Sequence Analysis of Silarylene–Siloxane Copolymers

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ABSTRACT: A series of nine different silarylene–siloxane copolymers were prepared by condensation polymerization of 1,4-bis(dimethylhydroxysilyl)benzene with a mixture of different bis(dimethylamino)- and dichlorodialkylsilanes. The structural characterization of the copolymers was carried out by ^{1}H, ^{29}Si, and ^{13}C NMR spectroscopy, differential scanning calorimetry, and gel permeation chromatography. ^{29}Si NMR gives the siloxane distribution of alternating, diad, and triad sequences. Polymers prepared from dichlorosilane show greater randomization than those prepared from bis(dimethylamino)silanes. ^{13}C NMR gives detailed information about the sequence distribution analysis and shows that the alternating silarylene–siloxane copolymers follow Bernoullian statistics.

I. Introduction

The development of silarylene–siloxane polymers in the early 1960s was a major breakthrough in the search for high-temperature-performance elastomers.[1] Incorporation of the phenylene moiety into the siloxane backbone minimizes the depolymerizability of poly(dimethylsiloxane) to cyclic trimers and tetramers. The most useful methods currently employed for the synthesis of silarylene–siloxane polymers are homocondensation of 1,4-bis(dimethylhydroxysilyl)benzene (BHB) with an active silane monomer such as bis(amino)silanes,[2] chlorosilanes,[3] siloxazanes,[4] or acetoxysilanes.[5] All the leaving groups yield a byproduct that causes chain cleavage producing low molecular weight polymers. Dvornic and Lenz[6–8] reported the synthesis of high molecular weight exactly alternating polymers by condensation of BHB with bis(uriedo)silane. The byproduct of the reaction is urea, a neutral species, which does not participate in the chain-cleavage process. Recently, we prepared high molecular weight silarylene–siloxane polymers by using Stewart's multistep polymerization technique.[9] Synthesis of silarylene–siloxane copolymers enables one to tailor the polymer properties. Arrangement of repeating blocks in the polymer chain also affects the properties of the polymers. In the present paper, we report the detailed sequence analysis of copolymers by ^{29}Si and ^{13}C NMR spectroscopy.

II. Experimental Section

^{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. Chemical shifts are given relative to tetramethylsilane, 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. Quantitative ^{29}Si spectra, were obtained after adding approximately 0.02 M Cr(acac)$_3$ to each sample to serve as a relaxation agent.[9]

^{13}C spectra were obtained on samples without relaxation reagent in order to minimize the carbon line widths. The widths (at half-height) of the ipso carbons were typically 0.7–1.0 Hz in these samples. These ^{13}C spectra line widths doubled at the Cr(acac)$_3$ levels used in the samples prepared for the ^{29}Si spectral analysis. Typical carbon relaxation times for the ipso carbon were estimated from inversion–recovery experiments, 180°–τ–90°, on 1 and 3. The carbons were nulled at τ = 3.5 s, indicating T_1 is approximately 5 s. The quantitative NOE-suppressed ^{13}C spectra of 1–4 were obtained with 5-s acquisition times on expanded sweeps (2000 Hz) with a 20-s relaxation delay in 10-mm NMR tubes.

Materials. 1,4-Bis(hydroxydimethylsilyl)benzene (BHB), bis(dimethylamino)dialkylsilanes, and dichlorodialkylsilanes were obtained from Petrach Systems and Aldrich Chemical Co. The materials were purified as described in the preceding paper.[9]

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 refluxing over a sodium–benzophenone solution under a dry nitrogen atmosphere, followed by distillation.

Condensation of BHB with a Mixture of Bis(dimethylamino)dialkylsilanes. BHB (1 mol) and desired amounts of the mixture of bis(dimethylamino)dialkylsilanes (Table I) were added to toluene and allowed to react in an inert atmosphere at 105 °C in a manner similar to the procedure described in the preceding paper.[9] At the end of the reaction the polymer was refluxed with hexamethyldisilazane to give trimethylsilyl-terminated polymer.

Cocondensation of BHB with Chlorosilanes. The polymerizations were carried out according to the procedure described in the preceding paper.[9] The results are summarized in Table I.

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-3388 with GPC (REV2048) programming.

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 copolymers **1–4** were prepared by solution copolycondensation of 1,4-bis(hydroxydimethylsilyl)benzene with bis(dimethylamino)silanes at 105 °C. Similar copolymers **5–9** were prepared by the condensation of BHB with analogous dichlorosilanes.

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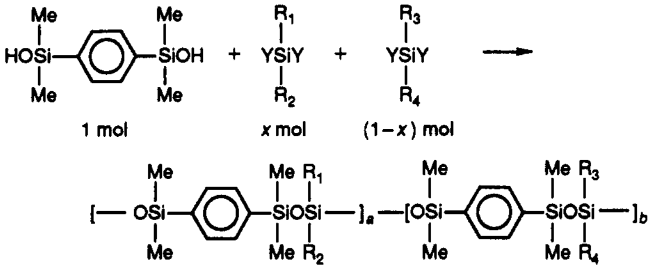
Table I
Compositions, Molecular Weights, and Glass Transition Temperatures of Silarylene–Siloxane Copolymers[a]

	monomer content, mole fraction charge						
polymer	DMS	DPS	MPS	MVS	$\bar{M}_w$	MWD	T_g, °C
1	0.75	0.25	0	0	21 400	2.0	-44
2	0.25	0.75	0	0	16 300	1.4	-38
3	0.50	0	0	0.50	32 900	2.4	-61
4	0	0.50	0	0.50	14 700	2.4	-31
5	0.50	0.50	0	0	42 000	3.1	-31
6	0.50	0	0	0.50	44 300	2.8	-67
7	0	0.50	0	0.50	41 700	3.2	-31
8	0	0.50	0.50	0	42 300	3.1	-19
9	0.50	0	0.50	0	39 300	2.7	-50

[a] All polymers were prepared as 1.00 silarylene/siloxane. DMS, bis(dimethylamino)dimethylsilane or dichlorodimethylsilane; DPS, bis(dimethylamino)diphenylsilane or dichlorodiphenylsilane; MPS, bis(dimethylamino)methylphenylsilane or dichloromethylphenylsilane; MVS, bis(dimethylamino)methylvinylsilane or dichloromethylvinylsilane. Polymers 1–4 are made with bis(dimethylamino)silanes and polymers 5–9 are made with dichlorosilanes.

Table II
Molar Ratios of Silarylene (BHB)–Siloxane ($SiMe_2O$, SiMePhO, SiMeVinO, or $SiPh_2O$) Copolymers from ^{29}Si NMR

	charge					mole ratios from ^{29}Si NMR					mole ratios from ^{1}H NMR				
	BHB	Me_2	MePh	MeVin	Ph_2	BHB	Me_2	MePh	MeVin	Ph_2	BHB	Me_2	MePh	MeVin	Ph_2
1	50	37.5			12.5	48	41			11					
2	50	12.5			37.5	49	12			39					
3	50	25		25		50	25		24						
4	50			25	25	50			26	23					
5	50	25			25	52	24			24	51	24			25
6	50	25		25		48	24		28		49	25		26	
7	50			25	25	48			22	30	49			22	30
8	50		25		25	41		32		27					
9	50	25	25			46	25	29			45	26	29		
10	50		50			46		54							



1, 2: Y = NMe_2, R_1 = R_2 = Me, R_3 = R_4 = Ph
3: Y = NMe_2, R_1 = R_2 = Me, R_3 = Me, R_4 = Vin
4: Y = NMe_2, R_1 = R_2 = Ph, R_3 = Me, R_4 = Vin
5: Y = Cl, R_1 = R_2 = Me, R_3 = R_4 = Ph
6: Y = Cl, R_1 = R_2 = Me, R_3 = Me, R_4 = Vin
7: Y = Cl, R_1 = R_2 = Ph, R_3 = Me, R_4 = Vin
8: Y = Cl, R_1 = R_2 = Ph, R_3 = Me, R_4 = Ph
9: Y = Cl, R_1 = R_2 = Me, R_3 = Me, R_4 = Ph

The GPC data (Table I) indicate that polymers 5–9 prepared with chlorosilanes have higher molecular weights than the polymers 1–4 prepared with bis(dimethylamino)silanes. Further, the polydispersity of 5–9 is higher than 1–4, indicating the possibility of greater equilibration of the former than the latter.

Structural Characterization. We have reported the use of ^{29}Si NMR to determine the siloxane sequences in silarylene–siloxane polymers[9] and in copolymers of dimethylsiloxane with diphenylsiloxane.[10] The sequence arrangements in copolymers of dimethylsiloxane with methylvinylsiloxane have been reported by Ziemelis and Saam.[11] An extension of the latter work provides an explanation for the complex multiplet patterns observed in the random copolymers 5–9, but does not describe the sequence about the silarylene moieties. However, ^{13}C NMR spectra enabled a complete description of the sequence in copolymers 1–4. The ^{13}C spectra were too complex to interpret at the same level in 5–9, but this is consistent with random structures observed in the ^{29}Si NMR spectra of these copolymers.

^{1}H NMR. The ^{1}H assignments have been reported by Dvornic, Lai, and Lenz.[3,6–8] Ratios of the silarylene (BHB) and siloxanes can be determined directly from the proton integration for all samples except 8, for which the absorptions overlap. The Me_2SiO and MeVinSiO levels are determined directly from the methyl and vinyl absorptions at 0.10 and 5.9–6.5 ppm, respectively. The MePhSiO and Ph_2SiO levels are determined from the absorption at 7.2 ppm assigned to the meta and para protons of the phenyl ring. The silarylene level is determined from the intensity of the 7.6 ppm absorption after correcting for the ortho protons of the phenyl groups when necessary. Results are given in Table II and compared to the charge.

^{29}Si NMR. The ^{29}Si chemical shifts of the major multiplets in the silarylene–siloxane copolymers 1–9 are readily assigned by comparison to the spectra of the homopolymers[9] and to the spectra of polysiloxanes.[12] Chemical shifts are given in Table III and the overall composition in Table II. The composition is in reasonable agreement with the feed for all samples except 8. The ratios determined from the ^{29}Si NMR agree with those calculated from the proton spectra, indicating that partial saturation of the silicon resonances, under the conditions employed to obtain the spectra of 5–9, is not a factor in the quantitative analysis. Figure 1 shows representative ^{29}Si spectra of 3 and 6. In polymer 3, expected to contain alternating triads of silarylene–siloxane–silarylene,[9] two absorptions are observed in the BHB region, one for BHB α to $SiMe_2O$ at −2.5 ppm and one for BHB α to SiMeVinO at −1.7 ppm. Absorptions at −19.6 and −33.6 ppm are assigned to $SiMe_2O$ and SiMeVinO between silarylenes in the alternating triads. The minor absorption at −1.2 ppm is attributed to the adjacent BHB silicons in the diad structure $ArSiMe_2OSiMe_2Ar$, which is present at about the 2% level. The intensity of this absorption gives the block BHB level. Minor ab-

Table III
Concentrations of Different Structures in Silarylene–Siloxane Copolymers, Normalized for Each Group

chemical shift	assignment[a]	1	2	3	4	5	6	7	8	9	10
0.03, −0.13	BHB/Ph_2	20	70		35	35		42	31		
−0.2 to −0.6	BHB/MeH										
−1.2	block BHB	2	6	2	10	42	52	36	23	76	100
−1.3	BHB/MePh								46		
−1.7	BHB/MeVin			47	56		26	23			
−2.5	BHB/Me_2	78	24	51		23	22			24	
−19.6	$SiMe_2O$ alter	95	98	100		55	27			23	
−20.7	$SiMe_2O$ diad	3				38	24				
−21.9	$SiMe_2O$ triad	2				8	4			8	
−20.0 to −21.5	$SiMe_2O$ other		2				45			69	
−33.0	SiMePhO alter								37	18	61
−33.44, −33.53	SiMePhO diad									29	34
−34.0	SiMePhO triad										5
−33.5 to −35.5	SiMePhO other								63	53	
−33.6	SiMeVinO alter			100	96		25	49			
−34.4	SiMeVinO diad						29				
−35.1	SiMeVinO triad						6				
−35.5 to −36.5	SiMeVinO other				4		40	51			
−46.0	$SiPh_2O$ alter	93	89		72	47		45	28		
−46.4	$SiPh_2O$ diad	7	11		22	19		22	21		
−46.8	$SiPh_2O$ triad								5		
−47.0 to −48.5	$SiPh_2O$ other				6	35		33	47		

[a] Diad, homonuclear diad α to arylene; triad, homonuclear triad α to arylene; other, diad or triad α to arylene containing different siloxane groups.

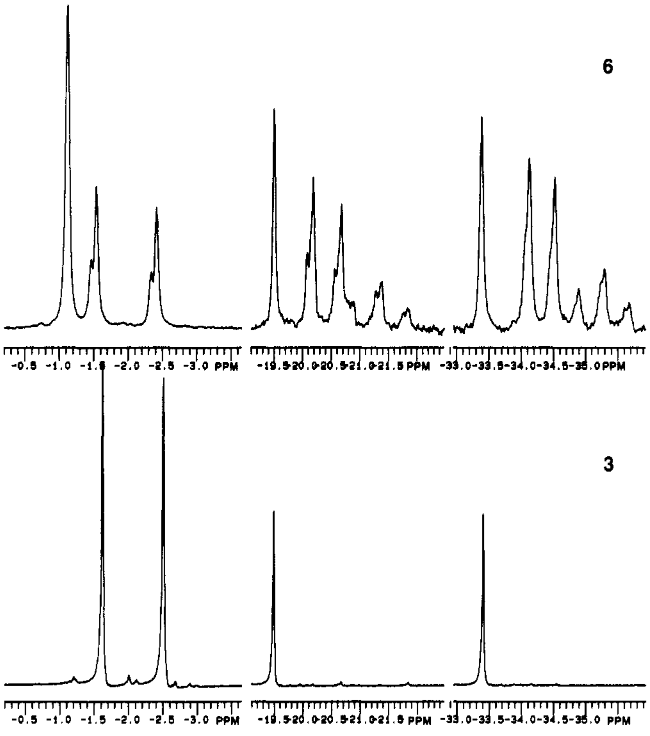


Figure 1. ^{29}Si NMR spectra of 3 and 6 at 79.5 MHz in $CDCl_3$ with 0.2 M $Cr(acac)_3$.

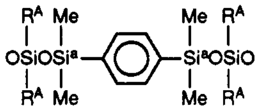
sorption at −46.4 ppm is due to $SiPh_2OSiPh_2$ diad in 1, 2, and 4, and low levels of $SiMe_2O$ diads are observed in 1. The overall diad concentration in the copolymers is 2-fold lower than the diad concentrations observed in the homopolymers prepared under similar conditions.[9] It is not surprising that the ^{29}Si NMR of 3 is a nearly alternating copolymer since the corresponding homopolymers are almost perfectly alternating.

The ^{29}Si NMR obtained on the analogous copolymers prepared with chlorosilanes show multiplets (Table III) for the siloxane resonances that can be attributed to randomization of the siloxane diads and triads, i.e., $SiR_1R_2OSiR_3R_4$-type diads. The 50:50 dimethylsiloxane–methylvinylsiloxane copolymer, 6, gives an excellent example of the copolymer sequence effects on the ^{29}Si chemical shifts (Figure 1). The most intense BHB resonance, at −1.2 ppm, is attributable to block BHB. The analogous resonance in 3 is under 2% of the intensity of the other BHB resonances. Six absorptions are observed (Figure 1) for the SiMeVinO between −33 and −37 ppm, and six similarly spaced multiplets are observed for the $SiMe_2O$ between −19.6 and −21.9 ppm. The absorptions are assigned to the following sequences based on the following analogies to reference material:

chemical shift, ppm	assignment
−19.6	$ArSiMe_2O\mathit{Si}Me_2OSiMe_2Ar$
−20.2	$ArSiMe_2O\mathit{Si}Me_2OSiMeVinO$
−20.8	$ArSiMe_2O\mathit{Si}Me_2OSiMe_2O$
−21.0	$OSiMeVinO\mathit{Si}Me_2OSiMeVinO$
−21.4	$OSiMe_2O\mathit{Si}Me_2OSiMeVinO$
−21.9	$OSiMe_2O\mathit{Si}Me_2OSiMe_2O$
−33.6	$ArSiMe_2O\mathit{Si}MeVinOSiMe_2Ar$
−34.4	$ArSiMe_2O\mathit{Si}MeVinOSiMeVinO$
−34.6	$ArSiMe_2O\mathit{Si}MeVinOSiMe_2O$
−35.0	$OSiMeVinO\mathit{Si}MeVinOSiMeVinO$
−35.4	$OSiMeVinO\mathit{Si}MeVinOSiMe_2O$
−35.8	$OSiMe_2O\mathit{Si}MeVinOSiMe_2O$

The assignments of the triads at −19.6, −20.8, and −21.9 ppm are identical with those found in the homopolymer,[9] in which a 1.1 ppm upfield shift is observed when $SiMe_2Ar$ is replaced by $SiMe_2O$ in the alternating sequence. Since 0.7 ppm upfield shifts are observed when $SiMe_2Ar$ is replaced by SiMeVinO in homopolymers of the silarylene with methylvinylsiloxane,[9] the absorptions at −20.2 and −21.4 ppm are assigned to the mixed siloxane diads. The assignment in the SiMeVinO region of the spectrum follows identical reasoning and the shifts, relative to the perfectly alternating homopolymer, are the same. The assignment of the methylvinylsiloxane/dimethylsiloxane triads agrees with those reported for the siloxane copolymer prepared by Ziemelis and Saam.[11] The absorptions in the dimethylsiloxane region of the spectrum are multiplets due to tacticity of the adjacent methylvinylsiloxane units and/or pentad sequence effects. Similar assignments exist in all of the copolymers, except that in most cases the absorptions overlap and assignments to diads and triads are not possible. Copolymerization of BHB with chlorosilanes, irrespective of the kind of substituent on the chlorosilane, produced random polymer. Reasoning similar to that used with the homopolymers[9] can be extended to copolymers; i.e., the acid produced in the polymerization causes equilibration leading to random structures.

^{13}C NMR Spectra of Copolymers. The sequence analysis in the silarylene–siloxane copolymers is identical with the analysis used in polyesters prepared from terephthalate, ethylene glycol, and butane diol.[13] Sequence determination requires observation of silarylene absorptions that distinguish the following three structures: where $SiR_2{}^AO$ and $SiR_2{}^BO$ are two different siloxane units, such as $SiMe_2O$ and $SiPh_2O$ in 1.



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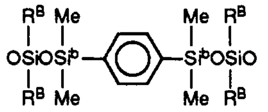

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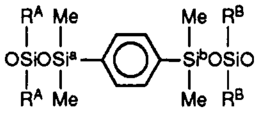


III

The ^{13}C or ^{29}Si spectra of the dimethylsilyl units in structures I and II are singlets because, to the triad level shown, the structure is symmetrical. The two dimethylsilyl groups in structure III are intrinsically different since one is α to the $SiR_2{}^B$ whereas the other is α to $SiR_2{}^A$. To first order, these chemical shifts should be similar to the analogous shifts in I and II, respectively. Unless there is a long-range effect on the chemical shifts, they will in fact be identical with the analogous silicons in I and II and the only information available from the spectra will be the ratio of components A and B. Note, for example, that Si^a in I differs from Si^a in III by the substitution of R_B for R_A eight bonds away from Si^a. It is not surprising, therefore, that the ^{29}Si spectra of the silarylene $SiMe_2$ shows only two types of $SiMe_2Ar$ resonances independent of sequence in all the copolymers. The −46.0 ppm absorption assigned to the diphenylsiloxy in the silarylene copolymer containing dimethyl and diphenylsilyl units is a closely spaced multiplet, which is presumably due to long-range sequence effects, but the resolution is insufficient to determine the relative areas of the peaks. The carbon spectra of the ipso arylene carbons of the copolymers do show absorptions that are sensitive to sequence. The observation of chemical shift effects over eight bonds is almost certainly a long-range conformational effect on the bond angles and γ-carbon shifts in the copolymer.[14] The ^{13}C spectra of the BHB ipso carbon in copolymers 1–4 show four different absorptions for sequences I and III. A typical example is given in Figure 2. The integrated peak intensities of the quaternary aromatic carbons of different silarylene–siloxane copolymers are listed in Table IV. The middle two absorptions have chemical shifts nearly identical with the singlets observed in the homopolymers. The outer two absorptions are new absorptions attributable to sequence III, which are assigned to the nonequivalent carbons by comparison of their chemical shifts to those of the homopolymers. The ratio of $SiR_2{}^A$ to $SiR_2{}^B$ in the copolymer is given by the ratio of the areas of $a + a'/b + b'$. This ratio, determined from the ipso carbons in the ^{13}C spectra, is similar to that determined from the ratios of the SiR_2 peaks in the ^{29}Si spectrum and confirms the ^{13}C assignment. Ipso peak areas were determined for four different copolymers with the three different possible combinations of R^A,R^B = Me_2, Ph_2, and MeVin. The ^{13}C spectra of 1 and 2 show numerous minor extraneous absorptions attributed to the presence of low levels of diphenylsiloxane diad. The observed R^A/R^B ratios, peak areas for the four ipso carbon peaks, and triad

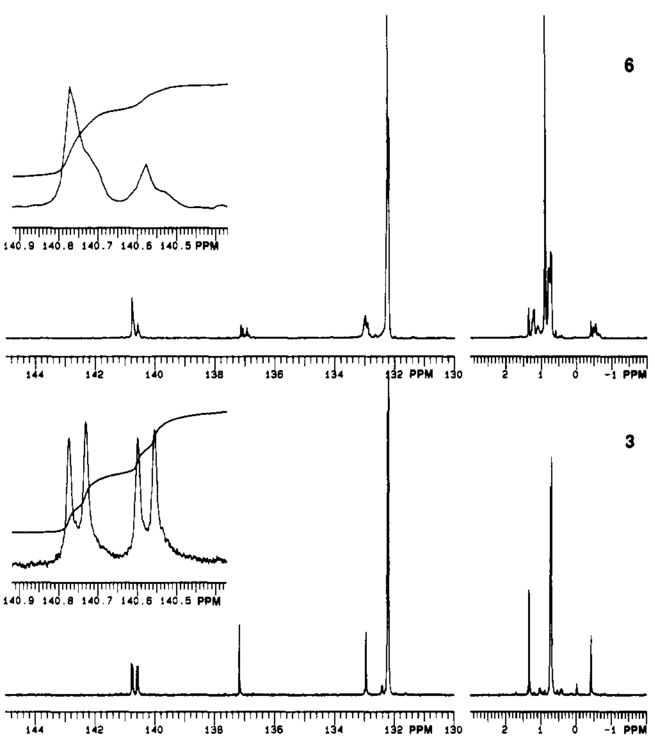


Figure 2. ^{13}C NMR spectra at 100.6 MHz of 3 and 6 in $CDCl_3$. The expansion of 3 is from a separate spectrum with an acquisition time of 4.0 s. The two strongest absorptions in 3 are off scale; their true intensities are 4-fold higher than shown.

Table IV
^{13}C NMR Chemical Shifts and Relative Intensities of Ipso Carbon Peaks in Silarylene–Siloxane Copolymers[a]

polymer	areas (normalized)			
1				
chem shift	140.09	140.20	140.68	140.80
	Ph-Ar-Me	Ph-Ar-Ph	Me-Ar-Me	Me-Ar-Ph
obsd	19	50	10	21
calcd	21	48	10	21
2[b]				
obsd	16	6	60	18
calcd	17	5	61	17
3				
chem shift	140.07	140.15	140.50	140.58
	Ph-Ar-Vin	Ph-Ar-Ph	Vin-Ar-Vin	Vin-Ar-Ph
obsd	25	18	35	22
calcd	24	18	33	24
4				
chem shift	140.54	140.59	140.72	140.76
	Vin-Ar-Me	Vin-Ar-Vin	Me-Ar-Me	Me-Ar-Vin
obsd	26	26	23	25
calcd	25	27	23	25
10				
chem shift	140.24	140.29	140.61	140.65
	Mp-Ar-D	Mp-Ar-Mp	D-Ar-D	D-Ar-Mp
obsd	19	5	58	20
calcd	18	6	58	18

[a] Chemical shifts (ppm) are given for the first ipso carbon in the sequence, in which, for example, PhArMe is short for $SiPh_2OMe_2SiArSiMe_2OSiMe_2O$. Mp is a SiMePhO alternating unit and D is the diad, SiMePhOSiMePhO. This is a copolymer of 78% $SiMePh_2O$ units and 22% $SiMePh_2OSiMePh_2O$ units with BHB.
[b] Chemical shifts same as with 1.

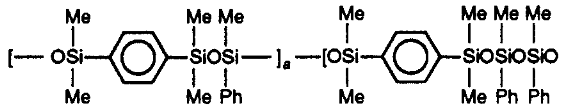
Table V
Molar Ratios and Triad Probabilities of Silarylene–Siloxane Copolymers Obtained from ^{29}Si and ^{13}C Carbon Spectra

		diad ratios		triad probabilities		
polymer	charge	obsd ^{13}C	obsd ^{29}Si	R^ASiR^A	R^BSiR^B	R^ASiR^B
1	25:75	31:69	24:76	10	50	40
2	75:25	78:22	76:24	60	6	34
3	50:50	57:43	54:46	18	35	47
4	50:50	52:48	51:49	23	26	51
10[a]		76:24	78:22	58	5	39

[a] See footnote *a* in Table IV.

probabilities are given in Tables IV and V. Assuming a random distribution of A and B in the copolymer, the ratios of the four ipso carbon peaks are simply calculated as p_A^2, p_B^2, p_Ap_B, and p_Bp_A where p_A and p_B are the mole fractions of A and B determined from the ratio of the two pairs of ipso peaks. The calculated ratios are within experimental error of the observed values and prove that the copolymers are random.

The above analysis also explains the ^{13}C NMR spectra of nonalternating homopolymers containing only diad units, such as homopolymer **10** prepared from silarylene and methylphenylsiloxane.



This sample, analyzed as **3** in ref 9 shows a 61:34 ratio of silicons in alternating/diad SiMePhO units. But since each diad contains two SiMePhO groups, the actual ratio of alternating/diad SiMePhO units is 78:22 = *a*:*b* in structure **10**. The ^{13}C NMR spectrum appears identical with one of the copolymers, assuming this 3:1 distribution of two types of siloxanes, and the quantitative analysis is included in Tables IV and V. As expected, the homopolymer containing diads is perfectly random.

In conclusion, the byproducts liberated in the polymerization play an important role in determining the structure of the copolymers. The ^{13}C analysis proves **1–4** and **10** are random copolymers. The ^{13}C spectra of **5–9** (Figure 2 is illustrative of **6**) do not show resolved ipso absorptions, but this is expected because these samples have at least four different types of siloxane units instead of the two observable in **1–4** and **10** since the liberated acid in the synthesis causes extensive randomization to form siloxane diads as found in the homopolymers.[9] The resolution is insufficient to observe $4^2 = 16$ absorptions from the 16 possible sequences. As a result, ^{29}Si NMR is needed to unravel the microstructure in **5–9**, but it is not possible to prove by ^{13}C NMR that the sequences are random. However, observation of the random sequence in **10** strongly suggests that the copolymers with siloxane diads are also random copolymers.

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