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Sequence Distribution in Poly(dimethylsiloxane-*co*-methylvinylsiloxanes)

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ABSTRACT: ^{29}Si NMR studies of copolymerized mixtures of octamethylcyclotetrasiloxane and 1,3,5,7-tetramethyltetravinylcyclotetrasiloxane showed random sequence distribution of comonomer units at equilibrium. The same random sequencing seen in the copolymer chains could be seen in the vicinity of the chain ends as well as in the byproduced cocyclosiloxanes. This persisted over a wide range of compositions and equilibrium temperatures. The results, consistent with homopolymerization, infer the absence of enthalpic driving forces in the copolymerization. Chemical shift data from the ^{29}Si NMR are reported for various sequences of comonomer units.

Introduction

Sequence distribution of repeat units in copolymers, which is crucial in determining both their properties and applications, can be derived from an understanding of the kinetic copolymerization parameters that are typically arrived at from the Mayo–Lewis model which presumes an irreversible process.[1-3] Although copolymerizations of cyclosiloxanes are reversible, previous studies either ignored this or sought to circumvent the difficulty by limiting the copolymerization to low conversions[4,5] or by selecting strained ring monomers and mild catalysts which do not readily induce siloxane redistribution.[6,7] Such approaches are not germane to common practice where the copolymerizations are usually taken to equilibrium. The present study focuses on a siloxane copolymerization at equilibrium through interpretation of the ^{29}Si NMR spectra of equilibrated copolymers in terms of simple linkage probabilities.[8] These are calculated from the relative intensities of signals from various triad sequences and are expressed in terms of run number, sequence length, or simply probability.[9,10] Emphasis is on copolymers containing dimethylsiloxy (D) and methylvinylsiloxy (V) units made by equilibration of octamethylcyclotetrasiloxane (D_4) and 1,3,5,7-tetramethyltetravinylcyclotetrasiloxane (V_4) initiated by potassium silanolate at various compositions and equilibrium temperatures. The copolymers were chosen because of their importance in cross-linking silicone rubber[11] and because they supplement recent studies of poly(dimethylsiloxane-*co*-diphenylsiloxane) made with a similar initiator and presumably also taken to equilibrium.[12,13] The latter studies, however, did not consider the composition and sequencing of the byproduced cocyclosiloxanes which can be an important or even dominant part of the equilibrate. The present investigation focuses on these as well as on the comonomer units located in both the main chain and near the chain ends.

Table I
Cocyclotetrasiloxanes Synthesized for ^{29}Si NMR Peak Assignments

compd	unit	δ, ppm from TMS	rel intensity
D_4	D	−19.10	
$D_{(1)}D_{(2)}D_{(1)}V$	D(1)	−18.58	2.0
	D(2)	−18.99	1.0
	V	−33.50	0.9
DDVV	D	−18.44	2.0
	V	−33.02	2.0
DVDV	D	−18.01	2.0
	V	−33.39	2.0
$DV_{(1)}V_{(2)}V_{(1)}$	D	−17.91	1.0
	V(1)	−32.95	2.1
	V(2)	−32.55	1.1

Experimental Section

Spectra. ^{29}Si NMR spectra were obtained on a Varian XL-200 FT spectrometer at 39.74 MHz using proton noise decoupling and $CDCl_3$ as an interal lock. The 90° pulse width was determined to be 19 μs. Throughout the experiments a simple pulse sequence was used with a pulse width of 16 μs and an aquisition time of 0.8 s and 2.2-s delay. The spectral width was 10 000 Hz using 16K data points. Samples were prepared as 30 wt % solutions in $CDCl_3$. $Cr(AcAc)_3$ (0.8 wt %) was added as a relaxation agent and TMS as an internal reference standard. A 16-mm sample tube was used with accumulation of 300–8000 scans. These

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Table II
^{29}Si NMR Chemical Shifts[a] for Comonomer Sequences in Cocyclic Tetramers

sequence	D units	V units
$\llcorner\overline{\mathrm{DDDD}}\lrcorner$	−19.10	
$\llcorner\overline{\mathrm{VD\underline{D}D}}\lrcorner$	−18.99	−33.50
$\llcorner\overline{\mathrm{V\underline{D}D\underline{D}}}\lrcorner$	−18.58	−33.50
$\llcorner\overline{\mathrm{VDDV}}\lrcorner$	−18.44	−33.02
$\llcorner\overline{\mathrm{VDVD}}\lrcorner$	−18.01	−33.39
$\llcorner\overline{\mathrm{D\underline{V}V\underline{V}}}\lrcorner$	−17.91	−32.95
$\llcorner\overline{\mathrm{DV\underline{V}V}}\lrcorner$	−17.91	−32.55
$\llcorner\overline{\mathrm{VVVV}}\lrcorner$		−32.44

[a] In ppm from TMS.

Table III
Trimethylsilyl End-Stopped Cooligomers Synthesized for ^{29}Si NMR Peak Assignments

compound	unit[a]	δ, ppm from TMS	rel intensity
MD_3VD_3M	M	7.28	2.0
	D(1,2,3)	−21.35 to −21.96	6.1
	V	−35.87	0.95
$MD_3V_2D_3M$	M	7.22	2.0
	D(1,3)	−21.42	3.9
	D(2)	−21.99	2.1
	V	−35.47	2.0
$MD_3V_3D_3M$	M	7.23	2.0
	D(1,3)	−21.41	3.9
	D(2)	−21.99	2.2
	V(1)	−35.41	2.0
	V(2)	−35.07	1.1
$MD_3V_4D_3M$	M	7.23	2.0
	D(1,3)	−21.41	3.9
	D(2)	−21.99	2.1
	V(1)	−35.40	2.0
	V(2)	−35.02	2.0
$MD_3V_5D_3M$	M	7.24	2.0
	D(1,3)	−21.40	4.0
	D(2)	−21.99	2.3
	V(1)	−35.40	2.1
	V(2,3)	−34.99	3.4
$MD_3V_6D_3M$	M	7.24	2.0
	D(1,3)	−21.41	4.1
	D(2)	−21.99	2.0
	V(1)	−35.41	2.1
	V(2,3)	−34.95, −35.00	4.2
MD_6VD_6M	M	7.25	2.0
	D(1,6)	−21.42	3.8
	D(2)	−22.06	2.0
	D(3,4,5)	−21.91, −21.84	5.7
	V	−35.84	1.0
$MD_6V_4D_6M$	M	7.25	2.0
	D(1,6)	−21.42, −21.35	4.0
	D(2)	−22.05	2.2
	D(3,4,5)	−21.92, −21.81	5.7
	V(1)	−35.38	2.0
	V(2)	−34.99	2.0
MVD_nVM	M	8.26	2.0
	D_n	−21.92	147
	V	−35.25	2.0
$MDVD_nVDM$[b]	M	7.34	2.0
	D(1)	−21.00	2.0
	V	−36.09	
	D_n	−21.93	

[a] Numbering for D begins at D adjacent to M unit. Numbering for V units begins at V adjacent to D unit. [b] Sample contaminated with about 15% MDVDM.

Table IV
^{29}Si NMR Chemical Shifts of Comonomer Sequences in the Chains

sequence	ppm from TMS[a]	sequence	ppm from TMS[a]
$\mathrm{VV\underline{D}VV}$	(−20.82)	$\mathrm{DD\underline{V}DD}$	−35.84
$\mathrm{VV\underline{D}VD}$	(−20.89)	$\mathrm{DD\underline{V}DV}$	(−35.74)
$\mathrm{DV\underline{D}VD}$	(−20.96)	$\mathrm{VD\underline{V}DV}$	(−35.64)
$\mathrm{VV\underline{D}DV}$	(−21.28)	$\mathrm{DV\underline{V}DD}$	−35.47
$\mathrm{DV\underline{D}DV}$	(−21.35)	$\mathrm{DV\underline{V}DV}$	(−35.38)
$\mathrm{VV\underline{D}DD}$	−21.35	$\mathrm{VV\underline{V}DD}$	−35.38
$\mathrm{DV\underline{D}DD}$	−21.42	$\mathrm{VV\underline{V}DV}$	(−35.28)
$\mathrm{VD\underline{D}DV}$	(−21.77)	$\mathrm{DV\underline{V}VD}$	−35.07
$\mathrm{VD\underline{D}DD}$	−21.84	$\mathrm{VV\underline{V}VD}$	−34.99
$\mathrm{DD\underline{D}DD}$	−21.91	$\mathrm{VV\underline{V}VV}$	−34.89

[a] Values in parentheses are estimated.

Table V
^{29}Si NMR Chemical Shifts for Chain Ends

sequence	ppm from TMS	sequence	ppm from TMS
$\mathrm{\underline{M}DD}$	7.25	$\mathrm{\underline{M}VD}$	8.26
$\mathrm{\underline{M}DV}$	7.34	$\mathrm{\underline{M}VV}$	8.40

conditions allowed quantitative integration. This was confirmed by the integral ratios obtained on isolated low molecular weight species listed in Tables I and III. Identification of sequences present in the copolymers was based on recognition of the characteristic triplet of triplets pattern observed for pentad structures in siloxane copolymers.[14] ^{29}Si NMR spectra of the copolymers show signal splitting due to triad as well as pentad structure in the D and V regions as shown in Figure 1 for a copolymer containing 30 M % V units. These patterns can be recognized in the linear chain, cocyclic tetramer and chain ends as seen in the expanded spectra. Chemical shift assignments for the sequences were confirmed by comparison to spectra of specially synthesized low molecular weight linear, cocyclic, and chain-ended Me_2SiO–MeViSiO species having known structural sequencing. The assigned chemical shifts can be found in Tables I–III. Signal intensities from the triad or diad sequences were determined by integration. Diad sequences were determined for structures near the chain ends. Accurate integration of the pentad sequences was not possible.

Distribution of cocyclics in the copolymers was determined on a Hewlett-Packard 5890A gas chromatograph equipped with a 20-m capillary column and flame ionization detector. Identification of individual cocyclic species was confirmed by mass spectrometry as well as isolation by distillation and ^{29}Si NMR spectroscopy.

Materials. D_4 from a commercial source was redistilled to give >99.8% purity, bp 173 °C at 760 mmHg. V_4 was also from a commercial source and fractionally redistilled at 39–40 °C at 1.5 mmHg to give >99.7% purity. Decamethyltetrasiloxane was obtained from a commercial source and redistilled to give >99.7% purity, bp 191 °C at 760 mm.

Cocyclosiloxanes were prepared from a mixture of 38.7 g (0.3 mol) of dimethyldichlorosilane and 141.0 g (1.0 mol) of methylvinyldichlorosilane which was slowly added with stirring to 1425 g (18 mol) of pyridine and 75 g of water (4.16 mol) cooled with an ice bath. The precipitate was filtered, and the pyridine was removed in a rotary evaporator. The crude cocyclosiloxanes were then fractionally distilled and separated into fractions, but due to the close boiling points of the positional isomers complete separation was not possible. Indentification of the components in the fractions was by GC/MS and ^{29}Si NMR spectra. Chemical shifts were then assigned on the basis of the relative amount of isomer present and the relative signal intensities of the D and V units. Table I exemplifies chemical shifts for the cocyclotetrasiloxanes isolated here. These were the basis of the peak assignments in Table II.

A series of low molecular weight trimethylsilyl (M) end-stopped poly(dimethylsiloxane-*co*-methylvinylsiloxanes) were prepared whose sequencing of comonomer units was known. This enabled peak assignments in the high molecular weight copolymer chains as well as the chain ends. Individual members of the series were prepared in essentially the same way be reaction of MD_xOH (x = 0, 1, 3, 6) with ClV_yCl (y = 1–6) in a 2/1 mole ratio in an excess of pyridine. Most of the products were not sufficiently volatile to distill but could be isolated in >90% purity from their reaction

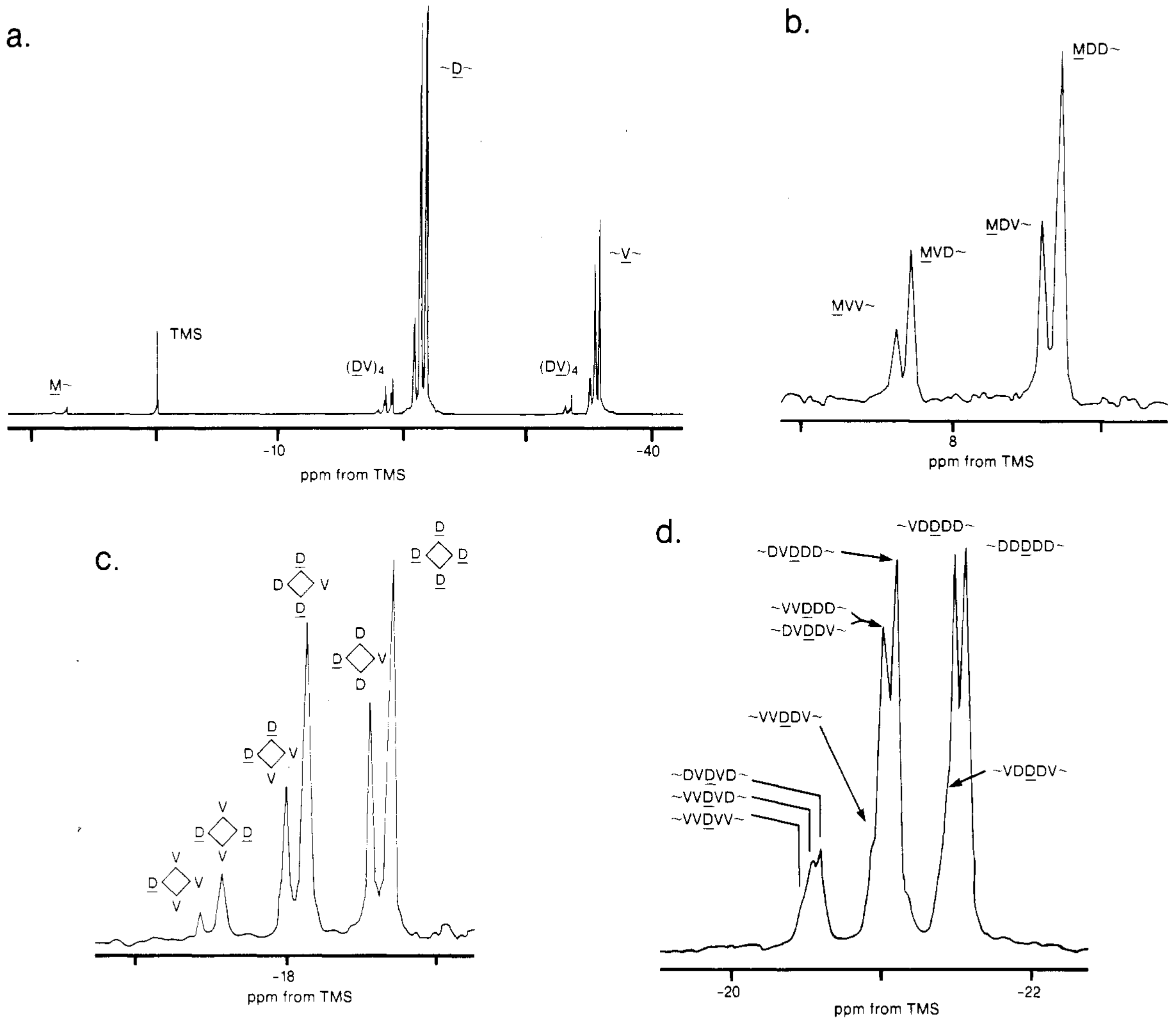

Figure 1. Typical ^{29}Si NMR spectrum. The equilibrated copolymer contains 30 mol % V units, and peak assignments are shown: (a) overall spectrum; (b) enlargement of 8.0 ppm; region; (c) enlargement of −18 ppm region; (d) enlargement of −21 ppm region.

mixtures. This purity was sufficient for ^{29}Si NMR peak assignment. All compounds exhibited ^{29}Si NMR spectra consistent with their structure. These are summarized in Table III, and the chemical shift data served as the basis for the peak assignments in Tables IV and V.

Coequilibration. Me_2SiO–MeViSiO copolymers were prepared by coequilibration of freshly distilled D_4 and V_4. Decamethyltetrasiloxane (MD_2M) was used as an end stopper to control molecular weight. Potassium silanolate was used as an initiator at 0.2 wt %. The catalyst was prepared by reaction of KOH and D_4 in refluxing cyclohexane, removing water by azeotropic separation, and had a neutral equivalent of 1375 g/mol K^+. Progress of the copolymerizations was followed by viscosity measurement and the distribution of cocyclics by GC until equilibrium was attained. This typically required 12–18 hours at 130 °C. Trimethylsilyl benzoate was added at the equilibration temperature to neutralize the catalyst and terminate the copolymerization. The copolymers were cooled to room temperature and filtered. Samples were withdrawn periodically during the polymerization of a 10 M % MeViSiO containing copolymer, terminated, and analyzed to determine how microstructure changed during equilibration.

Calculations of Run Number *R*. Integral ratio factors for D units and V units, f_d and f_v, respectively, were calculated from the relative intensities of the D-centered and V-centered triads whose chemical shift assignments in the ^{29}Si NMR spectrum were obtained from Tables II, IV, and V. Two commonly used relationships were

$$f_D = \frac{2F_{DDV}}{F_{DDV} + 2F_{DDD}} \qquad f_V = \frac{2F_{VVD}}{F_{VVD} + 2F_{VVV}} \tag{1}$$

where F_{DDV}, F_{DDD}, F_{VVD}, and F_{VVV} were integral areas of the indicated D-centered and V-centered triads. Other equally valid relationships can be used that include F_{VDV} and F_{DVD}.[9,10] The run number, *R*, or the average number of comonomer sequences in 100 repeat units is related to the integral ratio factors by

$$R = f_D \text{ (mol \% D)} = f_V \text{ (mol \% V)} \tag{2}$$

Only diad structures were resolved in the region of the ^{29}Si NMR spectra which corresponded to the chain ends, and it was necessary to calculate *R* from

$$R = 2\text{(mol \% D)}(1 - F_{DD}) = 2\text{(mol \% V)}(1 - F_{VV}) \tag{3}$$

where F_{DD} and F_{VV} are the relative intensities of the DD and VV diads, respectively.

Results

Immediately after initiation with potassium silanolate, V_4 polymerized first to the nearly complete exclusion of the D_4. Only after the complete consumption of V_4 was any significant D_4 polymerization observed. Figure 2 illustrates a copolymerization with 10 mol % V_4 at 130 °C followed by GC. This shows the consumption of monomers as well as the formation of byproduced cyclosiloxanes and cocyclosiloxanes. In the early stages cocyclosiloxanes with a high content of V units were formed, reached a maximum, and then decreased to an equilibrium level after 5–8 h. The composition of the copolymer chain reflected that seen in the cocyclosiloxanes. This is illustrated in Figure 3 which is based on the ^{29}Si NMR of the copolymer and shows the V units originally in block structures which later disperse along the chain as the system approaches equilibrium. Thus, the sequence distribution early in the

Table VI
Microstructure of Me_2SiO-MeViSiO Copolymers Equilibrated at 130 °C

	MeViSiO, mol %											
	10			30			50			70		
	chains	cyclic tetramers	chain end	chains	cyclic tetramers	chain end	chains	cyclic tetramers	chain end	chains	cyclic tetramers	chain end
% Me_2SiO (D)	89.6	90.5		67.2	68.8	69.8	49.2	50.0	49.2	29.1	29.7	30.1
% MeViSiO (V)	10.4	9.5		32.8	31.2	30.2	50.8	50.0	50.8	70.9	70.3	69.9
R_D[a]	18.8	17.2		44.4	44.7	48.3	49.7	50.5	51.7	41.0	42.1	38.8
R_V[a]	18.7	17.1		44.3	44.6	40.6	49.8	50.5	50.8	41.1	42.2	45.1
R_{rnd}[a]	18.6	17.2		44.1	42.9	42.4	50.0	50.0	50.0	41.3	41.7	42.1

[a] R_D, determined from Me_2SiO region. R_V, determined from MeViSiO region. R_{rnd}, calculated for a random distribution of comonomer units based on total compositions of D and V measured on ^{29}Si NMR. See ref 8.

Table VII
Microstructure of 30 mol % MeViSiO Copolymers Equilibrated at Varied Equilibrium Temperatures

	temp, °C (time, h)											
	150 (23)			130 (23)			90 (186)			22 (432)[a]		
	chains	cyclic tetramers	chain end	chains	cyclic tetramers	chain end	chains	cyclic tetramers	chain end	chains	cyclic tetramers	chain end
% Me_2SiO (D)	67.3	70.2	70.1	67.2	68.8	69.8	66.0	69.1	68.9	66.1	70.3	67.7
% MeViSiO (V)	32.7	29.8	29.9	32.8	31.2	30.2	34.0	30.9	31.1	33.9	29.7	32.3
R_D[b]	45.7	42.8	40.7	44.4	44.7	48.3	46.0	43.3	48.8	45.1	40.1	37.2
R_V[b]	45.8	42.9	41.9	44.3	44.6	40.6	45.6	43.4	40.1	45.1	40.1	44.3
R_{rnd}[b]	44.0	41.8	41.9	44.1	42.9	42.4	44.8	42.7	42.8	44.8	41.8	43.7

[a] 1% DMSO used as a promoter. [b] Definitions in footnote *a*, Table VI.

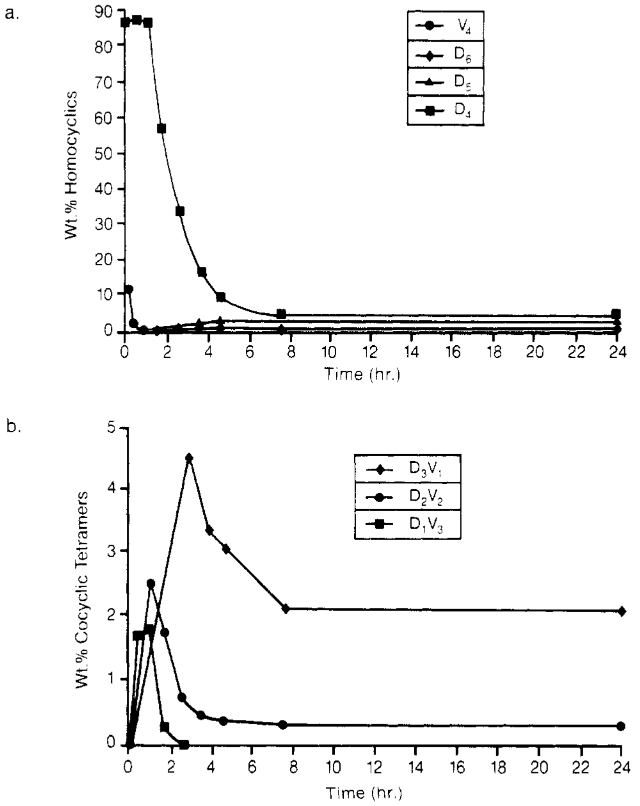

Figure 2. Consumption and reformation of cyclolosiloxanes during the copolymerization of D_4 with 10 mol % V_4 at 130 °C measured by GC: (a) Consumption of D_4, V_4 and formation of $D_{5,6}$; (b) formation of cocyclosiloxanes. MD_2M also present in samples taken at 2 and 4 h.

process is quite different than when the system achieves a steady state. Care was taken in each run, therefore, to ensure that the system was at equilibrium by terminating the copolymerization only well after there was no further change noted in bulk viscosity as well as in the composition of the volatile cyclosiloxanes which was measured intermittently.

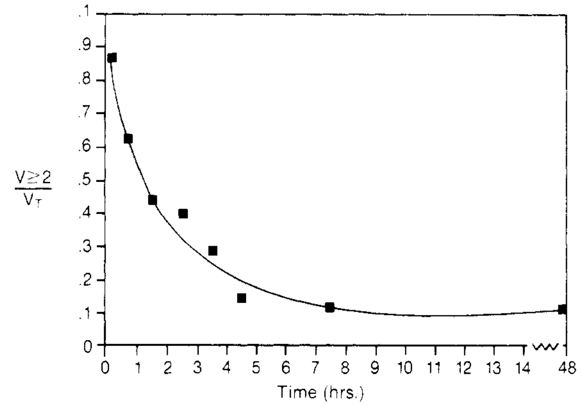

Figure 3. Relative amounts of multiple V units to total V units ($V_{>2}/V_T$) during an equilibration of a 10 mol % V copolymer at 130 °C.

Regions of the ^{29}SiNMR spectra from the equilibrates corresponding to the sequence distributions of D and V units in the chains, near the chain ends, and in the rings were each distinct but showed very similar patterns of relative signal intensities. An example of a system equilibrated with 30 mol % V units is given in Figure 1. A run number, *R*, was therefore independently determined[9,10] for the part of the system corresponding to the rings, chains, and the vicinity of the chain ends. Also, for each part of the system *R* was independently calculated from the region of the spectrum corresponding to the D units, R_D, and V units, R_V, and results were cross-checked.

Table VI shows results from copolymerizations where V is varied from 10 to 70 mol % in equilibrated copolymerizations at 130 °C while Table VII shows results for a series where temperature at equilibrium is varied from 22 to 150 °C in a copolymer with 30 mol % V. The two tables show that at a given composition the values of *R* corresponding to the copolymer chains and the chain ends but, with one exception, are very similar. Also *R* is very close to the value R_{rnd} calculated for a random distribution of comonomer units.[8] The exception was the value for R_D measured at the chain ends in the copolymer

Table VIII
Distribution of Cocyclics in Me_2SiO-MeViSiO Copolymers

% Me_2SiO (D)	90.5		68.8		50.0		29.7	
% MeViSiO (V)	9.5		31.2		50.0		70.3	
	predicted[a]	determined[b]	predicted[a]	determined[b]	predicted[a]	determined[b]	predicted[a]	determined[b]
cyclic tetramers								
D_4	0.656	0.628	0.240	0.248	0.0625	0.064	0.081	0.009
D_3V_1	0.292	0.320	0.412	0.406	0.250	0.242	0.076	0.084
D_2V_2	0.049	0.051	0.264	0.270	0.375	0.378	0.264	0.252
D_1V_3	0.004		0.076	0.075	0.250	0.254	0.412	0.412
V_4	0.0001		0.0081		0.0625	0.062	0.240	0.252
cyclic pentamers								
D_5	0.590	0.56	0.168	0.15	0.031	0.02	0.0024	
D_4V_1	0.328	0.35	0.360	0.34	0.156	0.14	0.0284	0.02
D_3V_2	0.0729	0.08	0.309	0.32	0.313	0.30	0.132	0.11
D_2V_3	0.0081		0.132	0.14	0.313	0.32	0.309	0.29
D_1V_4	0.0005		0.0284	0.03	0.156	0.17	0.360	0.38
V_5	0.0001		0.0024		0.031	0.04	0.168	0.19

[a] Predicted values based on eq 4. [b] Determined by GC area %.

equilibrated at 130 °C with 10 mol % V units (Table VI) where there was difficulty in obtaining accurate integration for this portion of the ^{29}Si NMR spectrum. Table VII also shows that R is independent of temperature and that randomness persists over a 130 °C range as evidenced by unchanging R_D and R_V and their close agreement with R_{md}.

The distribution of compositions of individual species for a given copolymer at equilibrium also appears to be random. This can be seen in the distribution of compositions of individual cocyclosiloxanes which can be readily determined by GC. The distributions are closely predicted by the binomial distribution (eq 4) which requires the absence of any selective reactivity in the copolymers at equilibrium

$$P_i = \frac{N!}{(N_{D_i}!)(N_{V_i}!)}(D)^{N_{Di}}(V)^{N_{Vi}} \tag{4}$$

where P_i is the probability of individual species i in a copolymer whose overall composition is given by D, the average mole fraction of D units, and V = 1 − D, the average mole fraction of V units, and where the number of D and V units in species i is N_{D_i} and N_{V_i}, respectively, which total to the degree of polymerization, N. Table VIII shows that for compositions ranging from 10 to 70 mol % V the amounts of each individual cocyclosiloxane were predicted by eq 4. Equation 4 could not be tested with the copolymer chains since individual species could not be isolated. It seems reasonable, however, that the binomial distribution will apply here as well since the sequence distribution of the copolymer chains closely parallel that of the cocyclosiloxanes.

Discussion

Two equilibria occur during cyclosiloxane polymerizations initiated by strong acids or bases which consist of redistributions of siloxane units between rings and chains and redistribution between chains.[15,16] The equilibria for the homopolymerization of D_x can be represented as

$$\sim D^*_n + D_x \rightleftarrows \sim D^*_{(n+x)} \tag{5}$$

$$\sim D_n\sim + \sim D_m\sim \rightleftarrows \sim D_{(n+y)}\sim + \sim D_{(m-y)}\sim \tag{6}$$

where x and y are integers. Thus, when equilibrium is established, every repeat unit in the system is effectively a participant whether it is located in the rings or the chains. It is then possible to construct a model for cyclosiloxane copolymerization at equilibrium which resembles the Mayo–Lewis scheme but where the competing rate constants are replaced by equilibrium constants and where comonomer concentrations represent *total* concentrations of each comonomer repeat unit regardless of their locations in the rings or chains

$$\begin{aligned} &\sim D^* + D \xrightleftharpoons{K_{DD}} \sim DD^* \\ &\sim D^* + V \xrightleftharpoons{K_{DV}} \sim DV^* \\ &\sim V^* + V \xrightleftharpoons{K_{VV}} \sim VV^* \\ &\sim V^* + D \xrightleftharpoons{K_{VD}} \sim VD^* \end{aligned} \tag{7}$$

where units with an asterisk represent an active end and D and V represent comonomer units anywhere in the rings or chains. This scheme combined with the same type of equilibria outlined in reactions 5 and 6 provides a pathway that allows comonomer units to distribute throughout the entire system and give essentially the same composition of comonomer units in the rings as well as in the copolymer chains.

Table IX
Diad Probabilities and Equilibrium Constant Ratios from Me_2SiO-MeViSiO Copolymers Equilibrated at 130 °C[a]

	MeViSiO, mol %			
	10	30	50	70
P_{DD}[b]	0.89	0.67	0.49	0.29
P_{VV}[b]	0.10	0.32	0.51	0.71
P_{DV}[b]	0.10	0.33	0.50	0.70
P_{VD}[b]	0.90	0.67	0.49	0.29
r_D	0.95	0.99	1.01	1.02
r_V	0.92	0.99	1.00	1.0

[a] Based on R_D and R_V observed in the chains (Table VI). [b] Conditional probabilities, i.e., the probability of a D unit given a D or V unit or a V unit given a D or V unit etc. See ref 3.

The equilibrium constant for homopolymerization, K_{DD}, has been shown by several investigators to be independent of temperature and hence driven only by entropy,[17-19] but in copolymerization the possibility of enthalpic contributions from the V units in K_{DV}, K_{VV}, and K_{VD} is possible. The lack of selectivity and the absence of a temperature effect in the present system, however, implies that such contributions are absent at least at the diad and triad levels. This can be stated more formally be defining ratios for the equilibrium constants r_D and r_V.

$$r_D \equiv K_{DD}/K_{DV} \qquad r_V \equiv K_{VV}/K_{VD} \tag{8}$$

Values of r_D and r_V can be estimated from diad probabilities by well established procedures,[3] and these in turn are readily calculated from R_D and R_V.[8] Results are summarized in Table IX where compositions of the copolymers

Table X
Diad Probabilities and Equilibrium Constant Ratios from 30 mol % MeViSiO Copolymer Equilibrated at Varied Temperatures[a]

	temp, °C (time, h)			
	150 (23)	130 (23)	90 (186)	22 (432)
P_{DD}[b]	0.66	0.67	0.65	0.66
P_{VV}[b]	0.30	0.32	0.35	0.33
P_{DV}[b]	0.34	0.33	0.33	0.34
P_{VD}[b]	0.70	0.68	0.67	0.67
r_D	0.94	0.99	0.97	0.99
r_V	0.88	0.99	0.95	0.98

[a] Based on R_D and R_V observed in the chains (Table VII). [b] Conditional probabilities. See ref 3.

are varied and in Table X where the equilibrium temperature is varied. Since r_D and r_V are close to unity regardless of composition or temperature, this simply restates that there is no selectivity in the equilibrated copolymerization and means that

$$\Delta H_{DD} = \Delta H_{DV} \qquad \Delta S_{DD} = \Delta S_{VD} \tag{9}$$

and

$$\Delta H_{VV} = \Delta H_{VD} \qquad \Delta S_{VV} = \Delta S_{VD} \tag{10}$$

since r_D and $r_V \cong 1$ and

$$\ln r_D = -\frac{\Delta\Delta H_D}{RT} + \frac{\Delta\Delta S_D}{R} \cong 0 \tag{11}$$

$$\ln r_V = -\frac{\Delta\Delta H_V}{RT} + \frac{\Delta\Delta S_V}{R} \cong 0 \tag{12}$$

where $\Delta\Delta H_D = \Delta H_{DD} - \Delta H_{DV}$, $\Delta\Delta S_D = \Delta S_{DD} - \Delta S_{DV}$, $\Delta\Delta H_V = \Delta H_{VV} - \Delta H_{VD}$, and $\Delta\Delta S_V = \Delta S_{VV} - \Delta S_{VD}$ and where the subscripts refer to the individual equilibria in eq 7. The enthalpy terms are zero because r_D and r_V are independent of temperature, but the individual entropy terms in the process must be equal but nonzero.

The close similarity of the sequence distributions at the chain ends with those in the rest of the chain seen at a variety of compositions and temperatures implies little influence from the trimethylsiloxy (M) units. Similar conclusions of an entropically driven process can therefore be drawn on the equilibrium copolymerization of M units with D or V units. Comparison of Figures 2 and 3 indicates that although the process is initially specific, the system quickly randomizes and that the composition of the rings and chains roughly match as this occurs. This, combined with the close similarity of composition and sequence distribution in the equilibrated polymer, polymer chain ends, and rings, implies a very dynamic system where no segment can be considered inert or isolated from the process.

Registry No. (Octamethylcyclotetrasiloxane)(1,3,5,7-tetramethyltetravinylcyclotetrasiloxane) (copolymer), 26659-55-2.

References and Notes

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