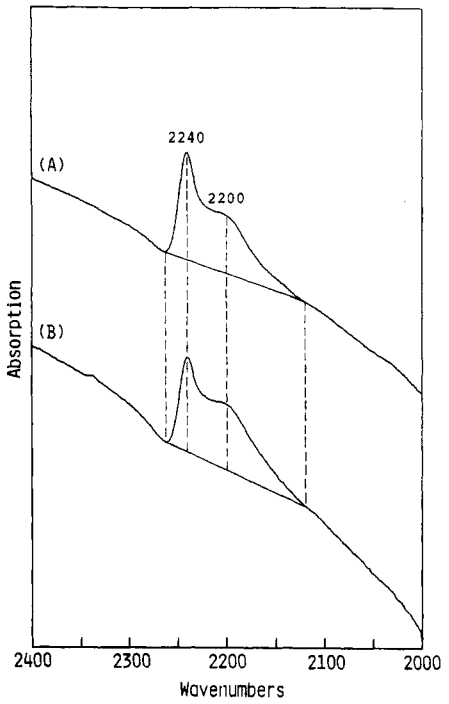

Figure 8. Partial FT-IR spectra in the C≡N region for two comparably stabilized PAN fiber samples: (A) S-6, (B) S-10.

the latter severely but shortly treated PAN sample (S-10) has much more conjugated nitrile content than the former softly and slowly treated one (S-6).

In conclusion, the main stabilization mechanism of PAN fibers under oxidative thermal degradation to form cyclic ladder structures was indirectly and directly confirmed by PyGC and CP/MAS ^{13}C NMR and FT-IR, respectively. In addition, the contribution of dehydrogenation and/or dehydrocyanide reactions to form the conjugated polyene structures suggested by the data of PyGC especially for the PAN fibers treated at relatively higher stabilization temperatures was also supported by those of CP/MAS ^{13}C NMR and FT-IR.

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Registry No. PAN (copolymer), 26202-14-2.

Microstructural Analysis of Polysilapropynylene Copolymers by ^{13}C and ^{29}Si Nuclear Magnetic Resonance

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ABSTRACT: The sequence distribution of poly(dimethylsilapropynylene-*co*-diphenylsilapropynylenes) $[[(Me_2SiC{\equiv}C-)_x(Ph_2SiC{\equiv}C-)_y]_n]$ has been studied by NMR spectroscopy. It is shown that the silylethynyl units are randomly distributed within the copolymer cyclic and linear chains at equilibrium. The distributions of triad and pentad sequences in the ^{29}Si NMR and of diad and tetrad sequences in the ^{13}C NMR have been determined theoretically and compared with experimental spectra. Rearrangement reactions leading to the randomized products occur and have been shown to compete with condensation reactions. This randomization process is independent of the nature of substituents on the silicon atom and temperature. The ratio of specific copolymerization equilibrium constants has been calculated, and the whole process of copolymerization is shown to be entropy driven.

Introduction

Silicon-containing polymers are finding an increasing number of applications in many areas of technology and research. The particular electronic structure of the silicon atom compared to that of carbon atom gives special properties to these polymers. The ability of the silicon atom to transmit electronic effects in silicon ethynyl derivatives has been known for many years.[1,2] We have recently reported the synthesis of pericyclynosilanes,[3] a class of cyclic compounds of the type $[(R_2SiC{\equiv}C-)_x(R'_2SiC{\equiv}C-)_y]_n$. These compounds are synthesized by the addition of a diorganodichlorosilane to a dilithium derivative of a diorganodiethynylsilane (Scheme I).

When R = R′, homopolymers can be prepared using this procedure, and when R ≠ R′ copolymers containing equimolar quantities of the two silylethynyl units are formed. Single-crystal X-ray diffraction analysis confirmed the cyclic nature of $(Me_2SiC{\equiv}C-)_6$, which adopts a chair conformation similar to cyclohexane.[4] Copolymers containing different mole ratios of silylethynyl units, $-R_2SiC{\equiv}C-$ to $-R'_2SiC{\equiv}C-$, may be prepared by a coequilibration process (Scheme II).

Herein we describe the sequencing of (dimethylsilyl)-

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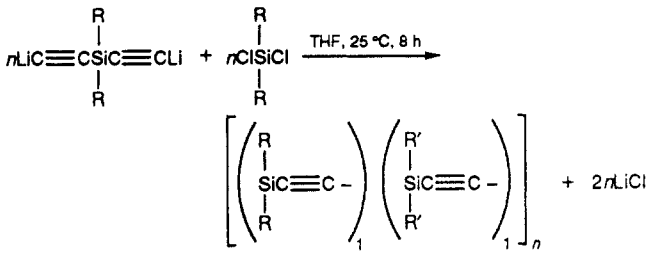
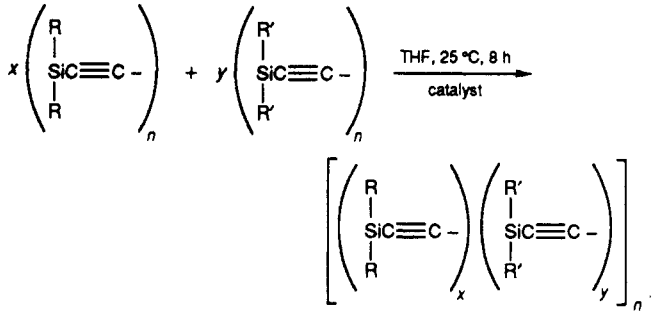
Scheme I



Scheme II



ethynyl (R = Me) and (diphenylsilyl)ethynyl (R′ = Ph) units within the chains of poly(dimethylsilapropynylene-*co*-diphenylsilapropynylenes). These units are represented by A and B, respectively, in the following text.

Experimental Section

SEC. Size-exclusion chromatography (SEC) was performed using a series of Waters ultrastyragel columns (30 cm × 7.8 mm) with average pore sizes of 10^5, 10^4, and 10^3 Å. Tetrahydrofuran (THF) was used as an eluent and was pumped at 1.0 $cm^3 \cdot min^{-1}$. Simultaneous detection was achieved by a Perkin-Elmer LC90 ultraviolet detector, the wavelength of which was set at 254 nm, and a Perkin-Elmer LC25 refractive index detector attached in series. Chromatogram analysis was performed using GPC-PRO software from the Viscotek Corp. The molecular weight distribution and the related average molecular weights were calculated on the basis of a polystyrene calibration.

NMR. Quantitative $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were recorded using a Bruker WM-360 spectrometer operating at 90 and 72 MHz, respectively. The spectra were acquired with gated proton decoupling. $Cr(acac)_3$ (0.02 M) was added to the sample solutions as a relaxation reagent and NOE suppressor. A total of 300–500 mg of compound was dissolved in 3 mL of $CDCl_3$. All chemical shifts were externally referenced to TMS. The 90° pulse width was set at 15 μs, and a typical relaxation delay of 15 s allowed more than 95% spin–lattice relaxation of ^{13}C and ^{29}Si nuclei to occur. Quantitative spectra were therefore obtained.

Materials. Diphenyldiethynylsilane was prepared according to a published procedure[5] and stored under nitrogen. Dimethyldichlorosilane and tetrahydrofuran were freshly distilled under nitrogen, from calcium hydride and potassium benzophenone, respectively.

Synthesis. Poly(dimethylsilapropynylene-*co*-diphenylsilapropynylene). To a solution of diphenyldiethynylsilane (5 g, 21.6 mmol) in THF (100 cm^3), magnetically stirred and cooled to −78 °C, was added a solution of 2.75 M BuLi (15.7 cm^3, 43.1 mmol) in hexane. The resulting solution was stirred and allowed to warm to ambient temperature. A solution of dimethyldichlorosilane (2.78 g, 21.6 mmol) in THF (50 cm^3) was then added dropwise at ambient temperature. Afer the addition was complete, the reaction mixture was stirred overnight. The THF solution was added to a saturated aqueous solution of NH_4Cl (100 cm^3) with vigorous agitation. The organic layer was separated, and the aqueous layer was then extracted with ether (30 cm^3). The organic phase and the ether extract were combined and washed with a saturated aqueous solution of NaCl (50 mmol). The organic phase was separated and dried over Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure to leave a white solid. The white solid was washed with MeOH (100 cm^3), and the suspension was stirred for 3 h. The white precipitate was then filtered and dried under reduced pressure to give 5.52 g of product (88% yield).

Table I
Triad Sequences Centered around the Diphenylsilylethynyl (B) Unit and the Corresponding ^{29}Si NMR Chemical Shifts Relative to External TMS

signal	triad sequence	δ, ppm
[0]	—≡—B—≡—*B*—≡—B—≡—	−49.58
[1]	—≡—A—≡—*B*—≡—B—≡—	−49.95
[2]	—≡—A—≡—*B*—≡—A—≡—	−50.35

Coequilibration Reaction. In a typical reaction, solid $(Me_2SiC{\equiv}C{-})_n$ (0.22 g, 2.68 mmol) and $(Ph_2SiC{\equiv}C{-})_n$ (0.54 g, 2.62 mmol) were placed in a Schlenk tube, which was then evacuated and purged with nitrogen. Freshly distilled anhydrous THF (100 cm^3) was transferred via cannula to the reaction vessel. The resulting pale yellow solution was magnetically stirred at ambient temperature while a THF solution of the redistribution catalyst, $Ph_2Si(-C{\equiv}CLi)_2$ prepared as described below, was added via a gas-tight syringe (volume of catalyst solution added = 100 μL, equivalent to 6.25×10^{-6} mol of catalyst). The mixture was stirred at ambient temperature for 12 h, after which time a few drops of dilute HCl were added to quench the catalyst. The mixture was neutralized by adding solid sodium hydrogen carbonate and stirring for 1 h. After filtration the THF was removed from the filtrate under reduced pressure to yield a white solid. The solid was washed with methanol before drying under reduced pressure.

Preparation of the Catalyst Solution. Solid $Ph_2Si(-C{\equiv}CH)_2$ (0.59 g, 2.5 mmol) was dissolved in freshly distilled, anhydrous THF (40 cm^3) under inert atmosphere. The resulting solution was magnetically stirred while cooling to −78 °C in a solid carbon dioxide–acetone bath. BuLi (2.95 M; 1.7 cm^3, 5 mmol) was then added using a gas-tight syringe. The mixture was allowed to warm slowly to ambient temperature before use.

Results and Discussion

Macrostructure analyses by size-exclusion chromatography (SEC) and by ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopy show that the addition reaction of the dilithium derivative of diphenyldiethynylsilane with dichlorodimethylsilane (Scheme I) and the coequilibration reactions (Scheme II) both lead to a product that consists of a mixture of cyclic and linear macromolecules. The distribution of the cyclic species is mainly constituted of hexamers, and the number average molecular weight M_n of the linear chains as determined by SEC is around 3600 Da corresponding to about 26 silylethynyl units.

Simple $^{29}Si\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra, consisting of two signals, might have been expected from an alternating structure such as $[Me_2SiC{\equiv}CPh_2SiC{\equiv}C{-}]_n$ (Scheme I). However, complex asymmetric multiplets were observed. When the reaction is driven to thermodynamic equilibrium, symmetric patterns could be obtained, presumably arising from a statistical distribution of the two different silylethynyl units within the molecular backbone.

The statistical interpretation of NMR spectra recorded for cyclic copolymer species is relatively straightforward when ring strain is not a contributory factor. The cyclic species may then be considered as infinitely long chains. In the case of dimethyl-6-pericyclynosilane, the cyclic hexamer, the relative energies of the chair, twist-boat, and boat conformations have been calculated and found to be equal to 0.033, 0.255, and 0 kJ, respectively. The tor-

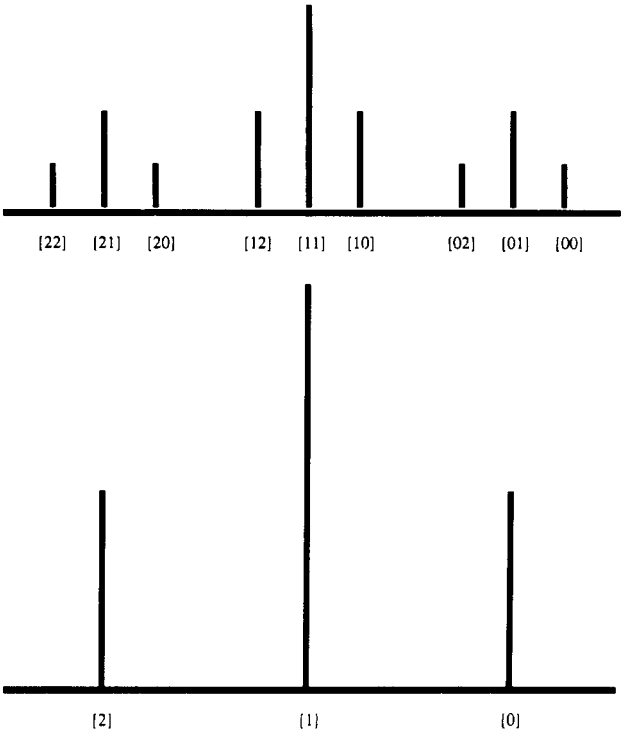


Figure 1. Theoretical ^{29}Si NMR spectrum of a given silylethynyl unit in an equimolar silylethynyl copolymer based on triad (bottom) and pentad (top) sequences and the respective labeling of the signals.[7]

sional effects that differentiate these conformations are therefore negligible and similar to those calculated for the 6-pericyclyne, the cyclohexameric carbon analogue.[6] These molecular mechanic calculations show that there is no ring strain present in pericyclynosilanes for the hexamer and consequently for higher cyclics. Similarly, the NMR spectra of linear chains can be readily interpreted by statistic models when the nature of the end groups in the linear chains does not significantly affect the chemical shifts of the adjacent silylethynyl units. Finally, the difference in chemical shifts between cyclic and linear species is small and in the order of the observed splitting due to a different adjacent silylethynyl unit.

For the silapropynylenes, the relative abundance of each sequence, composed of n units called n-ads built by the two silylethynyl units, was deduced from probabilistic considerations and directly compared with NMR spectra.[7]

For ^{29}Si nuclei, triad analysis of silylethynyl copolymers predicts three sequences in which the cenral silicon atom has three distinct microenvironments.[8,9] Extension to pentad sequences predicts nine signals (Figure 1). The relative intensities of these signals calculated from Bernoullian or first-order Markovian statistics are a function of the mole ratio of the silylethynyl units.

The ^{29}Si NMR spectrum of a poly(dimethylsilapropynylene-*co*-diphenylsilapropynylene) with an equimolar ratio of (dimethylsilyl)- to (diphenylsilyl)ethynyl units is shown in Figure 2. Signals around −40.56 ppm are attributed to the (dimethylsilyl)ethynyl units and those around −49.95 ppm to the (diphenylsilyl)ethynyl units. Triad microstructures are observed for the $Ph_2SiC{\equiv}C-$ units, with the particular sequence −ABA− showing some further second-order splitting. For the $Me_2SiC{\equiv}C-$, however, pentad microstructures were detected. The sensitivity of the ^{29}Si chemical shift to the nature of adjacent units appears to be higher in the (dimethylsilyl)ethynyl unit. The exact character of the chemical bond in organosilicon compounds is still the subject of controversy, and the origin

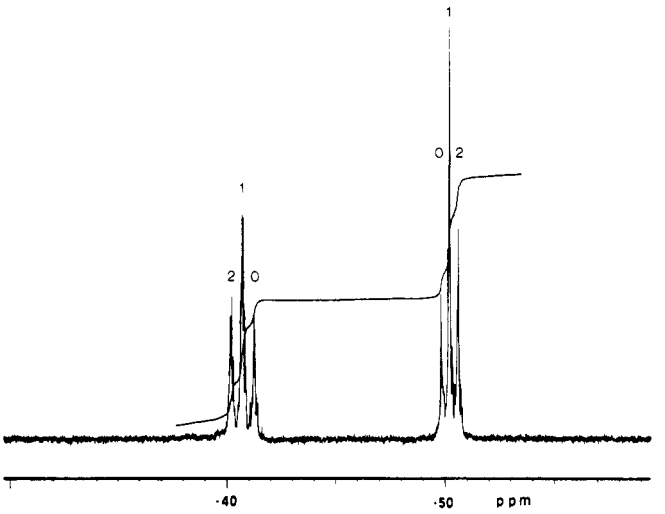


Figure 2. Experimental ^{29}Si NMR spectrum of 1:1 dimethyl- and diphenyl-*n*-pericyclynosilanes. At −40 ppm, a pentad pattern is observed and is attributed to the $Me_2SiC{\equiv}C-$ units. At −50 ppm, a triad pattern is observed and is attributed to the $Ph_2SiC{\equiv}C-$ units. The labeled signals correspond to triad and pentad sequences described in Tables I and II.

of the variation of ^{29}Si chemical shifts is still not fully understood.[10]

Each of the ^{29}Si signals in the poly(dimethylsilapropynylene-*co*-diphenylsilapropynylenes) has been attributed to triad and pentad sequences for (diphenylsilyl)ethynyl and (dimethylsilyl)ethynyl units, respectively, by comparison of spectra of model compounds with each other. Assuming chemical shift additivity in the sequences, statistical analysis correctly predicted the observed spectral patterns (Tables I and II). Consistent results have also been obtained by the analysis of spectra recorded for copolymers containing different mole ratios of (dimethylsilyl)- and (diphenylsilyl)ethynyl units.

The probability of various linkages P_{AA}, P_{AB}, P_{BA}, and P_{BB}, the number average sequence lengths l_A and l_B, and the experimental run numbers R_{exptl} have been calculated for the poly(dimethylsilapropynylene-*co*-diphenylsilapropynylenes). These microstructure parameters[8] are compared with the theoretical values for a statistical distribution of copolymer sequences in Table III. These results show quantitatively that total randomization has occurred.

Analysis of the microstructure occurring around $-C{\equiv}C-$ from ^{13}C NMR considers, at first order, the pseudodiad sequences of dimethylsilyl (A) and diphenylsilyl (B) groups.[7] The $-C{\equiv}C-$ units situated between the silyl groups are useful probes for the three pseudodiad microstructures, AC≡CA (I), AC≡CB (II), and BC≡CB (III). Four distinct signals would be expected, one from I, two from II, and one from III (Table IV and Figure 3). Each of these signals will be further split when the influence of second and third neighboring $R_2SiC{\equiv}C-$ groups is significant, leading to a complex pattern.

The distribution of these sequences, within the copolymer chains, can be predicted by Bernoullian statistics. For an equimolar copolymer the relative abundance of the pseudodiads, I, II, and III, will be 1, 2, and 1, respectively. Each of the two symmetric diads (I and III) has a single probability of occurrence and is made of two identical carbon atoms. The asymmetric diad (II) has two different carbon atoms with each having a double probability of occurrence. Therefore, a characteristic four-signal pattern with equal intensities (1:1:1:1) is observed (Figure 3).

Table II
Pentad Sequences Centered around the Dimethylsilylethynyl (A) Unit and the Corresponding ^{29}Si NMR Chemical Shifts Relative to External TMS

signal	pentad sequence	δ, ppm
[22]	—≡—B—≡—B—≡—*A*—≡—B—≡—B—≡—	-39.97
[21]	—≡—A—≡—B—≡—*A*—≡—B—≡—B—≡—	-40.03
[20]	—≡—A—≡—B—≡—*A*—≡—B—≡—A—≡—	-40.11
[12]	—≡—B—≡—A—≡—*A*—≡—B—≡—B—≡—	-40.63
[11]	—≡—B—≡—A—≡—*A*—≡—B—≡—A—≡—	-40.56
	—≡—A—≡—A—≡—*A*—≡—B—≡—B—≡—	
[10]	—≡—A—≡—A—≡—*A*—≡—B—≡—A—≡—	-40.50
[02]	—≡—B—≡—A—≡—*A*—≡—A—≡—B—≡—	-41.03
[01]	—≡—A—≡—A—≡—*A*—≡—A—≡—B—≡—	-41.09
[00]	—≡—A—≡—A—≡—*A*—≡—A—≡—A—≡—	-41.15

Table III
Calculated and Experimental Microstructure Parameters of a 1:1 Poly(dimethylsilapropynylene-*co*-diphenylsilapropynylene)

theory		experiment	
$X_A = 0.50$	$X_B = 0.50$	$X_A = 0.49$	$X_B = 0.51$
$P_{AA} = 0.50$	$P_{BB} = 0.50$	$P_{AA} = 0.49$	$P_{BB} = 0.52$
$P_{AB} = 0.50$	$P_{BA} = 0.50$	$P_{AB} = 0.49$	$P_{BA} = 0.48$
$l_A = 2.00$	$l_B = 2.00$	$l_A = 2.05$	$l_B = 2.13$
$R_{theory} = 50$		$R_{expt} = 48$	

Table IV
Diad Sequences Centered around the Ethynyl Unit and the Corresponding Observed ^{13}C NMR Chemical Shift Range[a]

signal	sequence	Δδ, ppm
I	-A—*C*≡*C*—A-	109.87-111.35
II	-A—*C*≡*C*—B-	107.55-106.51
	-A—C≡*C*—B-	113.15-114.65
III	-B—*C*≡*C*—B-	109.87-111.35

[a] A and B represent dimethylsilyl and diphenylsilyl groups, respectively. A range is observed due to second and third neighboring units (not shown).

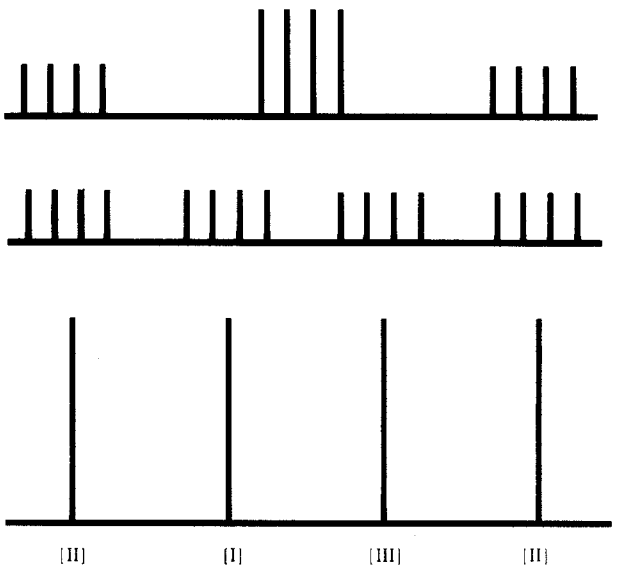


Figure 3. Theoretical ^{13}C NMR spectra of the ethynyl (-C≡C-) units in a 1:1 poly(dimethylsilapropynylene-*co*-diphenylsilapropynylene), calculated for diad (bottom) and tetrad (middle) sequences. The top spectrum would result from the exact overlapping of the two central sets of signals in the middle spectrum.

Surprisingly, however, the acetylenic region in the ^{13}C NMR spectrum of the poly(dimethylsilapropynylene-*co*-diphenylsilapropynylene) shows a pattern, consisting of three main signals, with a 1:2:1 relative intensity ratio (Figure 4). The carbon atoms in symmetric environments (I and III) are isochronous as shown by the NMR

Table V
Integrated ^{13}C NMR Intensities of Diad Sequences around -C≡C- Calculated from Bernoullian Statistics and Observed from NMR Spectra for Three Different Mole Ratios of Silylethynyl Units[a]

X_A	X_B	calcn	A—*C*≡*C*—B	A—*C*≡*C*—A / B—*C*≡*C*—B	A—*C*≡*C*—B
0.75	0.25	theory	0.27	0.46	0.27
		expt	0.23	0.55	0.23
0.50	0.50	theory	0.25	0.50	0.25
		expt	0.26	0.48	0.26
0.25	0.75	theory	0.27	0.46	0.27
		expt	0.21	0.48	0.21

[a] All values are normalized to unity. A = -Me_2Si- and B = -Ph_2Si-.

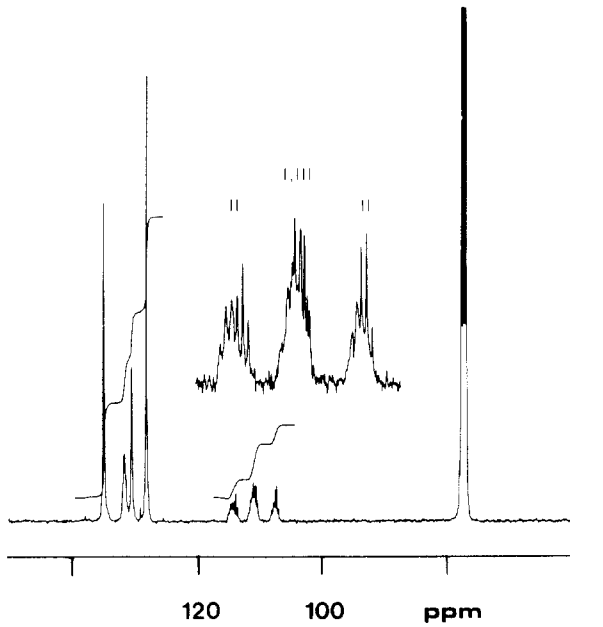


Figure 4. Experimental ^{13}C NMR spectrum of the ethynyl (-C≡C-) units in a 1:1 poly(dimethylsilapropynylene-*co*-diphenylsilapropynylene). Only the phenyl and ethynyl regions are displayed. The labeled signals correspond to diad sequences shown in Table IV.

spectra of the pure homopolymers $(Me_2SiC{\equiv}C-)_n$ and $(Ph_2SiC{\equiv}C-)_n$. Their signals overlap with each other and result in the 1:2:1 pattern. First-order assignment of the ^{13}C NMR signals to the diad microstructures is deduced from the homopolymers and is confirmed by the 3:1 and 1:3 mole ratio copolymers. The chemical shifts are collected in Table IV. The assignment of the tetrad sequences is impossible without the aid of precisely sequenced model compounds.

The probabilities of occurrence of the pseudodiads have been calculated and compared with ^{13}C NMR spectra for three different mole ratios of A and B silyl units. The

Table VI
Distribution of Hexameric Cocyclics Containing both Dimethyl- and Diphenylsilylethynyl Units[a]

	X_A		
	0.75	0.50	0.25
A_6	0.177	0.016	0.000
A_5B_1	0.355	0.094	0.004
A_4B_2	0.300	0.234	0.032
A_3B_3	0.132	0.313	0.132
A_2B_4	0.032	0.234	0.300
A_1B_5	0.004	0.094	0.355
B_6	0.000	0.016	0.177

[a] A = ($Me_2SiC{\equiv}C-$); B = ($Ph_2SiC{\equiv}C-$).

agreement is good, taking into account the error associated with the signal integration (Table V).

Both proton-decoupled ^{13}C and ^{29}Si NMR results showed that at equilibrium the silylethynyl units are randomly distributed within the polymeric cyclic chains.

Although the relative abundance of sequences at pentad levels may be determined by NMR, the distribution of compositions of individual cyclic or linear species could not be analyzed by either gas or supercritical fluid chromatography. Because of the equilibrium nature of this polymerization reaction, this distribution may be alternatively predicted by a binomial distribution described by the equation[11]

$$P_i = [N!/(N_A!)(N_B!)]X_A^{N_{Ai}}X_B^{N_{Bi}} \quad (1)$$

where P_i is the probability of occurrence of a polymeric species i, X_A and X_B are the mole fractions of A and B silylethynyl units, N_{Ai} and N_{Bi} are the number of A and B units in polymeric species i, and N is the ring size or the degree of polymerization. The distribution of hexameric cocyclics has been calculated for three different compositions (Table VI). These results show the complex mixture existing in these types of copolymers when randomization occurs.

Mechanism of Reaction

The statistical calculations and the NMR observations clearly show that a random redistribution of the silylethynyl units has occurred, whereas a regular alternating pattern might have been expected from a condensation reaction. The dilithium derivative of the diorganodiethynylsilane, which is always in excess in the course of the reaction, was proposed as the species responsible for the redistribution reactions. This was subsequently confirmed by the equilibration of the homopolymers $(Me_2SiC{\equiv}C-)_x$ and $(Ph_2SiC{\equiv}C-)_y$ in the presence of a catalytic amount of dilithium derivative of diphenyldiethynylsilane.

Several other copolymers have been synthesized, combining silylethynyl units bearing hydrogen, methyl, phenyl, and vinyl groups. In all cases, the ^{29}Si and ^{13}C NMR spectral patterns confirmed the occurrence of the redistribution process.[12]

The mechanism of redistribution reactions observed in this synthesis involves the nucleophilic attack of the silylethynyllithium species at the silicon atom of the rings or growing chains.[3] The repetition of the redistribution process allows the random exchange of silylethynyl units among the cyclic and linear species presumably in a mechanism similar to the one proposed for polysiloxane copolymers.[11]

Similarly to the equilibrium process described for poly(dimethylsiloxane-*co*-methylvinylsiloxanes), the equilibration process may be written as follows:

$$\sim\!A^* + A \overset{K_{AA}}{\rightleftharpoons} \sim\!AA^*$$

$$\sim\!A^* + B \overset{K_{AB}}{\rightleftharpoons} \sim\!AB^*$$

$$\sim\!B^* + A \overset{K_{BA}}{\rightleftharpoons} \sim\!BA^*$$

$$\sim\!B^* + B \overset{K_{BB}}{\rightleftharpoons} \sim\!BB^*$$

where K_{IJ} are the equilibrium constants of formation of an IJ diad. The ratios $r_A = K_{AA}/K_{AB}$ and $r_B = K_{BB}/K_{BA}$ can be estimated from the diad probabilities calculated from the ^{29}Si NMR spectra reported in Table III. Since the randomization process is independent of the substituent on the silicon atom and of the temperature in the measured range of 20–64 °C, we may deduce that the enthalpic contribution ΔH°_{IJ} to n-ads formation is negligible. Finally, since the ratios r_A and r_B have been found experimentally to be close to unity and independent of temperature, it would appear that the whole process of equilibration in polysilapropynylene copolymers is entropy driven.

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