCH_3); 3.44 (br m, 32 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (D_2O): δ -5.96 ($Si(\underline{C}H_3)(CH_2CH_2)_3$ (two types)), -3.69 ($Si(\underline{C}H_3)_2CH_2S$), 4.27 ($Si\underline{C}H_2CH_2SiCH_2S$), 5.0 ($Si(CH_2\underline{C}H_2)_4$, $Si(CH_3)\underline{C}H_2\underline{C}H_2Si(CH_3)CH_2CH_2SiCH_2S$), 6.82 ($SiCH_2\underline{C}H_2SiCH_2S$), 15.91 ($SiCH_2S$), 29.50 ($S\underline{C}H_2CH_2N$), 42.92 ($NCH_3$), 56.12 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (D_2O): δ 3.34 (16 Si, $SiCH_2S$); 7.5 ($SiCH_2CH_2\underline{Si}CH_3)_4$), 7.68 ($\underline{Si}(CH_3)CH_2CH_2SiCH_2S$) (overlapped, 12 Si); 9.26 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of ***1G$_{Vinyl}$-4NMe$_3$I*** *(SWK VI/18B)*

In an Ar-filled 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar and two glass stoppers were combined 0.223 g (0.264 mmol) of **1G$_{Vinyl}$-4NMe$_2$**, *ca.* 25 mL of absolute ethanol and 0.10 mL (0.23 g, 1.6 mmol) of methyl iodide. The reaction mixture was heated to reflux in an oil bath for 3.5 h. After cooling to room temperature, *ca.* 20 mL of anhydrous diethyl ether was added to precipitate the quaternary ammonium salt. The resulting fine white precipitate was collected by suction filtration, washed twice with 5 mL portions of ether and dried 21 h at room temperature and 0.005 torr. Yield 0.372 g (99%). Anal. Calcd for $C_{40}H_{100}I_4N_4S_4Si_5$ (1413.546 g/mol): C, 33.99; H, 7.13%. Found: C, 33.51; H, 7.20%.

^{1}H NMR (CD_3OD): δ 0.14 (s, 24 H, $SiCH_3$), 0.57 (s, 16 H, $SiCH_2CH_2Si$), 2.13 (s + sh, 8 H, $SiCH_2S$), 3.03 (m, 8 H, $SC\underline{H}_2CH_2N$), 3.28 (s + 2 sh, 36 H, NCH_3), 3.76 (m, 8 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (CD_3OD): δ -3.54 ($SiCH_3$), 3.85 ($Si\underline{C}H_2CH_2Si$), 8.30 ($SiCH_2\underline{C}H_2Si$), 17.97 ($SiCH_2S$), 29.47 ($S\underline{C}H_2CH_2N$), 54.11 (t + sh, $J_{N\text{-}C}$ = 4.2 Hz, NCH_3), 66.90 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (CD_3OD): δ 4.10 (4 Si, $SiCH_2S$), 9.74 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of $2G_{Vinyl}$-$8NMe_3I$ *(SWK VIII/15A)*

The above procedure for the preparation of **$1G_{Vinyl}$-$4NMe_3I$** was followed, using 0.622 g (0.319 mmol) of **$2G_{Vinyl}$-$8NMe_2$** and 0.20 mL (0.46 g, 3.2 mmol) of MeI. The product, a white powder, was dried at room temperature and 0.003 torr for 20 h. Yield: 0.945 g (96%). Anal. Calcd for $C_{92}H_{228}I_8N_8S_8Si_{13}$ (3083.703 g/mol): C, 35.83; H, 7.45%. Found: C, 35.93; H, 7.55%.

^{1}H NMR (CD_3OD): δ -0.027 (s, 12 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$), 0.10 (s, 48 H, $Si(C\underline{H}_3)_2CH_2S$), 0.43 (br s, 16 H, $Si(C\underline{H}_2C\underline{H}_2)_4$), 0.52 (br s, 32 H, $SiC\underline{H}_2C\underline{H}_2SiCH_2S$), 2.07 (s + sh, 16 H, $SiCH_2S$), 2.97 (m, 16 H, $SC\underline{H}_2CH_2N$), 3.22 (s, 72 H, NCH_3), 3.69 (m, 16 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (CD_3OD): δ -5.93 ($Si(\underline{C}H_3)(CH_2CH_2)_3$), -3.33 ($Si(\underline{C}H_3)_2CH_2S$), 3.61 ($Si(\underline{C}H_2CH_2)_4$), 5.50 ($Si\underline{C}H_2CH_2SiCH_2S$), 5.82 ($Si(CH_2\underline{C}H_2)_4$), 8.26 ($SiCH_2\underline{C}H_2SiCH_2S$), 17.74 ($SiCH_2S$), 29.40 ($S\underline{C}H_2CH_2N$), 54.05 (t, $J_{N\text{-}C}$ = 3.5 Hz, NCH_3), 66.72 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (CD_3OD): δ 4.10 (8 Si, $SiCH_2S$), 8.14 (4 Si, $Si(CH_3)(CH_2CH_2)_3$), 9.52 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of $3G_{Vinyl}$-$16NMe_3I$ *(SWK VI/68)*

The above procedure for the preparation of **$1G_{Vinyl}$-$4NMe_3I$** was followed, using 0.226 g (0.054 mmol) of **$3G_{Vinyl}$-$16NMe_2$** and 0.10 mL (0.23 g, 1.6 mmol) of MeI. The product, a white powder, was dried at room temperature and 0.02 torr for 14.5 h. Yield: 0.309 g (89%). Anal. Calcd for $C_{196}H_{484}I_{16}N_{16}S_{16}Si_{29}$ (6424.018 g/mol): C, 36.65; H, 7.59%. Found: C, 36.62; H, 7.63%.

^{1}H NMR (CD_3OD): δ 0.053 (br, 36 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$ (two types)), 0.19 (s, 96 H, $Si(C\underline{H}_3)_2CH_2S$), 0.50 (br s, 48 H, $SiC\underline{H}_2C\underline{H}_2Si(CH_3)(CH_2CH_2)_2$) (two types)), 0.59 (br s, 16 H, $SiC\underline{H}_2C\underline{H}_2Si(CH_3)_2CH_2S$)), 2.19 (s, 32 H, $SiCH_2S$), 3.08 (m, 32 H, $SC\underline{H}_2CH_2N$), 3.37 (br s, 144 H, NCH_3), 3.84 (m, 32 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (CD_3OD): δ -5.33 ($Si(\underline{C}H_3)(CH_2CH_2)_3$ (two types)), -2.91 ($Si(\underline{C}H_3)_2CH_2S$), 3.7 (br, $Si(\underline{C}H_2CH_2)_4$), 5.72 ($Si\underline{C}H_2CH_2SiCH_2S$), 6.06 (br, $Si(CH_2\underline{C}H_2)_4$, $Si(CH_3)\underline{C}H_2\underline{C}H_2Si(CH_3)CH_2CH_2SiCH_2S$), 8.44 ($SiCH_2\underline{C}H_2SiCH_2S$), 18.02 ($SiCH_2S$), 29.67 ($S\underline{C}H_2CH_2N$), 54.34 (t, $J_{N\text{-}C}$ = 4.6 Hz, NCH_3), 66.90 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (CD_3OD): δ 4.04 (16 Si, $SiCH_2S$); 8.00 ($SiCH_2CH_2\underline{Si}CH_3)_4$), 8.18 ($\underline{Si}(CH_3)CH_2CH_2SiCH_2S$) (overlapped, 12 Si); 8.77 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of ***1G$_{Vinyl}$-4NMe$_3$Cl*** *(SWK VI/64)*

A suspension of 0.134 g of **1G$_{Vinyl}$-4NMe$_3$I** (0.095 mmol) and 0.193 g (1.35 mmol) of AgCl in *ca.* 15 mL of deionized water was heated to 65°C for 4 h in a 25 mL round-bottomed flask equipped with a magnetic stir bar. After cooling to room temperature, solids were removed by filtration followed by centrifugation. Water was removed at reduced pressure, leaving a brown solid (0.107 g). Addition of *ca.* 6 mL of deionized water to this solid formed a suspension which was centrifuged once more. The centrifugate was decanted from the solids, and water was removed at reduced pressure. Drying for 18 h at 55°C and 0.01 torr left **1G$_{Vinyl}$-4NMe$_3$Cl** as a hygroscopic, colorless solid. Yield 0.097 g (97%). Anal. Calcd for $C_{40}H_{100}Cl_4N_4S_4Si_5$ (1047.740 g/mol): C, 45.85; H, 9.62; Cl, 13.54%. Found: C, 43.97; H, 9.87; Total Halogen (Calcd as Cl), 13.28%. Anal. Calcd for $C_{40}H_{100}Cl_4N_4S_4Si_5 \cdot 2H_2O$: C, 44.33; H, 9.67; Cl, 13.08%.

^{1}H NMR (D_2O): δ 0.10 (s, 24 H, $SiCH_3$), 0.534 (s, 16 H, $SiCH_2CH_2Si$), 2.008 (s, 8 H, $SiCH_2S$), 2.982 (m, 8 H, $SC\underline{H}_2CH_2N$), 3.170 (s + sh, 36 H, NCH_3), 3.582 (m, 8 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (D_2O): δ -4.01 ($SiCH_3$), 2.35 ($Si\underline{C}H_2CH_2Si$), 6.57 ($SiCH_2\underline{C}H_2Si$), 16.12 ($SiCH_2S$), 27.87 ($S\underline{C}H_2CH_2N$), 53.08 (t, $J_{N\text{-}C}$ = 3.3 Hz, NCH_3), 65.15 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (D_2O): δ 3.27 (4 Si, $SiCH_2S$), 9.56 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of $2G_{Vinyl}$*-8NMe*$_3$*Cl (SWK VIII/15B)*

The above procedure for the preparation of **$1G_{Vinyl}$-4NMe_3Cl** was followed, using 0.945 g (0.307 mmol) of **$2G_{Vinyl}$-8NMe_3I** and 1.44 g (10.0 mmol) of AgCl. The product, a slightly yellow solid, was dried at 60 °C and 0.003 torr for 24 h. Yield: 0.704 g (98%). Anal. Calcd for $C_{92}H_{228}Cl_8N_8S_8Si_{13}$ (2352.091 g/mol): Cl, 12.06%. Found: Total Halogen (Calcd as Cl), 11.55%.

^{1}H NMR (D_2O): δ 0.031 (br s, 12 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$); 0.18 (s, 48 H, $Si(C\underline{H}_3)_2CH_2S$); 0.48 (br s, $Si(C\underline{H}_2C\underline{H}_2)_4$), 0.54 (br s, $SiC\underline{H}_2C\underline{H}_2SiCH_2S$) (overlapped, 48 H); 2.07 (s, 16 H, $SiCH_2S$); 3.01 (m, 4 H, $SC\underline{H}_2CH_2N$); 3.24 (s + sh, 72 H, NCH_3); 3.64 (m, 16 H, $SCH_2C\underline{H}_2N$).

^{13}C NMR (D_2O): δ -6.34 ($Si(\underline{C}H_3)(CH_2CH_2)_3$); -4.21, -4.11 ($Si(\underline{C}H_3)_2CH_2S$); 2.34 (br, $Si(\underline{C}H_2CH_2)_4$); 3.90 ($Si\underline{C}H_2CH_2SiCH_2S$); 4.30 (br, $Si(CH_2\underline{C}H_2)_4$); 6.39 ($SiCH_2\underline{C}H_2SiCH_2S$); 15.83 ($SiCH_2S$); 27.58 ($S\underline{C}H_2CH_2N$); 52.76 ($NCH_3$); 64.79 ($SCH_2\underline{C}H_2N$).

^{29}Si NMR (D_2O): δ 3.32 (8 Si, $SiCH_2S$), 7.57 (4 Si, $Si(CH_3)(CH_2CH_2)_3$), 8.75 (1 Si, $Si(CH_2CH_2)_4$).

Preparation of $3G_{Vinyl}$*-16NMe*$_3$*Cl (SWK VI/71B)*

The above procedure for the preparation of **$1G_{Vinyl}$-4NMe$_3$Cl** was followed, using 0.157 g (0.0244 mmol) of **$3G_{Vinyl}$-16NMe$_3$I** and 0.206 g (1.43 mmol) of AgCl. The product, a colorless solid, was dried at 60 °C and 0.04 torr for 19.75 h. Yield: 0.115 g (95%). Anal. Calcd for $C_{196}H_{484}Cl_{16}N_{16}S_{16}Si_{29}$ (4960.794 g/mol): Cl, 11.43%. Found: Total Halogen (Calcd as Cl), 10.98%.

^{1}H NMR (D_2O): δ 0.059 (br, 36 H, $Si(C\underline{H}_3)(CH_2CH_2)_3$ (two types)); 0.20 (s, 96 H, $Si(C\underline{H}_3)_2CH_2S$); 0.48 (br s, $SiC\underline{H}_2C\underline{H}_2Si(CH_3)(CH_2CH_2)_2$) (two types)), 0.57 (br s, $SiC\underline{H}_2C\underline{H}_2Si(CH_3)_2CH_2S$)) (overlapped, 112 H); 2.10 (br s, 32 H, $SiCH_2S$), 3.05 (br m, 32 H, $SC\underline{H}_2CH_2N$), 3.27 (br s, 36 H, NCH_3), 3.67 (br m, 32 H, $SCH_2C\underline{H}_2N$).
^{13}C NMR (D_2O): δ -6.00 ($Si(\underline{C}H_3)(CH_2CH_2)_3$ (two types)), -3.72 ($Si(\underline{C}H_3)_2CH_2S$), 2.5 (br, $Si(\underline{C}H_2CH_2)_4$), 4.28 ($Si\underline{C}H_2CH_2SiCH_2S$), 5.00 (br, $Si(CH_2\underline{C}H_2Si)_4$, $Si(CH_3)\underline{C}H_2\underline{C}H_2Si(CH_3)(CH_2CH_2)_2$), 6.77 ($SiCH_2\underline{C}H_2SiCH_2S$), 16.23 ($SiCH_2S$), 28.01 ($S\underline{C}H_2CH_2N$), 53.15 ($NCH_3$), 65.17 ($SCH_2\underline{C}H_2N$).
^{29}Si NMR (D_2O): δ 3.31 (16 Si, $SiCH_2S$); 7.36 ($Si(CH_2CH_2\underline{Si}CH_3)_4$), 7.62 ($\underline{Si}(CH_3)CH_2CH_2SiCH_2S$) (overlapped, 12 Si); 8.78 (1 Si, $Si(CH_2CH_2)_4$).

MALDI-TOF Measurements

Sample Preparation

Solutions of the compounds under study were prepared at concentrations of 50 pmol/μL to 10 nmol/μL in alcohols or water (see Table 2). For all compounds except **$1G_{Vinyl}$-4SO$_3$Na**, **$2G_{Vinyl}$-8SO$_3$Na** and **$3G_{Vinyl}$-16SO$_3$Na** a 2 μL aliquot of the dendrimer solution was mixed with an equal amount of a saturated solution of the appropriate matrix elements (see Table 2), and this mixture was loaded onto the MALDI sample plate. Aliquots (30 μL) of solutions of **$1G_{Vinyl}$-4SO$_3$Na**, **$2G_{Vinyl}$-8SO$_3$Na** and **$3G_{Vinyl}$-16SO$_3$Na**

were treated with an equal volume of cation exchange resin (AG50W-X8, purchased from Bio-Rad Laboratories) which had been converted to the ammonium form using a published procedure.[56] After filtering, the resulting solutions were mixed with 20 μL of matrix solution (10 mg/mL) and recombined with an equal volume of the cation exchange resin in its ammonium form. After thoroughly mixing and filtering, 0.5 - 1.0 μL samples of the filtrates were loaded onto the MALDI sample plate.

Solubilization Studies

Solubilization of Alkyl-Substituted Benzene Derivatives by $3G_{Vinyl}$-$16SO_3Na$ *(SWK VI/72)*

Solutions of **$3G_{Vinyl}$-$16SO_3Na$** in D_2O were prepared in 5.00 mL volumetric flasks with concentrations of 9.70×10^{-3}, 3.88×10^{-3} and 1.55×10^{-3} M. Nine mixtures were made in NMR tubes of the three solutions and the three alkyl-substituted benzene derivatives C_6H_5R (R = Me, Et, *n*-Pr); each mixture contained 1 mL of one of the three dendrimer solutions and 0.2 g of one of the three organic compounds. All samples were tightly sealed and sonicated at 50 °C for 16 h. After removing from the sonicator bath, samples were equilibrated 2 d in an oil bath whose temperature was maintained at 24 ± 1 °C. Samples were removed from the oil bath, cleaned and quickly transferred to the probe of an NMR spectrometer. Concentrations of solubilized alkylbenzenes were determined from the averages of the ratios of the integrated areas of the alkylbenzene alkyl resonances to the dendrimer amphiphilic group resonances. The results are plotted in Figure 14.

REFERENCES

1. Jones, M. N.; Chapman, D. *Micelles, Monolayers, and Biomembranes;* John Wiley & Sons: New York, 1995, pp 1-23.
2. Dunaway, C. S.; Christian, S. D.; Scamehorn, J. F. "Overview and History of the Study of Solubilization," In *Solubilization in Surfactant Aggregates;* Christian, S. D. and Scamehorn, J. F., Eds.; Marcel Dekker: New York, 1995; Vol. 55, pp 3-34.
3. Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems;* Academic Press: New York, 1975.
4. Attwood, D.; Florence, A. T. *Surfactant Systems: Their Chemistry, Pharmacy and Biology;* Chapman and Hall: London, 1983, pp 72-123.
5. Elworthy, P. H.; Florence, A. T.; Macfarlane, C. B. *Solubilization by Surface-Active Agents and Its Applications in Chemistry and the Biological Sciences;* Chapman & Hall: London, 1968.
6. Newkome, G. R.; Yao, Z.-q.; Baker, G. R.; Gupta, V. K. "Cascade Molecules: A New Approach to Micelles. A [27]-Arborol," *J. Org. Chem.* **1985**, *50*, 2003-4.
7. Newkome, G. R.; Yao, Z.-q.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. "Cascade Molecules: Synthesis and Characterization of a Benzene[9]^3-Arborol," *J. Am. Chem. Soc.* **1986**, *108*, 849-50.
8. Newkome, G. R.; Young, J. K.; Baker, G. R.; Potter, R. L.; Audoly, L.; Cooper, D.; Weis, C. D.; Morris, K.; Johnson Jr., C. S. "Cascade Polymers. pH Dependence of Hydrodynamic Radii of Acid Terminated Dendrimers," *Macromolecules* **1993**, *26*, 2394-6.
9. Young, J. K.; Baker, G. R.; Newkome, G. R.; Morris, K. F.; Johnson Jr., C. S. "'Smart' Cascade Polymers. Modular Syntheses of Four-Directional Dendritic Macromolecules with Acidic, Neutral, or Basic Terminal

Groups and the Effect of pH Changes on their Hydrodynamic Radii," *Macromolecules* **1994**, *27*, 3464-71.

10. Kuzdzal, S. A.; Monnig, C. A.; Newkome, G. R.; Moorefield, C. N. "Dendrimer Electrokinetic Capillary Chromatography: Unimolecular Micellar Behavior of Carboxylic Acid Terminated Cascade Macromolecules," *J. Chem. Soc. Chem. Comm.* **1994**, 2139-40.
11. Shah, G.; Dubin, P. L.; Kaplan, J. I.; Newkome, G. R.; Moorefield, C. N.; Baker, G. R. "Size-Exclusion Chromatography of Carboxyl-Terminated Dendrimers as a Model for Permeation of Charged Particles into Like-Charged Cavities," *J. Colloid Interface Sci.* **1996**, *183*, 397-407.
12. Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. "Alkane Cascade Polymers Possessing Micellar Topology: Micellanoic Acid Derivatives," *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1176-8.
13. Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Saunders, M. J.; Grossman, S. H. "Unimolecular Micelles," *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1178-80.
14. Newkome, G. R.; Moorefield, C. N.; Keith, J. M.; Baker, G. R.; Escamilla, G. H. "Chemistry within a Unimolecular Micelle Precursor: Boron Superclusters by Site- and Depth-Specific Transformations of Dendrimers," *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 666-8.
15. Tomalia, D. A.; Durst, H. D. "Genealogically Directed Synthesis: Starburst™/Cascade Dendrimers and Hyperbranched Structures," In *Topics in Current Chemistry;* Weber, E., Ed.; Springer-Verlag: Berlin, 1993; Vol. 165, pp 193-313.

16. Tomalia, D. A.; Berry, V.; Hall, M.; Hedstrand, D. M. "Starburst Dendrimers. 4. Covalently Fixed Unimolecular Assemblages Reminiscent of Spheroidal Micelles," *Macromolecules* **1987**, *20*, 1164-7.

17. Ottaviani, M. F.; Montalti, F.; Turro, N. J.; Tomalia, D. A. "Characterization of Starburst Dendrimers by the EPR Technique. Copper (II) Ions Binding Full Generation Dendrimers," *J. Phys. Chem. B* **1997**, *101*, 158-66.

18. Ottaviani, M. F.; Montalti, F.; Romanelli, M.; Turro, N. J.; Tomalia, D. A. "Characterization of Starburst Dendrimers by EPR. 4. Mn(II) as a Probe of Interphase Properties," *J. Phys. Chem.* **1996**, *100*, 11033-42.

19. Ottaviani, M. F.; Cossu, E.; Turro, N. J.; Tomalia, D. A. "Characterization of Starburst Dendrimers by Electron Paramagnetic Resonance. 2. Positively Charged Nitroxide Radicals of Variable Chain Length Used as Spin Probes," *J. Am. Chem. Soc.* **1995**, *117*, 4387-98.

20. Caminati, G.; Turro, N. J.; Tomalia, D. A. "Photophysical Investigation of Starburst Dendrimers and Their Interactions with Anionic and Cationic Surfactants," *J. Am. Chem. Soc.* **1990**, *112*, 8515-22.

21. Ottaviani, M. F.; Turro, C.; Turro, N. J.; Bossmann, S. H.; Tomalia, D. A. "Nitroxide-Labelled Ru(II) Polypyridyl Complexes as EPR Probes of Organized Systems. 3. Characterization of Starburst Dendrimers and Comparison to Photophysical Measurements," *J. Phys. Chem.* **1996**, *100*, 13667-74.

22. Turro, C.; Niu, S.; Bossmann, S. H.; Tomalia, D. A.; Turro, N. J. "Binding of $^*Ru(phen)_3^{2+}$ to Starburst Dendrimers and Its Quenching by $Co(phen)_3^{3+}$: Generation Dependence of the Quenching Rate Constant," *J. Phys. Chem.* **1995**, *99*, 5512-7.

23. Moreno-Bondi, M. C.; Orellana, G.; Turro, N. J.; Tomalia, D. A. "Photoinduced Electron-Transfer Reactions To Probe the Structure of Starburst Dendrimers," *Macromolecules* **1990**, *23*, 910-2.

24. Turro, N. J.; Barton, J. K.; Tomalia, D. A. "Molecular Recognition and Chemistry in Restricted Reaction Spaces. Photophysics and Photoinduced Electron Transfer on the Surface of Micelles, Dendrimers and DNA," *Acc. Chem. Res.* **1991**, *24*, 332-40.

25. Gopidas, K. R.; Leheny, A. R.; Caminati, G.; Turro, N. J.; Tomalia, D. A. "Photophysical Investigation of Similarities between Starburst Dendrimers and Anionic Micelles," *J. Am. Chem. Soc.* **1991**, *113*, 7335-42.

26. Hawker, C. J.; Fréchet, J. M. J. "Monodispersed Dendritic Polyesters with Removable Chain Ends: A Versatile Approach to Globular Macromolecules with Chemically Reversible Polarities," *J. Chem. Soc. Perkin Trans. 1* **1992**, 2459-69.

27. Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. "Unimolecular Micelles and Globular Amphiphiles: Dendritic Macromolecules as Novel Recyclable Solubilization Agents," *J. Chem. Soc. Perkin Trans. 1* **1993**, 1287-97.

28. Pollak, K. W.; Fréchet, J. M. J. "Nonionic Unimolecular Micelles: Poly(ethylene oxide)-Coated Dendrimers," *Polym. Prepr.* **1996**, *75*, 273-4.

29. Kim, Y. H.; Webster, O. W. "Water-Soluble Hyperbranched Polyphenylene: 'A Unimolecular Micelle'?," *J. Am. Chem. Soc.* **1990**, *112*, 4592-3.

30. Chapman, T. M.; Hillyer, G. L.; Mahan, E. J.; Shaffer, K. A. "Hydraamphiphiles: Novel Linear Dendritic Block Copolymer Surfactants," *J. Am. Chem. Soc.* **1994**, *116*, 11195-6.

31. van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; Elissen-Román, C.; van Genderen, M. H. P.; Meijer, E. W. "Polystyrene-poly(propyleneimine) Dendrimers: Synthesis, Characterization and Association Behavior of a New Class of Amphiphiles," *Chem.—Eur. J.* **1996,** *2,* 1616-26.

32. van Hest, J. C. M.; Baars, M. W. P. L.; Elissen-Román, C.; van Genderen, M. H. P.; Meijer, E. W. "Acid-Functionalized Amphiphiles Derived from Polystyrene-Poly(propyleneimine) Dendrimers, with a pH-Dependent Aggregation," *Macromolecules* **1995,** *28,* 6689-91.

33. Lee, J.-J.; Ford, W. T.; Moore, J. A.; Li, Y. "Reactivity of Organic Anions Promoted by a Quaternary Ammonium Ion Dendrimer," *Macromolecules* **1994,** *27,* 4632-4.

34. Sadamoto, R.; Tomioka, N.; Aida, T. "Photoinduced Electron Transfer Reactions through Dendrimer Architecture," *J. Am. Chem. Soc.* **1996,** *118,* 3978-9.

35. Dandliker, P. J.; Diederich, F.; Gisselbrecht, J.-P.; Louati, A.; Gross, M. "Water-Soluble Dendritic Iron Porphyrins: Synthetic Models of Globular Heme Proteins," *Angew. Chem. Int. Ed. Engl.* **1995,** *34,* 2725-8.

36. van der Made, A.; van Leeuwen, P. W. N. M. "Silane Dendrimers," *J. Chem. Soc. Chem. Comm.* **1992,** 1400-1.

37. van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brandes, R. A. C. "Dendrimeric Silanes," *Adv. Mater.* **1993,** *5,* 466-8.

38. Zhou, L.-L.; Roovers, J. "Synthesis of Novel Carbosilane Dendritic Macromolecules," *Macromolecules* **1993,** *26,* 963-8.

39. Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. "Synthesis of an Organosilicon Dendrimer Containing 324 Si-H Bonds," *Organometallics* **1994,** *13,* 2682.

40. Lorenz, K.; Mülhaupt, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. J. "Carbosilane-Based Dendritic Polyols," *Macromolecules* **1995**, *28*, 6657-61.

41. Perklev, T. "4-Trimethylsilyl-buten-(1)," *Svensk Kem. Tidskr.* **1953**, *65*, 216-9.

42. Brasen, W. R.; Hauser, C. R. "2-Methylbenzyldimethylamine," In *Organic Syntheses, Coll. Vol. 4;* Rabjohn, N., Ed.; John Wiley and Sons: New York, 1963, pp 585-8.

43. Ford-Moore, A. H. "Benzoylcholine Iodide and Chloride," In *Organic Syntheses, Coll. Vol. 4;* Rabjohn, N., Ed.; John Wiley and Sons: New York, 1963, pp 84-8.

44. Bovey, F. A. *High Resolution NMR of Macromolecules;* Academic Press: New York, 1972, p 462.

45. Dandliker, P. J.; Diederich, F.; Gross, M.; Knobler, C. B.; Louati, A.; Sanford, E. M. "Dendritic Porphyrins: Modulating Redox Potentials of Electroactive Chromophores with Pendant Multifunctionality," *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1739-42.

46. Kawaguchi, T.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. "Double Exponential Dendrimer Growth," *J. Am. Chem. Soc.* **1995**, *117*, 2159-65.

47. Leon, J. W.; Fréchet, J. M. J. "Analysis of Aromatic Polyether Dendrimers and Dendrimer-Linear Block Copolymers by Matrix-Assisted Laser Desorption Ionization Mass Spectrometry," *Polym. Bull.* **1995**, *35*, 449-55.

48. Leon, J. W.; Kawa, M.; Fréchet, J. M. J. "Isophthalate Ester-Terminated Dendrimers: Versatile Nanoscopic Building Blocks with Readily Modifiable Surface Functionalities," *J. Am. Chem. Soc.* **1996**, *118*, 8847-59.

49. Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. "Routes to Dendritic Networks: Bis-Dendrimers by Coupling of Cascade Macromolecules through Metal Centers," *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2023-6.

50. Sahota, H. S.; Lloyd, P. M.; Yeates, S. G.; Derrick, P. J.; Taylor, P. C.; Haddleton, D. M. "Characterisation of Aromatic Polyester Dendrimers by Matrix-assisted Laser Desorption Ionisation Mass Spectrometry," *J. Chem. Soc. Chem. Comm.* **1994**, 2445-6.

51. Walker, K. L.; Kahr, M. S.; Wilkins, C. L.; Xu, Z.; Moore, J. S. "Analysis of Hydrocarbon Dendrimers by Laser Desorption Time-of-Flight and Fourier Transform Mass Spectrometry," *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 731-9.

52. Broze, G. "Solubilization and Detergency," In *Solubilization in Surfactant Aggregates*; Christian, S. D. and Scamehorn, J. F., Eds.; Marcel Dekker: New York, 1995; Vol. 55, pp 493-516.

53. Ward, T. J.; Ward, K. D. "Solubilization in Micellar Separations," In *Solubilization in Surfactant Aggregates*; Christian, S. D. and Scamehorn, J. F., Eds.; Marcel Dekker: New York, 1995; Vol. 55, pp 517-40.

54. Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon: New York, 1963; Vol. I, p 533.

55. Almgren, M.; Grieser, F.; Thomas, J. K. "Dynamic and Static Aspects of Solubilization of Neutral Arenes in Ionic Micellar Solutions," *J. Am. Chem. Soc.* **1979**, *101*, 279-91.

56. Wang, B. H.; Biemann, K. "Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass-Spectrometry of Chemically-Modified Oligonucleotides," *Anal. Chem.* **1994**, *66*, 1918-24.

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BIOGRAPHICAL SKETCH

The author proudly hails from the great, wide-open expanses of South Dakota. He was born in Deadwood, S.D. on April 27, 1970 and was raised in Spearfish, S.D. He attended the South Dakota School of Mines and Technology in Rapid City, S.D. where he studied chemistry and physics. While there, he performed research in physical chemistry under Prof. Cathleen Webb. He spent the summer of 1991 as an N.S.F. R.E.U. Fellow at the Rensselaer Polytechnic Institute in Troy, NY, where he performed research in polymer chemistry with Prof. Gary Wnek. After receiving his B.S. in Chemistry from S.D.S.M.&T. in 1992, he moved to M.I.T. where he joined the Seyferth group in January 1993. Upon graduating from M.I.T., he will be joining the research group of Prof. Robert Bergman at the University of California, Berkeley as a postdoctoral research associate.