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POLYSILANES WITH VARIOUS ARCHITECTURES

by

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POLYSILANES WITH VARIOUS ARCHITECTURES

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Abstract: Copolymers and homopolymers containing silicon atoms connected to three and four other silicon atoms have been prepared and characterized. We report the first evidence of dendritic polymers with silicon backbones. Copolymers made from $RSiCl_3$ and $R^1R^2SiCl_2$ resemble hybrid materials of polysilyne and polysilanes. Polymers, which contain tetrasilyl-substituted Si atoms, $[(SiMe_2)_4Si]_n$ and $(Si)_m(Me_2Si)_n$, have also been synthesized. These molecules appear to be the first hyperbranched polymers, which have applications based on their electronic properties. The properties of these molecules fit into the hierarchy of 1-D to 3-D topologies known for Si materials.

INTRODUCTION

The discovery of hyperbranched and dendritic polymers is one of the most important recent developments in polymer science (Ref. 1). Hyperbranched polymers are soluble up to high molecular weights and have potential for new inclusion and cluster chemistry because of the large amount of empty space in such compounds. Until now there has been very little attention paid to the applications of dendritic structures to the field of conducting and semiconducting polymers. In this paper, we present the first study of the relationship of dendritic structure to electrical properties of polymers. We will focus on the hyperbranched structure in polysilanes.

POLYSILANES

Polysilanes are interesting materials that show electronic delocalization along the silicon chain (Refs. 2, 3, 4). Chains of silicon atoms make intrinsic semiconducting polymers and even conducting materials when doped. Applications for photoconductors and nonlinear optical materials are also well documented. Polysilanes can also serve as probes for studies of polymer chain conformation since the UV absorption properties of the polymer are dependent on Si-Si-Si-Si dihedral angle and thus on the chain conformation. In a broader sense, polysilanes can also be used to elucidate the relationship between structure and photoemission of semiconductors. Figure 1 shows the photoemission wavelengths of silicon materials in different forms. Crystalline silicon exists in a tetrahedral lattice. Because of the indirect band-gap, photoluminescence is not allowed. If crystalline silicon is processed by HF etching and then anodized in an O_2 plasma, the new material, "porous" silicon becomes photoemitting between 600-900 nm (1-2 eV), which may be due to a quantum size effect (Ref. 5). These nanoscopic clusters are postulated to behave as quantum dots (Ref. 6).

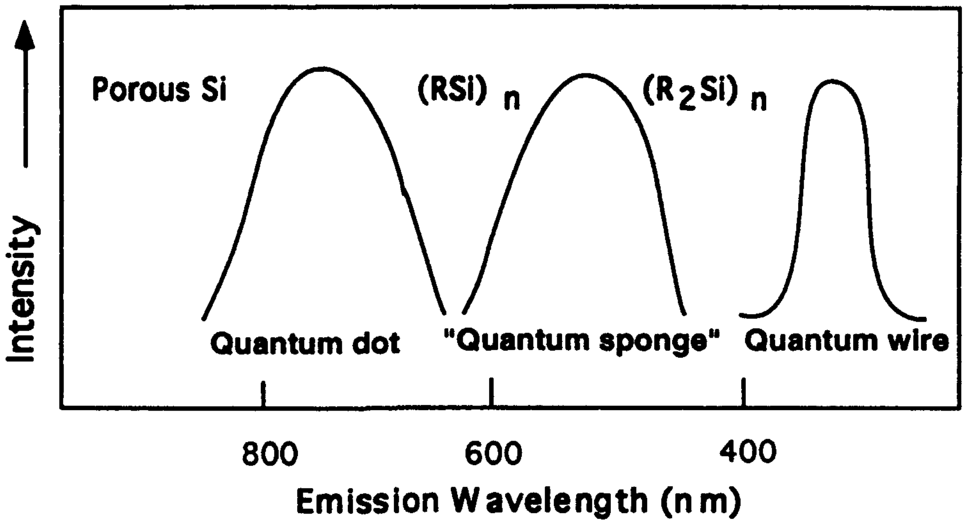


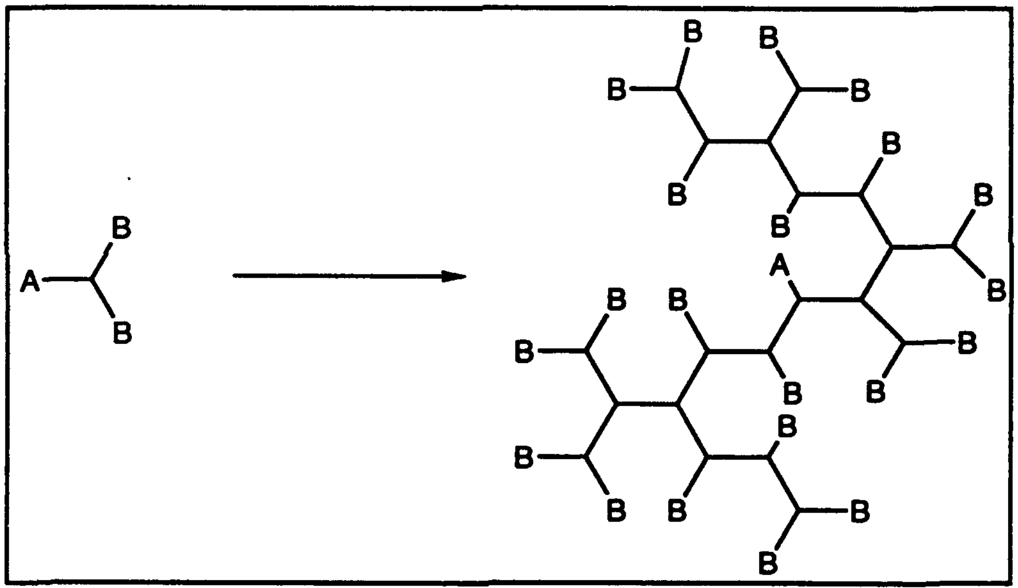
Figure 1. Emission spectra of various silicon containing compounds.

At higher energies, we find photo-emission from the organo-substituted polysilane materials. If the material is of low dimension, like in a single very long polymer chain, $(R^1R^2Si)_n$, then the photoemission is at the highest energies, around 350 nm (3.5 eV). This material could then be called a quantum wire. Intermediate photo-emission at between 400-700 nm (2-3 eV) is observed from $(RSi)_n$ or polysilynes (Ref. 7), polymers synthesized from $RSiCl_3$, because these materials have a 2-D or 3-D structure and the mixing of the electronic states becomes altered (Ref. 8). Since quantum size effects may be unique inside a highly branched material, we have deemed that these materials may be "quantum" sponges, because the shape of these molecules is thought to be like a hyperbranched dendrimer. Moreover, by understanding how to control the structure of the materials we can control their electronic properties.

MORPHOLOGY OF POLYSILYNES

Polysilanes made from condensation of $R^1R^2SiCl_2$ are linear chains. If the monomer functionality is increased to 3, as for $RSiCl_3$, high molecular weight products are formed called polysilynes, but the structure is very complicated. These materials are certainly not regular chains of $(RSi)_n$, as in polyacetylene. Earlier workers were surprised that these compounds are soluble in organic solvents, even at high molecular weights, and suggested that polysilyne had a 2-D structure (Refs. 9, 10). They imagined a folded, sheet-like structure with many interconnected rings. In their scheme, the folds are soluble because the organic groups separate the planes from each other creating the soluble polymer. However, no concrete evidence has been presented for the formation of a 2-D structure. Also, it is not easy to imagine a mechanism that would propagate the structure in only two dimensions since in a network of interpenetrating rings there would be unreacted bonds that could propagate growth of the molecule in directions orthogonal to the plane of the ring.

In light of what we now know about the properties of hyperbranched structures, it seems more reasonable that polysilynes are soluble because of their dendritic nature. Still, we must explain how polysilyne can become hyperbranched, but not crosslinked. To build a hyperbranched polymer, one starts with a multi-functional monomer, e.g. AB_2 (Refs. 11, 12). Intuitively, one might expect that the reaction of this trifunctional monomer would lead to a crosslinked gel. Instead, because of the growth mechanism of the reaction, as shown in Scheme 1, the A functionality of the initiating monomer becomes buried inside the growing structure and cannot react anymore. Very early on in the course of the reaction, the growing molecule has an effective reaction surface which consists of only B functionality. As the chain grows, each A reacts with a B on the surface, regenerating a new surface B site. Since the B functions cannot react with each other, the growing molecules cannot crosslink.

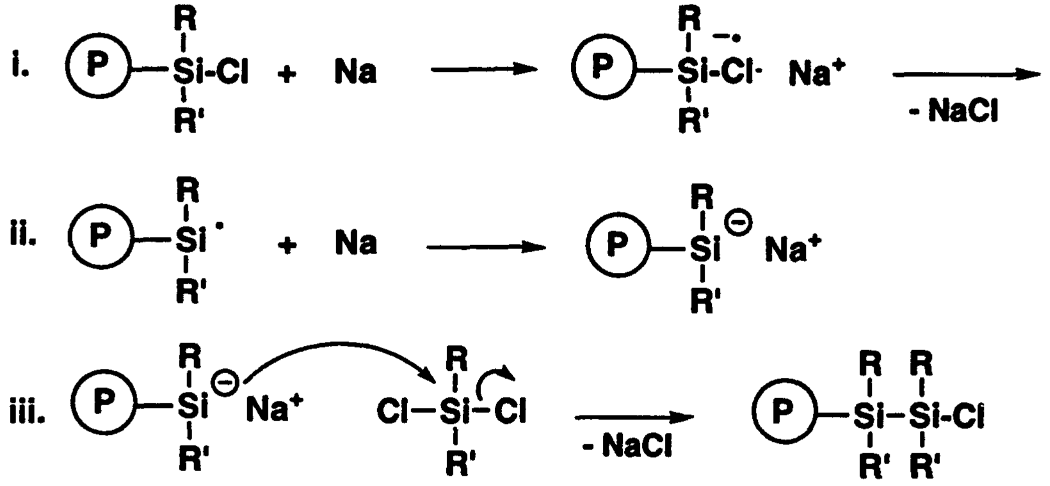


Scheme 1. The hypothetical growth mechanism of an AB_2 monomer into a hyperbranched polymer.

Since the monomer for polysilyne, $RSiCl_3$, appears to be an A_3 system, how can we understand the polysilyne reaction in terms of an AB_2 system? A careful analysis of the polysilane growth mechanism yields a valuable insight to this question. Although the polymerization of polysilanes is formally a condensation reaction involving consumption of two moles of Na per monomer unit, it behaves like a chain growth process. The actual mechanism is very complicated because the reaction is heterogeneous, taking place on the surface of the sodium in solution. Two important phenomena in the polymerization of polysilanes are:

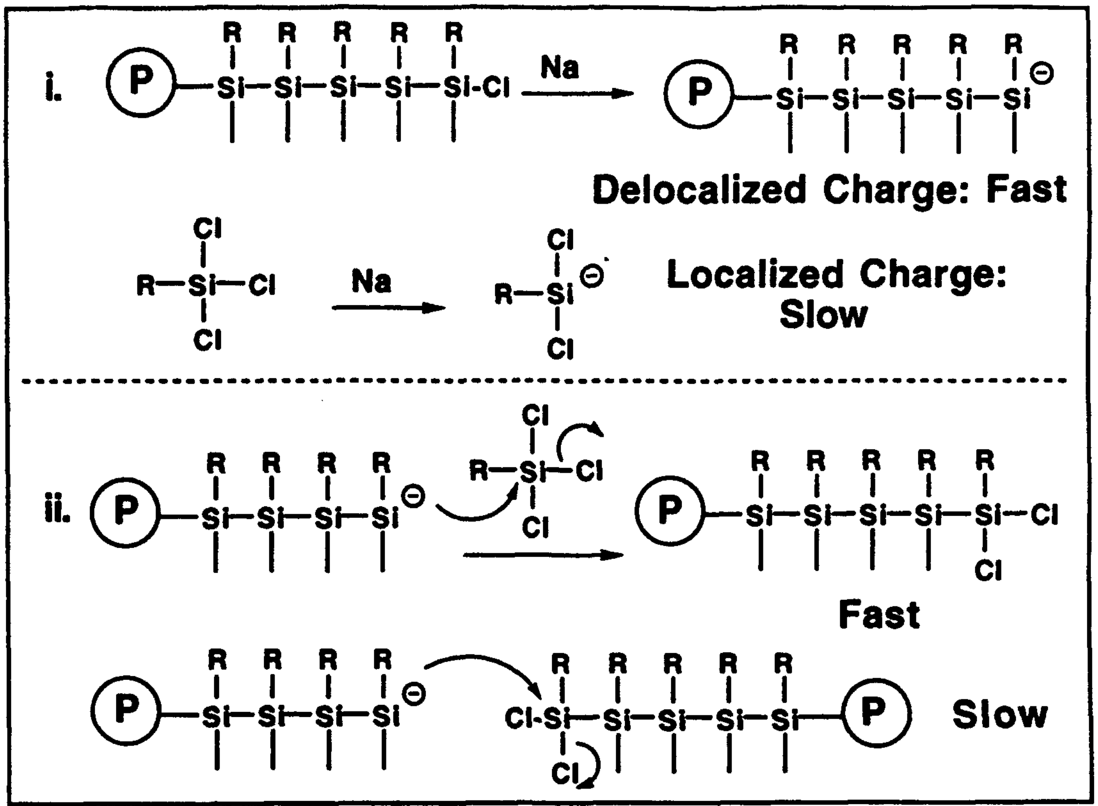
(1) high-molecular-weight products are observed at the beginning of the reaction and (2) the molecular weights and rate of polymerization do not depend on the ratio of the monomer to the metal. Consistent with these data is a chain growth mechanism, in which monomer at the alkali metal surface is continually being added to polymer, but cross-reactions between monomer-monomer and polymer-polymer are disfavored.

In Scheme 2, we show a rationalization for the reaction mechanism for the polymerization of polysilane. In accordance with a chain-growth mechanism, the reactivity of the monomer is differentiated with that of the polymer. The critical step in the polymerization is the formation of the silyl anion.



Scheme 2. Proposed propagation mechanism for polysilanes: i) Single electron transfer from Na metal to a growing polymer chain end; ii) Second electron transfer; iii) nucleophilic substitution.

Since the growing polymer chain has several Si-Si bonds over which the anion can be stabilized by delocalization, (Scheme 3) the formation of the anion on the polymer chain will be favored in comparison to the formation on the monomer, leading to the propagation of the chain. The Si-Cl bond on the end of the polymer chain will thus have a higher electron affinity towards the metal than the Si-Cl bond on the monomer. On the other hand, the Si atom in the monomer will be more electrophilic towards the reactive silyl anion than the Si atom on the end of another polymer chain. This is because the Si in the monomer is connected to three electron withdrawing Cl atoms. In addition, the monomer is at much higher concentration than the polymer and would diffuse much faster to the reaction site. This rationale is a basis for differentiating the Si-Cl groups on the ends of growing chains and on the monomer, making this system AB-type. Polysilyne could grow to high molecular weights without forming crosslinks as other hyperbranched dendrimers.



Scheme 3. Proposed initiation and propagation of polysilyne: the anion is stabilized on the polymer chain end and adds monomer much faster than crosslinking.

DENSITY OF SILICON CLUSTERS

As mentioned earlier, silicon compounds show photoemission, which is dependent on the nature of the structure of the silicon network and the substitution of the silicon atoms. Since there is a notable difference in the photoproperties of linear polysilanes, which photoluminesce in the far UV region and network polysilynes, which luminesce in the visible, it should be possible to further modify the properties of the emission by controlling the density of the silicon content of the hyperbranched structures. For this purpose, we have synthesized a variety of polysilanes in an effort to make dendritic or hybrid-linear-dendritic structures. First, we present studies of copolymers of $RSiCl_3$ with $RR'SiCl_2$ to make polysilane-polysilyne hybrid materials (Ref. 13); second, studies of copolymers of $SiCl_4$ and Me_2SiCl_2; and, third, studies of polymers based exclusively on $(SiMe_2X)_4Si$, which is a tetrafunctional monomer.

HYBRID POLYSILANE-POLYSILYNES

The copolymers we chose for our study were made from $RSiCl_3$ (R=n-hexyl, phenyl and methyl) and $PhMeSiCl_2$. The results of the sonochemical copolymerization of $PhSiCl_3$ and $PhMeSiCl_2$ are shown in Table 1.

Table 1. Copolymerization of Phenyltrichlorosilane (M_1) with Methylphenyldichlorosilane (M_2) in the Presence of Sodium.

M_1/M_2	1/0	1/1	1/5	1/10	0/1
yield, %	37.2	30.6	14.0	11.1	12
m_1/m_2	1/0	1/1.3	1/4	1/6	0/1
$M_n \cdot 10^{-3}$	3.2	2.0	2.3	2.5	104
M_w/M_n	1.73	1.10	1.18	1.32	1.50
λ_{max}, nm	<266	332	333	336	340
$\varepsilon_{Si\text{-}Si} \cdot 10^{-3}$	-	1.3	4.7	5.5	9.0

$[M]_0$=0.35 mol/L, $[Na]_0/[Si\text{-}Cl]_0$=1.02, 3 h, toluene, immersion type probe.

The polymer composition for the copolymers made from $PhMeSiCl_2$ and $PhSiCl_3$ is richer in (PhMeSi) units than the feed ratio would predict. This might be due to the higher reactivity of $PhMeSiCl_2$ or to the higher tendency of cyclization of $PhSiCl_3$. The general trends of going from 100% (PhSi) to 0% are consistent with a composition that increasingly becomes more like linear $(PhMeSi)_n$. If the dendritic structures are formed, then molecular weights based on polystyrene standards could be underestimated. The molecular weights and polydispersities of all the polymers are almost the same, 2-3 x 10^{-3}, except the 100% $(PhMeSi)_n$. The UV absorption spectra of the various $(PhSi)_m(PhMeSi)_n$ copolymers show the expected peaks for each component of the copolymer, suggesting that the polymer may contain blocks of each.

Table 2 shows the results of the copolymerization of n-Hexyl$SiCl_3$ and $PhMeSiCl_2$. This copolymer incorporates *almost the same* composition of (PhMeSi), 10:1, regardless of the feed ratio of the two components. The properties of these materials seem quite similar to each other, which according to λ_{max} of the material, seems to be a result of the polymer consisting almost entirely of blocks of $(PhMeSi)_n$.

Table 2. Copolymerization of n-Hexyltrichlorosilane (M_1) with Methylphenyldichlorosilane (M_2) in the Presence of Sodium.

M_1/M_2	1/0	1/1	1/5	1/10	0/1
yield, %	23.8*	7.6	10.5	11.2	12
m_1/m_2	1/0	1/10	1/13	1/15	0/1
$M_n \cdot 10^{-3}$	3.0	40	69	70	104
M_w/M_n	2.4	1.68	1.69	1.60	1.50
λ_{max}, nm	<266	338	-	340	340
$\varepsilon_{Si\text{-}Si} \cdot 10^{-3}$	-	1.3	-	7.6	9.0

$[M]_0$=0.35 mol/L, $[Na]_0/[Si\text{-}Cl]_0$=1.02, 3 h, toluene, immersion type probe.
* - 15 h, after 3 h no polymer was formed.

In Table 3, the results from the copolymerization of $MeSiCl_3$ and $PhMeSiCl_2$ are presented. It is worth noting that incorporation of (MeSi) units into the polymer leads to insoluble products if the feed ratio of $PhMeSiCl_2$ is less than 5:1. For the two soluble copolymers produced, the properties are quite similar and seem to show more of a mixed structure, because the λ_{max} of these materials is not like either of the homopolymers.

Table 3. Copolymerization of Methyltrichlorosilane (M_1) with Methylphenyldichlorosilane (M_2) in the Presence of Sodium.

M_1/M_2	1/0	1/1	1/5	1/10	0/1
yield, %	90*+	20.1+	10.8	11.6	12
m_1/m_2	1/0	-	1/4	1/6	0/1
$Mn \cdot 10^{-3}$	-	-	2.3	2.4	104
M_w/M_n	-	-	1.4	1.4	1.50
λ_{max}, nm	-	-	330	332	340
$\varepsilon_{Si\text{-}Si}\ 10^{-3}$	-	-	2.5	3.5	9.0

$[M]_0$=0.35 mol/L, $[Na]_0/[Si\text{-}Cl]_0$=1.02, 3 h, toluene, immersion type probe.
* - yield after 15 h.
\+ - insoluble polymer.

POLYMERS FROM TETRAFUNCTIONAL MONOMERS

Two previously described polymers are polysilanes in which there are Si atoms bonded to two other Si atoms (linear polysilanes) and polymers in which Si atoms are bonded to three other Si atoms (globular polysilynes). In order to extend our study of dendritic materials, we polymerized tetrafunctional monomers which should lead to structures with Si atoms bonded to four other Si atoms. Our two strategies are the copolymerization of a tetrafunctional silane, $SiCl_4$ with a difunctional silane, Me_2SiCl_2; and the homopolymerization of a tetrafunctional silane, $(SiMe_2X)_4Si$ (X = Cl and Br). The former should provide soluble $(Si)_n$ clusters; the latter should lead to the separation of tetrasilyl-substituted Si atoms by $SiMe_2$ groups.

$(SiMe_2X)_4Si$ (X = Cl and Br) (Ref. 14) was synthesized in two steps according to Scheme 4. First, we coupled Me_2HSiCl to $SiCl_4$ with Li metal in THF to form $(SiMe_2H)_4Si$ (Ref. 15), *1*. *1* was then converted easily to either the chloro- *2* or bromo- *3* derivative by reaction with either CCl_4 or n-bromobutane, respectively(Ref. 14).

$$1)\ SiCl_4 + 8Li + 4HMe_2SiCl \xrightarrow{THF} Si(SiMe_2H)_4$$

$$2)\ Si(SiMe_2H)_4 \xrightarrow[reflux]{CCl_4} Si(SiMe_2Cl)_4$$

$$3)\ Si(SiMe_2H)_4 \xrightarrow[reflux]{n\text{-}BuBr} Si(SiMe_2Br)_4$$

Scheme 4. Two-step synthesis of tetrakis(halodimethylsilyl)silane.

Some properties of a copolymer, $(Si)_m(Me_2Si)_n$ (Ref. 16), are shown in Table 4 along with data from $[(SiMe_2)_4Si]_n$, made from the chloro monomer (Ref. 17).

Table 4. Properties of Polysilanes Containing Tetrasilyl-substituted Si.

Polymer	$(Si)_m(Me_2Si)_n$	$[(SiMe_2)_4Si]_n$
Appearance	yellow powder	waxy-orange solid
yield, %	1	≈90
$M_n \cdot 10^{-3}$	6.3	3.1
M_w/M_n	2.5	4.3
Absorption*	243, 295	239, 290
Emission*	328, 456	weak

* λ_{max} in nm

Both polymerizations were carried out in THF with Li. The rates of the reactions differed radically. $(Si)_m(Me_2Si)_n$ can be made by adding the monomers to a suspension of Li in THF at room temperature in one day. However, on work up with H_2O, more than 90% of the material gelled, leaving extractable polymer of only about 1% yield. $(SiMe_2Cl)_4Si$ reacts much more slowly with Li and requires more than three days in refluxing THF.

We also examined the thermal properties of $(Si)_m(Me_2Si)_n$ and $[(SiMe_2)_4Si]_n$. Both materials decompose from 400 to 450°C. $(Si)_m(Me_2Si)_n$ decomposes in two stages, associated with the two segments of polymers in the copolymer. $[(SiMe_2)_4Si]_n$ decomposes smoothly.

Structural assignment for these compounds comes from polarization transfer ^{29}Si NMR as shown in Figure 2. For $[(SiMe_2)_4Si]_n$, there are three main peaks, at +10, -43 and -120 ppm. The peak at +10 ppm, we assign to end groups; -43 ppm to $SiMe_2$ units and -120 ppm to $(Si)Si_4$ units. The polarization transfer condition was especially chosen to transfer polarization from the protons on $SiCH_3$ not to the Si two bonds away, but the $(Si^*)Si_4$, which is connected by three bonds (Ref. 18). Under these conditions, we expect to see resonances for both two- and three-bonded silicons, but the intensity of the Si, three bonds away should be enhanced relative to the Si, two bonds away from the ^1H. There are two peaks around -43 ppm, in the proper range for Me_2Si and is fairly narrow indicating that there must be free rotation and a similar magnetic environment for the Si nuclei. The very broad peak centered at -120 ppm is typical for $(Si^*)Si_4$ and indicates restricted motion and many different environments for the Si nuclei.

The polarization transfer ^{29}Si NMR spectrum for $(Si)_m(Me_2Si)_n$ is also shown in Fig. 2. Only a slightly broadened peak at -37 ppm, typical for free Me_2Si chains can be seen. This indicates that $(Si^*)Si_4$ must be isolated as clusters, attached to "arms" of Me_2Si chains. No end groups are observed for the copolymer.

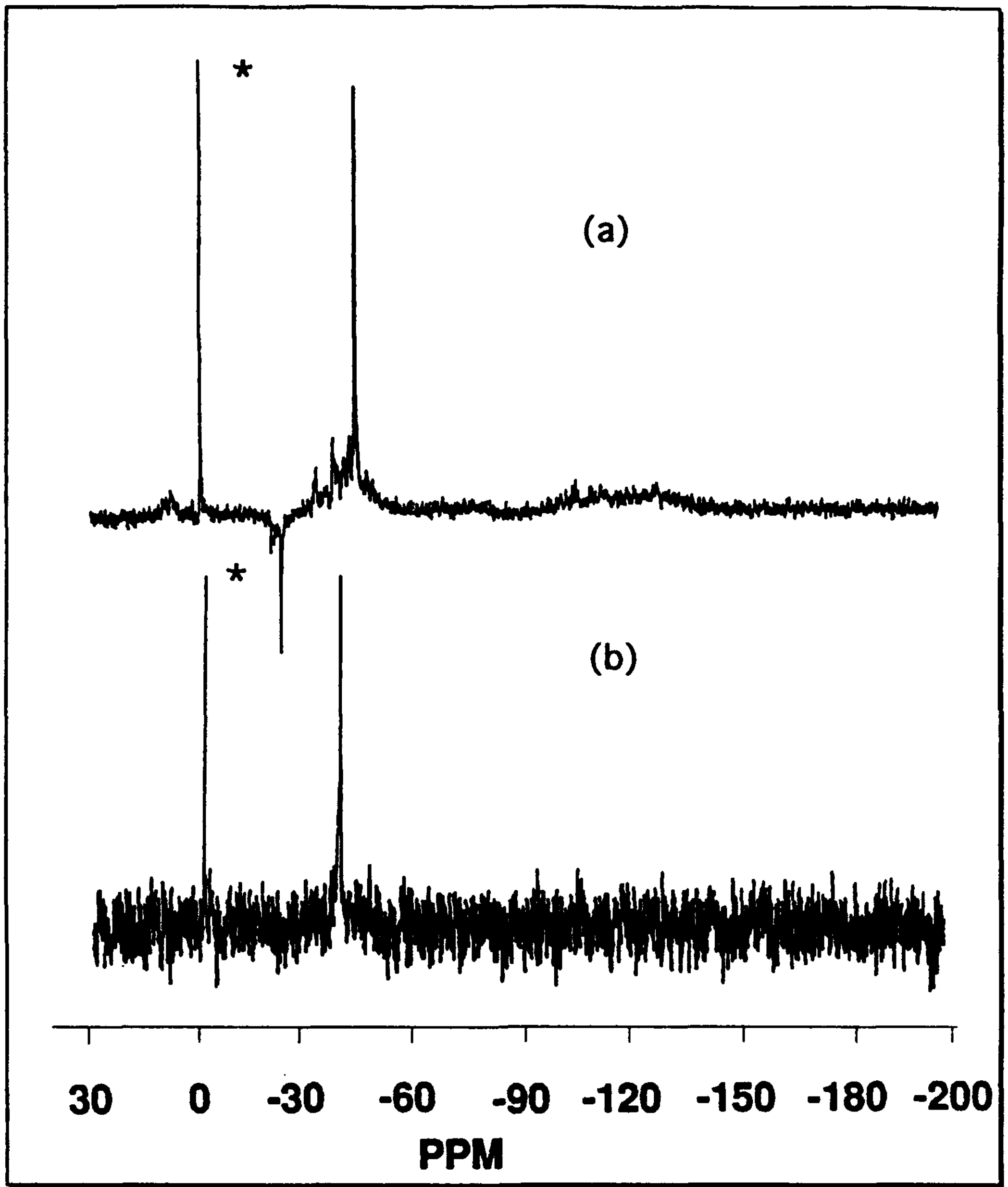


Figure 2. The Polarization transfer ^{29}Si NMR of (a) $[(SiMe_2)_4Si]_n$ and (b) $(Si)_m(Me_2Si)_n$. The * marks tetramethylsilane, used as an internal standard. The negative peak in (a) is from a siloxane impurity.

PHOTOCHEMISTRY

The photochemistry of polysilanes depends significantly on the structure of the materials. Polysilanes normally have an intense rather narrow $\sigma - \sigma^*$ transition, which occurs in the far UV range of the spectrum at 300 - 350 nm. Naturally, strong fluorescence is observed from this band, which is usually observed as a narrow band with a small Stokes shift making the emission 350 - 400 nm.(Ref. 2) In addition, a broad luminescence peak has been observed for some materials in the visible spectrum around 500 nm and a number of explanations have been proposed. Although there is no consensus on the origin of the broad luminscence, a reasonable assignment is to a band associated with short segments of Si, which are structurally or conformationally isolated from the rest of the polymer σ system. Structurally, this might translate to a polysilane that contains isolated short segments along the chain or branched off the chain. This view is supported by recent experiments in which branches are introduced into the polysilane chain by making copolymers with trifunctional and difunctional silanes (Ref. 19). Indeed, increasing the density of branches along the polysilane chain, by increasing the feed ratio of tri- to difunctional monomer, results in a rise in the intensity of the emission.

The UV absorption spectra of $[(SiMe_2)_4Si]_n$ and $(Si)_m(Me_2Si)_n$ are shown in Figure 3. Both have similar absorptions, near 250 nm and 300 nm, only the shape of the peaks differs slightly. $(Si)_m(Me_2Si)_n$ shows a much stronger absorption at lower energy mixing with and obscuring the peak near 250 nm. $[(SiMe_2)_4Si]_n$, which has a regular structure, shows more symmetrical peak shapes. Tentatively, we assign the peak near 300 nm to the typical polysilane $\sigma - \sigma^*$ transition and the peak near 250 nm to a more localized $\sigma - \sigma^*$ transition over only a few silicon atoms.

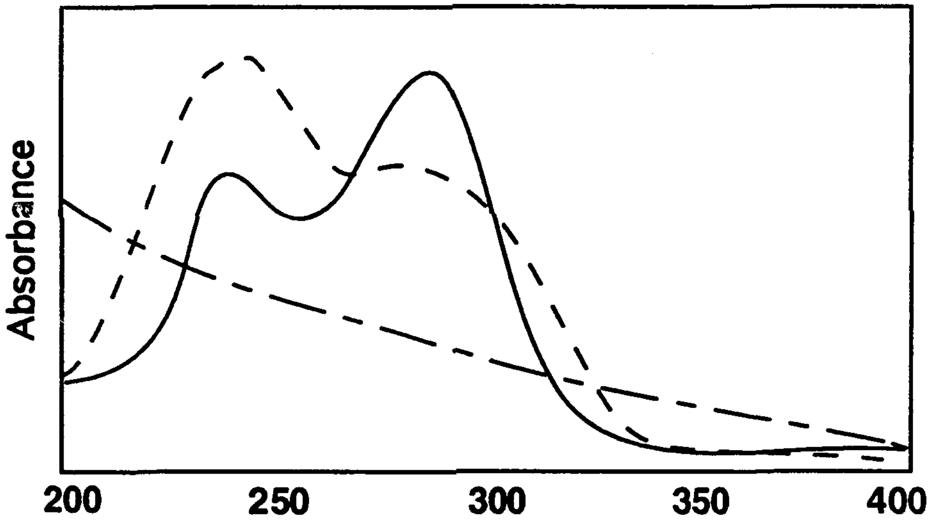


Figure 3. The UV absorption spectrum of $(Si)_m(Me_2Si)_n$ —; $[(SiMe_2)_4Si]_n$ - - -; and $(PhSi)_n$ — -. The intensity of the peaks is not normalized and represented in arbitrary units.

Excitation at 250 nm and 295 nm both produce similar emissions, (Figure 4) except for differences in intensities. $(Si)_m(Me_2Si)_n$ shows the expected Stokes shifted emission from the 295 nm absorption band at 328 nm, typical of polysilanes. More importantly a visible emission at 456 nm is also observed. The difference between (a) and (b) in Figure 4 is that the excitation at 295 nm produces peaks that are about 200 times more intense. $[(SiMe_2)_4Si]_n$ shows much weaker emission than $(Si)_m(Me_2Si)_n$, at a level not much above the solvent emission. We conclude that the delocalized $\sigma - \sigma^*$ transition is much more effective in $(Si)_m(Me_2Si)_n$ than $[(SiMe_2)_4Si]_n$ and thus the photoemission of the copolymer is much more intense, due to effective energy transfer from the Me_2Si arms to the silicon cluster.

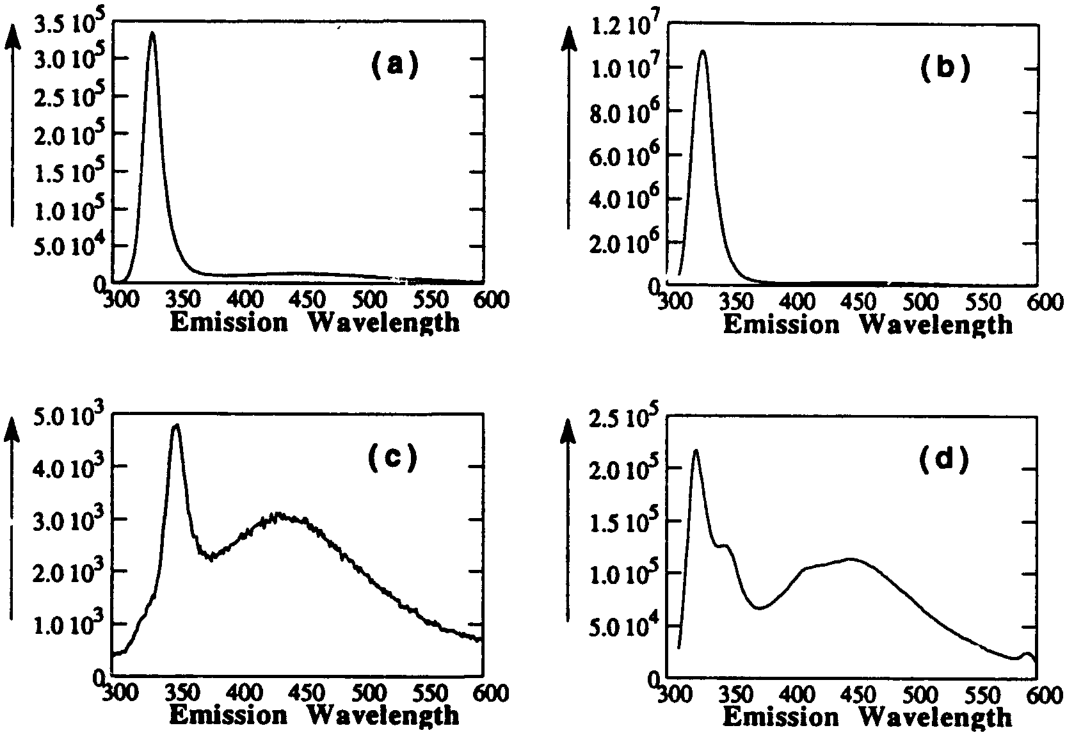


Figure 4 Emission spectra of $(Si)_m(Me_2Si)_n$, (a) 250 nm excitation and (b) 295 nm excitation and $[(SiMe_2)_4Si]_n$, (c) 250 nm excitation and (d) 295 nm excitation.

SPIRO AND BICYCLIC STRUCTURES

Our first thought about the structure $[(SiMe_2)_4Si]_n$ was that this polymer should have spiro or bicyclic architecture, as depicted in Figure 5. These structures seemed very appealing to us, because we felt that these architectures might stabilize a soluble polysilane structure because the backbone consists of 6-member rings, alternating in a fused spiro-structure. It is well known that the main products of polysilane synthesis are 5- and 6-member rings, and that polymer is usually only present in at most 30% (Refs. 20, 21). Therefore, if polysilane could be stabilized by the inclusion of the six-member rings imbedded in the backbone, the polymer might be formed under thermodynamic conditions, leading to high conversions of polymer. A spiropolysilane might also have interesting properties because the silicon rings would run orthogonally to each other down along the chain, perhaps giving the hypothetical compound different photochemistry or enhanced thermal stability.

Our original idea, however, did not take into account the strain that might exist in 1,4-disilyl-substituted rings. Moreover, under thermodynamic conditions the strained rings might be vulnerable to attack from silyl anions, leading to a random redistribution of products, ultimately to dendrimers. Although there is some evidence that spiro compounds are formed at low conversions (Ref. 22), we have not yet been able to isolate pure spiro polymer.

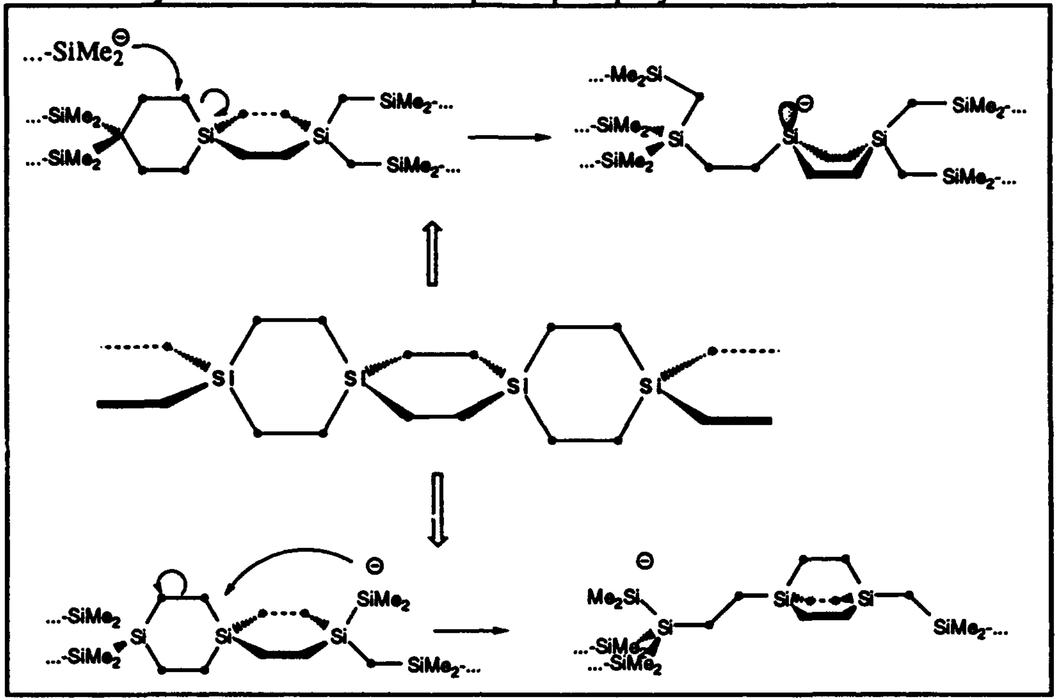


Figure 5. Potential reaction pathways for products of $(SiMe_2Cl)_4Si$ and Li in THF. • = $SiMe_2$.

Whatever the structure formed in the early stages of the reaction, the final product is hyperbranched. In Figure 6, we show our best guess to the structure of the polymers.

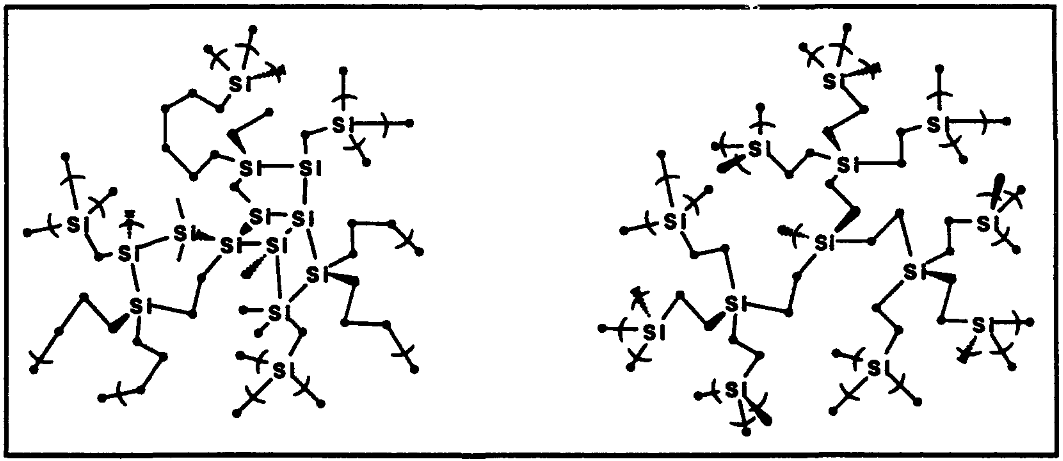


Figure 6. Hypothetical structures for $(Si)_m(Me_2Si)_n$ (left) and $[(SiMe_2)_4Si]_n$ (right). • = $SiMe_2$.

Finally, we should comment on the slow rate of polymerization of $(SiMe_2Cl)_4Si$ with Li, compared to the fast reaction rates of $RSiCl_3$ and R_2SiCl_2. First, chain propagation, obviously, must be slower for a spiro-polymer, since the silicon backbone is not in the correct geometry to form an effectively conjugated pathway to stabilize the anion on the polymer end. A contributing factor may be the slower addition of $(SiMe_2Cl)_4Si$ units because it is less reactive. The more reactive monomers are much more electrophilic because of the substitution by two or three chlorines. Also, $(SiMe_2Cl)_4Si$ should react slower because it is more sterically hindered.

Molecular weights for dendritic $[(SiMe_2)_4Si]_n$ are limited to M_w in the range of 15000, because under the reaction conditions, backbiting occurs leading to a broad distribution of lower-molecular-weight materials. Our reaction studies show that higher-molecular-weight materials are made during early reaction times, but in the course of the reaction, backbiting leads to redistribution of molecular weights. Under similar conditions, Li in THF, it is not possible to make linear polysilanes with high molecular weights, because of this facile backbiting reaction. One pathway of the backbiting reaction is shown in Figure 5. $SiSiMe_2$-$SiMe_2Si$ bonds might be cleaved as well as bonds between quaternary and secondary silicon atoms. This latter reaction will result in the formation of electronically stabilized tertiary silyl anions (Ref. 23), which can add another monomer unit. Thus, there should be two types of segments of Me_2Si units in the polymer: one segment has one unit between each tetrasilyl substituted Si and the other has two units. This structure is consistent with the two peaks near -43 ppm in the ^{29}Si NMR spectrum. Currently, we are studying methods, which control the structure, size and density of clustered polysilanes.

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