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Polymerization of 1,4-Bis(hydroxydimethylsilyl)benzene with (Dimethylamino)-/chlorosilanes: Structural Characterization by ^{29}Si NMR

Gaddam N. Babu* and Richard A. Newmark

I & E Sector Research Laboratory, and Corporate Research Laboratory, Building 201-4N-01, 3M Company, St. Paul, Minnesota 55144

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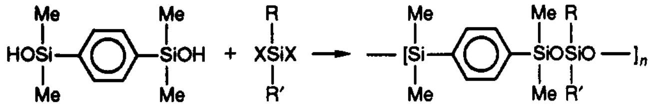
ABSTRACT: The solution polycondensations of 1,4-bis(hydroxydimethylsilyl)benzene (BHB) with dimethyldichlorosilane, diphenyldichlorosilane, phenylmethyldichlorosilane, and methylvinyldichlorosilane were carried out at 0–5 °C. The polymers were also prepared with analogous bis(dimethylamino)silanes. The polymers were characterized by ^{1}H, ^{29}Si, and ^{13}C NMR spectroscopy and ^{29}Si NMR spectroscopy was used to determine the polymer sequence. Polymers prepared from bis(dimethylamino)dimethylsilane and bis(dimethylamino)methylvinylsilane were almost perfectly alternating, whereas the other six polymers showed over 25% silarylene diads, indicating considerable randomization. In all cases the polymer prepared from dichlorosilanes showed greater randomization than those prepared from bis(dimethylamino)silanes. However, the T_g is independent of the randomization.

I. Introduction

Silarylene–siloxane copolymers, which exhibit a wide range of physical properties depending on their composition and structure, have received considerable academic and commercial interest. The preparation of these polymers is carried out by a number of methods.[1-8] In order to prepare polymers with phenylene units in the backbone, step-growth reactions must be used. Most such polymerization reactions have been based on the condensation of silanol with an active silane monomer through a nucleophilic substitution reaction, as follows:


X = halo, acetoxy, or dialkylamino groups
R, R′ = alkyl, phenyl, or vinyl groups

A number of active silane monomers have been investigated for this purpose with different leaving groups X, particularly the dialkylamine, acetoxy, and chloro groups. All these methods have been reported to produce low molecular weight polymers with degree of polymerization ranging from 10 to 50. The formation of low molecular weights may be attributed to the acid- or base-catalyzed chain-cleavage reactions. Dvornic and Lenz[1-4] prepared exactly alternating silarylene–siloxane polymers by the reaction of 1,4-bis(hydroxydimethylsilyl)benzene (BHB) with dialkylbis(ureido)silanes and dialkyldichlorosilanes. The major advantage of the former synthetic route is reaction under milder conditions and the formation of a nonbasic substituted urea that does not react with the polymer. Synthesis of exactly alternating polymer with dialkyldichlorosilane requires very careful control of the reaction.[4]

The reactions of 1,4-bis(hydroxydimethylsilyl)benzene with bis(dimethylamino)dialkylsilanes produce polymers with molecular weights close to 1 million using Stewart's multistep polymerization technique.[9] While this work was in progress, Williams reported the use of ^{29}Si NMR to determine the sequence of polymers prepared from oligomers of dimethylsiloxane and 1,4-bis(hydroxydimethylsilyl)benzene.[10] We report a complete analysis of silarylene–siloxane polymer composition and the microstructure of the polymers using ^{29}Si and ^{13}C NMR.

II. Experimental Section

Spectra. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Varian XL-400 NMR spectrometer at 400 (^{1}H), 100.6 (^{13}C), and 79.5 MHz (^{29}Si), respectively, on very concentrated (50 wt %) solutions in $CDCl_3$. Chemical shifts are given relative to tetramethylsilane (TMS), but ^{1}H and ^{13}C shifts were determined by using the solvent resonance (7.27 and 76.91 ppm, respectively) as an internal reference. Silicon nuclei, even in polymers, typically show very long relaxation times as well as small negative nuclear Overhauser effects.[11] In order to obtain quantitative ^{29}Si spectra, approximately 0.02 M $Cr(acac)_3$ was added to each sample to serve as a relaxation agent. The T_1 values were all between 2.3 and 2.6 s in these solutions except for the end group $SiMe_3$ at 7.4 ppm in which T_1 = 0.6 s. A gated decoupled spectrum proved that the NOE enhancements were all reduced to zero by the addition of $Cr(acac)_3$. Based on these results, quantitative NOE-suppressed ^{29}Si NMR spectra were obtained with a 7-s recycle time and 90° pulses on the polymers prepared by using bis(dimethylamino)silanes. But since the relaxation times are all similar, quantitative spectra of the polymers prepared from the dichlorosilanes were obtained with a 2.7-s recycle time.

The proton–carbon correlations were determined by heteronuclear correlation experiments including a BIRD sequence to fully decouple all the protons.[12] The delay times in the pulse sequence were optimized for 120- (aliphatic) or 170-Hz (aromatic) J(CH) couplings. The aliphatic spectrum was accumulated by using 128 points and a 403-Hz sweep width in the ^{13}C dimension and 96 increments and a 313-Hz sweep width in the proton (t_1) dimension for a resolution of 3 Hz/point in the ^{1}H dimension in which the major absorptions were separated by 11 Hz. A total of 64 transients were accumulated for each t_1 FID, with a relaxation delay between acquisitions of 2.2 s; double-exponential apodization in both dimensions was applied after zero filling to a 512 × 512 data matrix. The aromatic ^{1}H, ^{13}C COSY experiment was obtained by using 1024 points and a 2400-Hz ^{13}C sweep width, 128 increments and a 700-Hz ^{1}H sweep width, and zero-filling to 2048 × 512. The ^{29}Si, ^{1}H COSY was obtained under conditions identical to the aliphatic ^{13}C, ^{1}H COSY except for a 1270-Hz sweep width and 256 points in the ^{29}Si dimension and with delay times optimized for a 10-Hz J(SiH) in the multipulse sequence. The latter is a compromise between the true ^2J(SiH) coupling constant (~7 Hz)[13] and the need to minimize the total time of the pulse sequence before T_2 relaxation attenuates the signal.[12]

Materials. 1,4-Bis(hydroxydimethylsilyl)benzene (BHB), bis(dimethyamino)dialkylsilanes, and dichlorodialkylsilanes were obtained from Petrarch Systems Silanes and Silicones and Al-

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drich Chemical Co. The purity of 1,4-bis(hydroxydimethylsilyl)benzene was checked by gel permeation chromatography on 100-Å ultraStyragel columns, with tetrahydrofuran (THF) as the mobile phase. The white crystals melted at 135–136 °C. All monomers were purified before use by fractional distillation either under nitrogen or under vacuum. Fractions used in polymerization reactions had the following boiling points: bis(dimethylamino)dimethylsilane 128 °C, bis(dimethylamino)diphenylsilane 110 °C (1 mmHg), bis(dimethylamino)methylphenylsilane 108 °C (10 mmHg), bis(dimethylamino)methylvinylsilane 146 °C, dichlorodimethylsilane 70 °C, dichlorodiphenylsilane 150 °C (10 mmHg), dichlorophenylmethylsilane 205 °C, and dichloromethylvinylsilane 92 °C. All samples were more than 99% pure by GC analysis.

Toluene (Fisher Scientific) was distilled from calcium hydride under a nitrogen atmosphere and stored over molecular sieves until used. The THF used as reaction solvent was dried before use by repeated refluxing over a sodium–benzophenone solution under a dry nitrogen atmosphere, followed by distillation.

Condensation of BHB with bis(dimethylamino)dialkylsilanes was carried out by two different methods:

Multistep Method. Poly[1,4-bis(oxydimethylsilyl)phenylenedimethylsilane] (**1A**), poly[1,4-bis(oxydimethylsilyl)phenylenediphenylsilane] (**2A**), and poly[1,4-bis(oxydimethylsilyl)phenylenemethylphenylsilane] (**3A**) were prepared by the method described below.

Prepolymer. 1,4-Bis(hydroxydimethylsilyl)benzene (19.6 g, 86.7 mmol) was placed in a three-necked 500-mL round-bottom flask dried overnight in a oven at 100 °C. The flask was fitted with a thermometer, a mechanical stirrer, and a two-outlet adaptor. The system was thoroughly purged with dry nitrogen for 30 min. While the positive pressure was maintained, 100 mL of freshly distilled dry toluene was added. The flask was slowly heated to a gentle reflux. Under nitrogen atmosphere, 3.83 g (26.2 mmol) of bis(dimethylamino)dimethylsilane was added to the reaction mixture. This addition was repeated four times (2.0 g, 13.7 mmol) over a 30-h period until 94.2 mol % of aminosilane (11.83 g, 81 mmol) had been added. The reaction mixture was allowed to reflux for an additional 10 h and then was precipitated in excess methanol. The product was dried under vacuum to constant weight at 100 °C.

High Molecular Weight Polymer 1A. A system was assembled similar to that for the prepolymer synthesis. The prepolymer was added to a 500-mL three-necked flask and dried overnight in a vacuum oven at 50 °C. The prepolymer was chain-extended with bis(dimethylamino)methylvinylsilane (0.61 g, 3.8 mmol). The amount of silane was added dropwise over a 30-h period. The reaction was further allowed to reflux for an additional 10 h. The molecular weight was monitored by GPC.

Prepolymers were prepared similarly by the reaction of BHB with bis(dimethylamino)diphenylsilane and bis(dimethylamino)methylphenylsilane followed by chain extension with bis(dimethylamino)methylvinylsilane to give **2A** and **3A**.

Single-Step Method. A single-step method, in which 1 mol of BHB and 0.95 mol of bis(dimethylamino)dialkylsilane were added to toluene and allowed to react without any further adjustments, was also used. At the end of the reaction the polymer was refluxed with hexamethyldisilazine to give trimethylsilyl-terminated polymer.

Condensation of BHB with Chlorosilanes. A system was assembled similar to the procedure described for prepolymer synthesis. The system was thoroughly purged with nitrogen. Bis(dimethylhydroxysilyl)benzene (2.97 g, 13.1 mmol) was transferred to the flask under nitrogen. The disilanol was dissolved in 20 g of dry THF. The flask was cooled to 0–5 °C. Dimethyldichlorosilane (1.67 g, 12.9 mmol) in 10 mL of THF was added drop by drop from a gas-tight syringe to the solution over a period of 1 h. The reaction temperature was maintained at 0–5 °C for an additional 3 h before the contents were allowed to warm to room temperature. Stirring was continued and the THF was allowed to evaporate slowly over a period of 24 h to obtain a gumlike polymer. The polymer was redissolved in THF, precipitated in methanol, and purified as above.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) was performed in duplicate on a Waters Model 200 GPC using THF at 30 °C. The samples were run through a series of Waters μ-Styragel GPC columns of mixed porosity and detected by using an ACS 750/14 mass detector. The molecular weights were calculated by using a Hewlett-Packard HP-3388A integrator with GPC (REV2048) programming.

Table I
Prepolymer/Polymer Molecular Weight Data

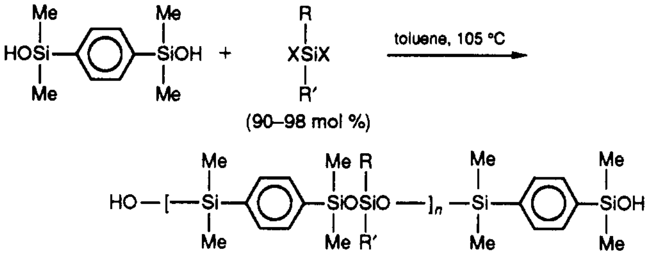
	prepolymers		
polymer	silane[a] (mole ratio), %	$10^{-4}\bar{M}_w$	polymers $10^{-5}\bar{M}_w$
1A	94.2	4.52	8.85
2A	97.7	5.46	9.16
3A	93.4	6.32	7.67

[a] Relative to BHB.

Thermal Transitions. To determine the transition temperatures of the polymers, a Perkin-Elmer DSC-4 with TADS was used. In all cases a temperature interval between −150 and +25 °C was covered at a heating rate of 20 °C/min. The samples analyzed ranged from 10 to 25 mg in weight, and a maximum sensitivity of 2 mcal/s was used.

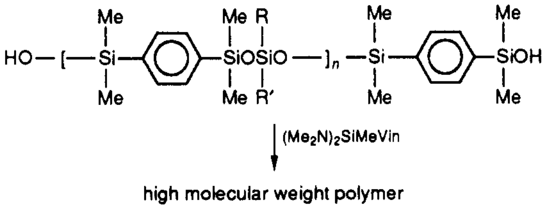
III. Results and Discussion

A series of silarylene–siloxane homopolymers have been prepared by solution polycondensation of 1,4-bis(hydroxydimethylsilyl)benzene with four bis(dimethylamino)silanes at 105 °C by use of Stewart's multistep polymerization technique with some modifications.[9] This technique enabled us to prepare prepolymers with molecular weights of ~50 000.



1: R = R′ = Me, X = NMe$_2$
2: R = R′ = Ph, X = NMe$_2$
3: R = Me, R′ = Ph, X = NMe$_2$
4: R = Me, R′ = Vin, X = NMe$_2$
5: R = R′ = Me, X = Cl
6: R = R′ = Ph, X = Cl
7: R = Me, R′ = Ph, X = Cl
8: R = Me, R′ = Vin, X = Cl

The prepolymers were isolated and purified and then chain extended with bis(dimethylamino)methylvinylsilane to higher molecular weights (**1A**, **2A**, and **3A**) by incremental addition of aminosilane utilizing the following reaction:



1A: R = R′ = Me
2A: R = R′ = Ph
3A: R = Me, R′ = Ph

The molecular weights are summarized in Table I. One-step condensation of BHB with bis(dimethylamino)dialkylsilanes (amine-deficient method) gave hydroxy-terminated silarylene–siloxane polymers **1–4**. These were end-capped with trimethylsilyl groups. The molecular weights of these polymers are in the range 10 000–30 000.

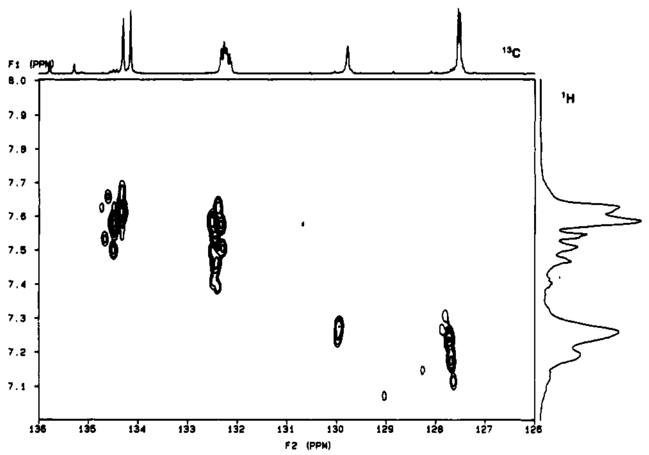


Figure 1. 2D $^1H,^{13}C$ COSY NMR of **6** (aromatic region).

Similar polymers **5**–**8** were prepared by the condensation of BHB with analogous dichlorosilanes by the one-step condensation route. The microstructures of **1**–**8** prepared by the one-step condensation process were studied and compared.

Structural Characterization. Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for the qualitative and quantitative analysis of polymers.[14-16] In particular, the advent of Fourier transform (FT) NMR facilitates the observation of low-natural-abundance nuclei such as ^{29}Si and ^{13}C. Since these nuclei exhibit relatively large chemical shift ranges, resolution of structurally similar atoms by this technique is quite good and FT NMR is particularly well suited to the analysis of polymer chains where structural changes are small.

There have been a number of reports related to silicones using ^{29}Si NMR.[17-19] Recently, we reported the sequence analysis of dimethylsiloxane–diphenylsiloxane copolymers and the effect of sequences on the structure–property relationship.[17] These studies have now been extended to siloxane polymers having phenylene groups on the backbone.

^1H NMR. The ^1H assignments and chemical shifts of chracteristic absorption peaks of silarylene–siloxane polymers have been reported by Dvornic, Lai, and Lenz.[2-4] Proton ratios of the siloxane/silarylene were determined from integrated peak intensities in **4** and **8** in which the concentration of vinyl groups is readily determined from the proton multiplets centered at 5.9 ppm and the silarylene determined from the singlet at 7.6 ppm. The $OSiMe_2$/silarylene ratios in **1** and **5** are determined from the intensity of the methyl peaks at 0.10 and 0.35 ppm.[3] The siloxane phenyl protons in **2**, **3**, **6**, and **7** show two broad absorptions at 7.2 and 7.6 ppm; the latter overlaps the silarylene protons at 7.6 ppm.[4] Since the carbon chemical shifts have been assigned,[4] these multiplets could be assigned from a H,C COSY experiment with **6** (Figure 1). The meta and para protons of the $SiPh_2O$ are at 7.2 ppm and the ortho protons and silarylene protons are at 7.6 ppm, from which the $SiPh_2O$/silarylene ratio could be determined by difference. The proton spectra of **1**–**8** confirmed the 50:50 charge of the siloxane and silarylene in the polymer.

^{29}Si NMR. We have found that ^{29}Si NMR provides detailed information about the structure of the polymers. The ^{29}Si chemical shifts of the $SiMe_2O$, $SiPh_2O$, SiMePhO, and SiMeVinO absorptions are similar to those observed in the literature for polysiloxanes.[11,18] The chemical shifts of the major peaks in silarylene–siloxane homopolymers **1**–**8** are thus readily assigned and are listed in Table II. Figures 2 and 3 show representative ^{29}Si NMR spectra of **1** and **5** and of **2** and **6**, respectively. The siloxane/silarylene ratio could be determined in all cases by direct integration. The observed molar ratio was within experimental error of the 50:50 charge for samples **1**–**8**. The silicon spectrum of **1** showed major absorptions at −2.7 and −19.5 ppm due to $ArSiMe_2O$ and $SiMe_2O$, respectively. In addition to this, the polymer showed weak absorptions at +7.6, −0.3, and −21.8 ppm, each at the 2% level, and a peak at −20.8 ppm at the 3% level. The peak at +7.6 ppm is attributed to the trimethylsilyl end groups. This absorption cannot be due to hydroxyl end groups, $HOSiMe_2ArSiMe_2O$, since the $ArSiMe_2$ absorption occurs at 3.3 ppm in BHB monomer. The additional peaks at −20.8 and −21.8 ppm indicate the presence of diad and longer segments of $SiMe_2O$ between the silarylene units in the polymer. In particular, the absorption at −21.8 ppm is similar to that observed in poly(dimethylsiloxanes).[11,17] The −20.8 ppm peak is thus assigned to siloxane diads (n = 0), to the end Si in triads (n = 1) or to longer units in the following structure:

$$SiMe_2ArSiMe_2O\mathit{SiMe_2O}(SiMe_2O\text{–})_n\text{–}\mathit{SiMe_2O}SiMe_2ArSiMe_2$$

The average value of n is given by twice the intensity of the −21.8 ppm absorption divided by the intensity of the −20.8 ppm absorption. Identical assignments have been given independently by Williams.[10] These assignments indicate that each silarylene substituent introduces a 1.0 ppm down field shift on the dimethylsiloxane, resulting in the progression −21.8, −20.8, and −19.5 ppm for the $SiMe_2O$ between 0, 1, and 2 silarylene, respectively. When n is greater than 2, the chemical shift differences due to dimethylsiloxy units are indistinguishable at 79 MHz. The minor absorption at −1.4 ppm is attributed to the adjacent BHB silicons in the diad structure $ArS\mathit{i}Me_2OS\mathit{i}Me_2Ar$. Absorption between −1.2 and −1.4 ppm is observed in **1**–**8** at varying intensities correlating to the diad plus triad siloxane units. This absorption is thus clearly assigned to silarylene diads and its intensity gives the block BHB level. The two absorptions of nearly equal intensity in the downfield region for **5** at −1.4 and −2.7 ppm are due to block and alternating structures, respectively. Polymer **5** shows an additional absorption at −18.2 ppm assigned to octamethylcyclotetrasiloxane (D_4). The intensities of the minor −1.4, −20.8, and −22.0 ppm absorptions are much greater in **5** than in **1** (Table II).

Because of the presence of various structural units in **1** and **5**, the condensation reaction of BHB with either chloro- or aminosilane does not lead to the expected perfectly alternating homopolymer. Several reactions are possible that explain the observed structures. A curious fact is that the concentration of block structures in **1** is only 1% as compared to 52% in **5** even though the reaction of the former was run at elevated temperatures, where the probability of condensation of BHB units is greater. According to Pike,[7] the reaction of a silanol and bis(dimethylamino)silane proceeds through a four-membered transition state such as

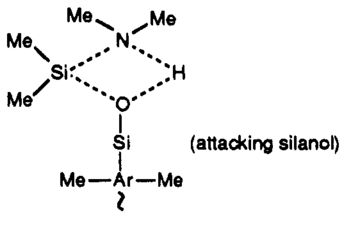


Table II
Chemical Shift Assignments and Peak Ratios of Silarylene–Siloxane Polymers 1–8 from ^{29}Si NMR Spectra[a]

$-Me_2SiArSi^1Me_2OMe_2SiArSiMe_2O-$

$-Me_2SiArSi^2Me_2OSi^4RR'OMe_2SiArSiMe_2O-$

$-Me_2SiArSi^3Me_2OSi^5RR'OSi^5RR'OMe_2SiArSiMe_2-O-$

$-Me_2SiArSi^3Me_2OSi^5RR'OSi^6RR'OSiRR'O-$

assgnmt	1	2	3	4[b]	5	6	7	8
ASi^1	−1.4 (0.01)	−1.2 (0.19)	−1.4[c] (1.00)	−1.2 (0.04)	−1.4 (0.52)	−1.2 (0.33)	−1.2 *b*	−1.3 (0.50)
ASi^2	−2.7 (0.99)	−0.1 (0.71)		−1.6 (0.96)	−2.7 (0.48)	−0.1 (0.39)	−1.1 *b*	−1.7 (0.50)
ASi^3		+0.1 (0.10)				+0.1 (0.25)		
ASi^4	−19.5 (0.95)	−46.0 (0.72)	−32.1 (0.61)	−33.5 (0.96)	−19.7 (0.24)	−46.0 (0.48)	−32.9 (0.26)	−33.5 (0.21)
ASi^5	−20.8 (0.03)	−46.3 (0.28)	−33.6 (0.34)	−34.2 (0.04)	−20.8 (0.46)	−46.3 (0.52)	−33.4 (0.57)	−34.2 (0.53)
ASi^6	−21.8 (0.02)		−35.1 (0.05)		−22.0 (0.22)		−33.9 (0.17)	−35.0 (0.26)

[a] Chemical shifts (ppm) from TMS. Si^2 and Si^3 only resolved in 2 and 6. [b] Contains 8% D_4. [c] Si^1 and Si^2 not resolved in 3 and insufficiently resolved for an integral in 7.

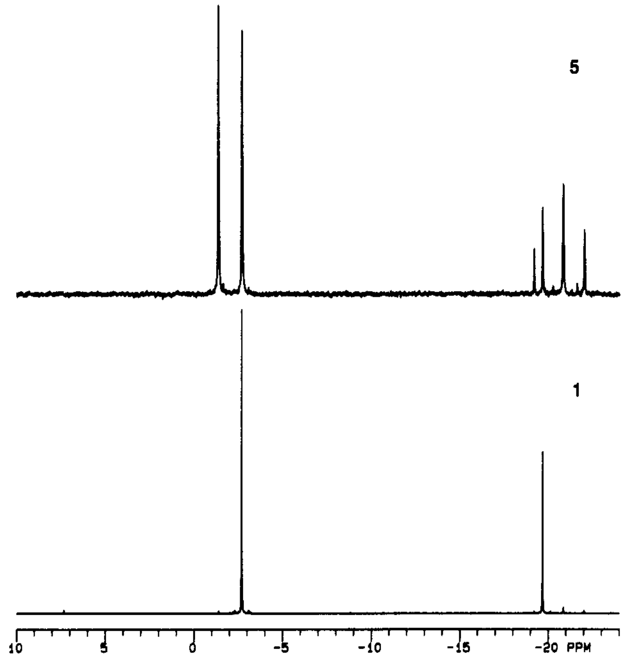
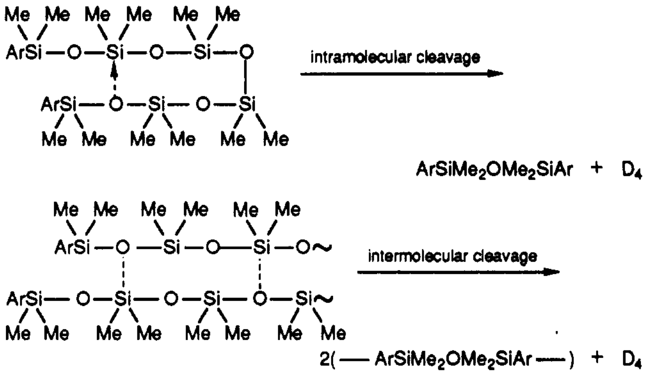
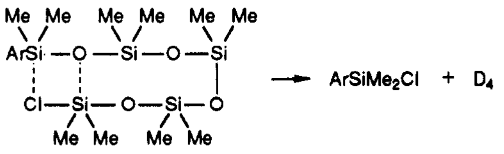


Figure 2. ^{29}Si NMR spectra of 1 and 5 at 79.5 MHz in $CDCl_3$.

where a cyclic structure promotes formation of the SiOSi polymer linkage while aiding the removal of the leaving group by the formation of neutral amine in the presence of a relatively nonpolar solvent. In the above transitional complex, formed as a result of nucleophilic attack, the silicon is more electronegative than in its initial state since it receives an additional electron pair from the oxygen. The high concentration of alternating structure in 1 suggests that the base, dimethylamine, is not sufficiently basic to invoke equilibration. This is a process whereby Si–O linkages of a siloxane or mixture of siloxanes are continuously broken and re-formed until the system reaches an equilibrium state at the thermodynamically most stable conditions. The presence of a very low concentration of block structure in 1 may be attributed to the self-condensation of BHB or BHB-terminated silarylene–siloxanes at elevated temperatures. Water liberated during this condensation may hydrolyze the Si–N bonds in the silane to the corresponding silanol. This silanol may either self-condense or react with another molecule of bis(dimethylamino)silane to produce diad and triad structures. On the other hand, 5 consists of a major proportion of nonalternating structures including ~8% D_4. The random nature of the polymer structure in 5 may be attributed to the equilibration caused by the HCl byproduct. The high concentration of block structure could be either from equilibration or from acid-catalyzed condensation of BHB or hydroxy-terminated BHB, since the self-condensation of BHB by thermal means will not occur as the reaction was carried out at 0–5 °C. Under acid equilibration conditions, D_4 may be obtained by either of the mechanisms described below:



The formation of D_4 in 5 may also result from the cleavage of the Si–O–Si bonds by HCl producing silanol-terminated dimethylsiloxy end units which in turn may react with the chlorosilane giving chlorine-terminated siloxane. The polar terminal Si–Cl bond may eliminate D_4 intramolecularly through a four-membered transition state as shown below:



At the suggestion one of the reviewers, a drop of concentrated HCl was added to 1. After 24 h the ^{29}Si

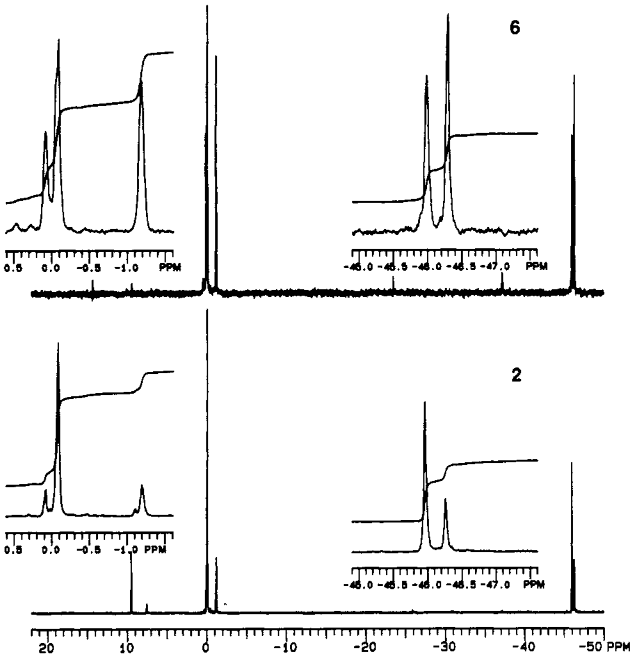


Figure 3. ^{29}Si NMR spectra of **2** and **6** at 79.5 MHz in $CDCl_3$.

spectrum showed rearrangements to a nonalternating polymer containing silarylene and dimethylsiloxane diads.

The ^{29}Si NMR of **2** and **6** show major absorptions at −0.1 and −46.0 ppm due to silarylene and diphenylsiloxy groups, respectively, in the polymer. Numerous minor absorptions are present including an absorption in **2** at +9.4 ppm consistent for trimethylsilyl end groups next to a diphenylsiloxane unit. A minor absorption at −46.3 ppm is attributed to $SiPh_2OSiPh_2$ diads in the polymers. Self-condensed product from arylenedisilanol is present in **2** and **6** at the 19% and 35% levels, respectively. Since block BHB formation consumes BHB, the excess silane must form diads and triads because monomer is not observed in the product. Therefore, we suggest that the water formed when two BHB molecules or BHB-terminated oligomers condense reacts with the Si–N bond as in **1** to produce the corresponding silanol which in turn should readily self-condense to give the observed diads. Unlike **1** and **5**, no $(SiPh_2O)_3$ blocks are observed in **2** and **6**. In addition to block silarylene units at −1.2 ppm, the $SiMe_2$ of the arylene shows two peaks in **2** and **6** that must be attributed to siloxane sequence effects. The absorption at −0.1 ppm is proportional to the alternating $SiPh_2O$ level and is twice the absolute intensity of the −46.0 ppm absorption, $\mathrm{OSiMe_2Ar}\mathit{Si}\mathrm{Me_2OSiPh_2OMe_2}\mathit{Si}\mathrm{ArSiMe_2O}$, the other silarylene resonance, at +0.1 ppm, is proportional to the diad level and is equal to the intensity of the −46.4 ppm absorption, $\mathrm{OSiMe_2Ar}\mathit{Si}\mathrm{Me_2OSiPh_2OSiPh_2OMe_2}\mathit{Si}\mathrm{ArSiMe_2O}$. This long-range siloxane sequence effect on the silarylene ^{29}Si chemical shifts is not observable in the other polymers; the anisotropy of the phenyl is probably a significant factor in increasing the dispersion of the chemical shifts of the silarylene.

Polymer **3** showed two peaks in a 3:2 ratio for the methylphenylsiloxane at −32.1 and −33.6 ppm, which are assigned to SiMePhO between two arylenes and SiMePhOSiMePh diads, respectively. Absorptions due to diads and triads of $(SiMePhO)_n$, $n = 2$ and 3 or higher, are observed at much greater levels in **7**. The absorption due to $SiMe_2$ of the silarylene in the strictly alternating polymer at −1.1 ppm partially overlaps the block silarylene peak at −1.2 ppm. It is not clear at this juncture how the

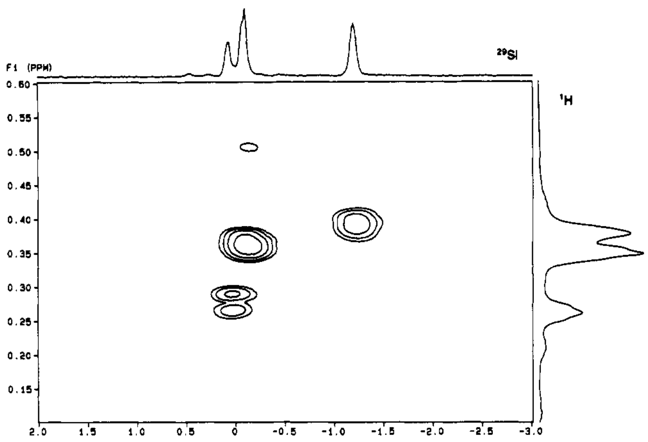


Figure 4. 2D ^{1}H,^{29}Si COSY NMR spectrum of **6**, run with the usual heteronuclear correlation pulse sequence but with delay times optimized for a 10-Hz ^2J(SiH).

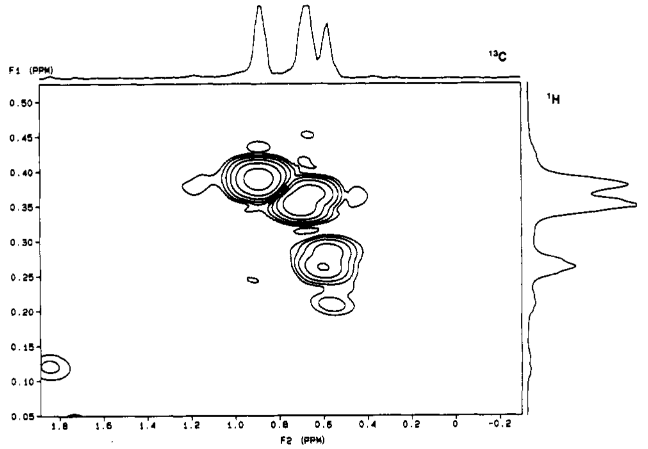


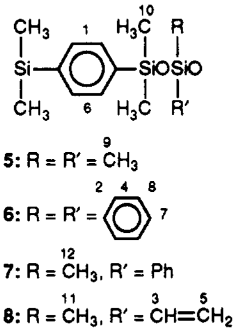
Figure 5. 2D ^{1}H,^{13}C COSY NMR spectrum of **6** (CH_3 region).

reactivity of methylphenyldichlorosilane toward disilanol monomer or SiOH terminated polymer might influence the observed structures.

The ^{29}Si NMR shows **4** to be quite pure with end group absorptions below 5% and a 4% concentration of block structures. A weak absorption at −34.2 ppm is attributed to a low level (~4%) of SiMeVinO diads. The vinyl group in the silane enhances the electropositive character of silicon, which should facilitate a rapid reaction between BHB and bis(dimethylamino)methylvinylsilane yielding alternate structures. In contrast, the ^{29}Si NMR spectrum of **8** showed two peaks at −1.3 and −1.7 ppm of equal intensity, which are assigned to block $[\mathrm{Ar}\mathit{SiMe}_2\mathrm{O}\mathit{SiMe}_2\mathrm{Ar}]$ and alternating $[\mathrm{Ar}\mathit{SiMe}_2\mathrm{OSiMeVinO}\mathit{SiMe}_2\mathrm{Ar}]$ structures, respectively. Three peaks at −33.5, −34.5, and −35.0 ppm are present in a 1:2:1 ratio due to alternating, diad, and triad methylvinylsiloxy block units in the polymer.

Much greater randomization is observed in **5**–**8** formed in the presence of acid-producing monomers as compared to polymers **1**–**4**, where the reactions are carried out with base-producing monomers. The nature of the substituent on the silane seems to have little effect in the formation of random polymers (**5**–**8**) with the reactions between chlorosilane and disilanol. Polymers **1** and **4** are over 95% alternating, whereas **2** and **3** are 75% and 60% alternating, respectively. The electronic and steric factors appear to influence the observed structural distribution, particularly in **1**–**4**. From the point of charges, the methyl group in silane in **1** is an electron donor, which should retard the substitution, but the less bulky methyl groups enhance

Table III
Chemical Shift Assignments of Silarylene–Siloxane Homopolymers from ^{13}C Spectra[a]



assgnmt		1	2	3	4	5	6	7	8
C_1		140.78	140.78	140.32	140.57	140.76	140.77	140.77	140.69
C_2			135.81	137.58			140.22	137.60	
C_3						137.12			137.23
C_4			134.17	133.04			134.17	133.20	
C_5					132.92				133.13
C_6		132.24	132.17	132.04	132.18	132.23	132.24	132.21	132.33
C_7			129.71	129.35			127.52	129.49	
C_8			127.52	127.41			127.64	127.53	
C_9	alt	1.32				1.34			
	diad					1.18			
	triad					1.04			
C_{10}	alt	0.72	0.66	0.48	0.69	0.76	0.62	0.63	0.80
	diad		0.54			0.70	0.53		0.74
	block		0.85			0.89	0.77	0.87	0.90
C_{11}	alt				−0.05				−0.01
	diad								−0.15
C_{12}	alt			−0.47				−0.43	
	diad							−0.50	
	triad							−0.55	

[a] Chemical shifts (ppm) relative to TMS.

Table IV
2D Heteronuclear Correlation of ^{29}Si, ^{1}H, and ^{13}C Chemical Shifts in 6

assignment	chemical shifts, ppm ^{29}Si	^{1}H	^{13}C
block BHB	−1.20	0.37	0.77
Ar*SiMe*$_2$OSiPh$_2$OSiMe$_2$Ar	−0.20	0.35	0.62
Ar*SiMe*$_2$OSiPh$_2$OSiPh$_2$O	0.00	0.26	0.53

the reaction between disilanol and the bis(dimethylamino)dimethylsilane as compared with the other silanes. In 1 and 4 the formation of nearly alternating polymers suggests that replacing a methyl with a vinyl in bis(dimethylamino)dimethylsilane has little effect on the product distribution. It appears that the differences in the steric and electronic effects between the two silanes are too small to see any appreciable differences in the product distribution (Table II). On the other hand, substitution of one or both methyls for phenyls in bis(dimethylamino)dimethylsilane increases the block and diad proportions. It may be argued that steric constraints around the silicon in methylphenyl- and diphenylaminosilanes encourages the self-condensation of BHB-terminated polymers even though the electron-withdrawing nature of the phenyl groups should favor the formation of alternating structures.

The nature of the substituent on the dichlorosilanes seems to have little effect in the formation of both alternating and random structures in 5–8. Acid equilibration of the condensation reactions seems to play a predominant role in the observed structural distribution in 5–8. Polymers 5–8 have nearly the same concentration of diad structures, which probably reflects similar experimental conditions in the synthesis.

^{13}C NMR. The ^{13}C assignments (Table III) for the major absorptions in the nearly alternating polymers 1, 3, and 4 agree with those reported earlier.[3,4] The aryl chemical shifts in 2 are very similar to those in 3. The methyl resonances in 1–4 are sharp singlets and readily assigned by comparison to 2 in which no OSiMeRO is present. The ^{13}C methyl assignments in 1, 3, or 4 are confirmed by the 2:1 or 4:1 intensity ratios of the arylene/siloxane absorptions. Multiplets are observed in the methylsilicon region in 5–8 due to the presence of diad siloxane and block silarylene units in addition to the alternating units found in 1–4. Three absorptions are observed in 6 that were unambiguously assigned via a pair of 2D NMR experiments. A ^{29}Si,^{1}H COSY experiment, utilizing a long-range 7-Hz $^{2}J(SiH)$ coupling for polarization transfer,[13] (Figure 4) correlates the ^{29}Si absorptions with the three major

Table V
Glass Transition Temperatures of Silarylene–Siloxane Polymers

polymers	T_g, °C bis(dimethylamino)silanes 1–4	dichlorosilanes 5–8	bis(ureido)silanes[a]
1, 5: R = R′ = CH_3	−61	−65 (−65)[b]	−62
2, 6: R = Ph, R′ = Ph	−9 (+1, −4)[c]	−14	
3, 7: R = CH_3, R′ = Ph	−35 (−32)[c]	−31 (−32)[b]	−32
4, 8: R = CH_3, R′ = Vin	−62	−65 (−76)[b]	−69

[a] Reference 3. [b] Reference 4. [c] Reference 5.

methyl resonances in the proton spectrum (Table IV). Then a normal ^{13}C,^{1}H COSY (Figure 5) experiment correlates the carbon shifts with the protons, also given in Table IV. Similar experiments are not possible in the other samples because distinct absorptions are not observed for the proton methyl resonances, nor are ^{29}Si absorptions resolved due to sequence effects on the silarylene resonances. Nevertheless, the ^{13}C resonances can be assigned in **5**, **7**, and **8** by comparison to **1**–**4** and the upfield shifts of approximately 0.2 ppm found in **6** when Me_2SiAr is replaced by Me_2SiO. These shifts are clearly found to be additive in **5** (Table III). Thus, the absorption at 1.34 ppm is assigned to the Me_2SiO in the alternating sequence. In the diad the absorption shifts upfield 0.16 ppm since the Me_2SiO has one α-silarylene and one α-siloxane. In the triad the Me_2SiO has two α-siloxanes and is shifted upfield an additional 0.14 ppm. The 1:2:1 intensity ratio for the three absorptions at 1.34, 1.18, and 1.04 ppm matches that found in the ^{29}Si spectrum (Table II).

The aromatic and olefinic regions of the ^{13}C NMR spectra of **5**–**8** are also much more complicated than those of **1**–**4** due to extensive randomization. Multiplets are also observed for all these absorptions due to the long-range effects of sequence on the chemical shifts.[17] The aromatic and olefinic chemical shifts reported in Table III are for the centers of multiplets.

Characterization of Silarylene–Siloxane Polymers. The glass transition temperatures of polymers **1**–**8** have been determined by differential scanning calorimetry. The data agree well with previous workers (Table V). The glass transition temperatures of exactly alternating polymers[3,4] are comparable to those of **1**–**4**. It is, however, surprising that the T_g of **1**–**4** are comparable to those of **5**–**8** despite the fact that the latter materials have substantial diad structures.

IV. Conclusions

Sequence analyses of **1**–**8** indicate that, under the reaction conditions employed, considerably greater randomization occurs in the products prepared from dichlorosilanes relative to bis(dimethylamino)silane. This confirms that the redistribution of silarylene–siloxanes under acid conditions is more facile than under basic conditions.[21]

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