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Polymeric Organosilicon Systems. 12. Synthesis and Anionic Ring-Opening Polymerization of 1,2,5,6-Tetrasilacycloocta-3,7-diynes

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Six 1,2,5,6-tetrasilacycloocta-3,7-diynes were synthesized by the reaction of the di-Grignard reagents of 1,2-diethynyldisilanes with 1,2-dichlorodisilanes. The reaction of the di-Grignard reagent of 1,2-diethynyl-1,2-dimethyldiphenyldisilane with 1,2-dichloro-1,2-dimethyldiphenyldisilane gave two isomers, *r*-1,*t*-2,*t*-5,*c*-6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (*cis–trans*-**1b**) and *r*-1,*t*-2,*c*-5,*t*-6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (*all-trans*-**1b**) whose configurations were determined by an X-ray diffraction study. *cis–trans*-**1b** crystallizes in the trigonal space group $R\bar{3}$ with cell dimensions $a = b = 21.671$ (6) Å, $c = 16.639$ (2) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6557$ (3) Å^3, and $D_{\text{calcd}} = 1.167$ Mg/m^3 ($Z = 9$), while *all-trans*-**1b** crystallizes in the monoclinic space group $P2_1/a$ with cell dimensions $a = 18.308$ (6) Å, $b = 11.339$ (3) Å, $c = 15.352$ (4) Å, $\alpha = \gamma = 90°$, $\beta = 94.50$ (2)°, $V = 3186$ (2) Å^3, and $D_{\text{calcd}} = 1.106$ Mg/m^3 ($Z = 4$). Treatment of 1,2,5,6-tetrasilacycloocta-3,7-diynes with a catalytic amount of *n*-butyllithium in THF at room temperature afforded poly[(disilanylene)ethynylenes] with high molecular weights. The reaction of poly[(1,2-dimethyldiphenyldisilanylene)ethynylene] (**1c**), whose molecular weight was determined to be 77 900, with a catalytic amount of *n*-butyllithium in THF at room temperature resulted in depolymerization of the starting polymer to give oligomers with M_w = 1 500. Treatment of poly[(tetraethyldisilanylene)ethynylene] (**5c**) with a catalytic amount of *n*-butyllithium under the same conditions led to redistribution to give the polymer which showed a very broad molecular weight distribution. Similarly, poly[(1,2-di-*n*-hexyldimethyldisilanylene)ethynylene] underwent redistribution in the presence of a trace of *n*-butyllithium, but the rate of the reaction was determined to be slow. Irradiation of a benzene solution of the poly[(disilanylene)ethynylenes] with a low-pressure mercury lamp resulted in homolytic scission of silicon–silicon bonds to give photodegradation products with low molecular weights. Irradiation of the films prepared from the polymers in air also led to the scission of the silicon–silicon bonds in the polymer backbone to give the products which have silanol and siloxy groups. Treatment of the films prepared from **1c**, **5c**, and poly[(1,2-diethyldimethyldisilanylene)ethynylene] with antimony pentafluoride vapor afforded conducting films.

Introduction

We have demonstrated that organosilicon polymers in which the regular alternating arrangement of a disilanylene unit and π-electron system is found in the polymer backbone are photoactive and show conducting properties when the polymers are doped by exposure to antimony pentafluoride vapor.

Alternating polymers containing the disilanylene-π-electron system can readily be accomplished by the sodium condensation reaction of compounds involving two chlorosilyl groups attached to the π-electron system.[2–6] However, the major problem of this method is, the lack of reproducibility for the product yields and molecular weights of the resulting polymers. In an attempt to develop a method that does not involve alkali-metal condensation for the preparation of the alternating copolymers, we discovered that 1,2,5,6-tetrasilacycloocta-3,7-diynes undergo anionic ring-opening polymerization to give poly[(disilanylene)ethynylenes] in the presence of a catalytic amount of *n*-butyllithium in THF. We now wish to report in detail the synthesis and ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes and some properties of the resulting poly[(disilanylene)ethynylenes].

Results and Discussion

Synthesis. The first strained eight-membered cyclic (disilanylene)ethynylene, octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne has been synthesized by Sakurai and his co-workers from the thermal and photochemical ring contraction of permethylated 1,2,3,6,7-pentasilacyclonona-4,8-diyne.[7] Recently, Iwahara and West have reported the preparation of three tetrasilacyclooctadiyne derivatives, 1,1,2,2,5,5,6,6-octamethyl-, 1,1,2,2,5,5,6,6-octa-*n*-butyl-, and 1,2,5,6-tetra-*n*-butyltetramethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne in high yields.[8] Their method involves the reaction of the di-Grignard reagents prepared from 1,2-diethynyldisilanes and ethylmagnesium bromide with 1,2-dichlorodisilanes. We have also found that the tetrasilacyclooctadiynes can readily be prepared by the reaction of the di-Grignard reagents of 1,2-diethynyldisilanes with 1,2-dichlorodisilanes.[9a]

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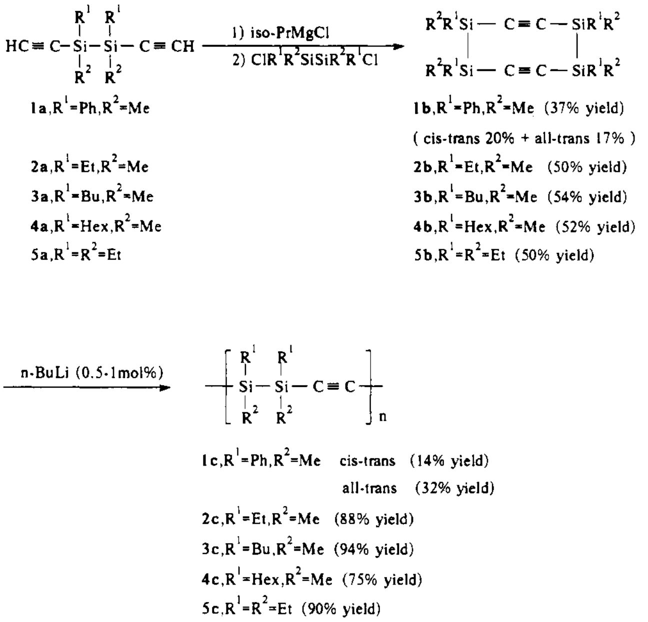
Scheme I



The starting 1,2-diethynyldisilanes were synthesized by the reaction of ethynylmagnesium bromide obtained from ethylmagnesium bromide and acetylene in THF, with 1,2-dichlorodisilanes. Using this method, 1,2-diethynyl-1,2-dimethyldiphenyldisilane (**1a**),[9b] 1,2-diethyl-1,2-diethynyldimethyldisilane (**2a**), 1,2-di-*n*-butyl-1,2-diethynyldimethyldisilane[8] (**3a**), 1,2-diethynyl-1,2-di-*n*-hexyldimethyldisilane (**4a**), and tetraethyl-1,2-diethynyldisilane (**5a**) were synthesized in 82, 87, 83, 48, and 84% yields, respectively. Compounds **1a**–**4a** were isolated as a mixture of *dl* and meso isomers, and the mixture of *dl* and meso isomers was used for the synthesis of the tetrasilacyclooctadiynes. The reaction of the di-Grignard reagents prepared from **1a**–**5a** and 2 equiv of isopropylmagnesium chloride in THF, with the corresponding 1,2-dichlorodisilanes afforded 1,2,5,6-tetrasilacycloocta-3,7-diynes **1b**–**5b** in 37–54% yields (Scheme I).

In the reaction of the di-Grignard reagent prepared from **1a** with 1,2-dichloro-1,2-dimethyldiphenyldisilane, two isomers of 1,2,5,6-tetrasilacycloocta-3,7-diyne were isolated as white crystals in 20 and 17% yields, respectively, after fractional recrystallization of the reaction mixture. Configurations of these two isomers were verified by an X-ray crystallographic analysis. One isomer which crystallized from benzene and melts at 202–203 °C was identified as *r*-1,*t*-2,*t*-5,*c*-6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (*cis–trans*-**1b**), that is, two phenyl groups on an Si–Si moiety are located in a trans fashion, but two phenyls on an Si—C≡C—Si group are cis each other. The other isomer which crystallized from benzene–hexane and melts at 155–156 °C was identified as *r*-1,*t*-2,*c*-5,*t*-6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (*all-trans*-**1b**) in which all phenyl groups are located in a trans fashion (see below).

Similar reactions of the di-Grignard reagents prepared from **2a**–**5a** with the corresponding 1,2-dichlorodisilanes gave 1,2,5,6-tetraethyltetramethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**2b**), 1,2,5,6-tetra-*n*-butyltetramethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne[8] (**3b**), 1,2,5,6-tetra-*n*-hexyltetramethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**4b**), and 1,1,2,2,5,5,6,6-octaethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**5b**) in 50, 54, 52, and 50% yields, respectively. ^{1}H and ^{13}C NMR spectra of **2b**–**4b** appear as if only one isomer is present in the isolated product (see Experimental Section). Tetrasilacyclooctadiyne **2b** thus obtained is colorless crystals but melts at 30–32 °C. Unfortunately, no single crystal, analogous to *cis–trans*-**1b** or *all-trans*-**1b**, could be obtained by fractional recrystallization, because of the low melting point of **2b**. Compounds **3b** and **4b** are colorless liquids, and therefore, we could not clarify whether or not the products **2b**–**4b** consist of a mixture of isomers. However, on the basis of the fact that the chemical shifts of the ^{1}H and ^{13}C NMR spectra of *cis–trans*-**1b** are the same as those of *all-trans*-**1b**, the products **2b**, **3b**, and **4b** are thought to be a mixture consisting of two isomers, analogous to *cis–trans*-**1b** and *all-trans*-**1b**. In ^{1}H and ^{13}C NMR spectra for **2b**–**4b**, the chemical shifts for two isomers would be accidentally overlapping.

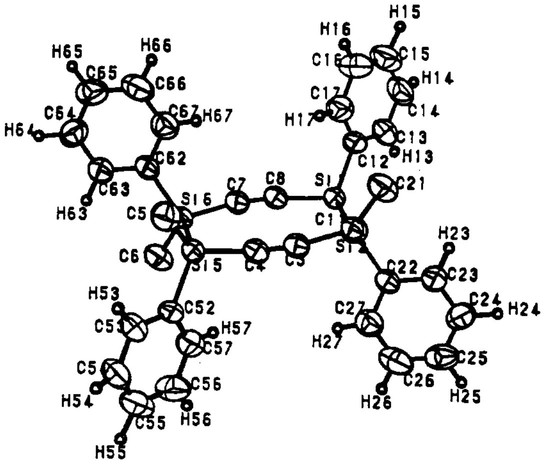


Figure 1. Molecular structure of *cis–trans*-**1b** with the atomic numbering system. The harmonic parts of the displacement ellipsoids for non-hydrogen atoms are drawn at the 50% probability level.

The structures of compounds **2b**–**5b** were confirmed by mass, IR, and ^{1}H and ^{13}C NMR spectroscopic analyses (see Experimental Section).

X-ray Analysis of *cis–trans*-1b and *all-trans*-1b. The molecular structures of *cis–trans*-**1b** and *all-trans*-**1b** were determined by the X-ray crystal structural analysis.[10] *cis–trans*-**1b** which is obtained by recrystallization from benzene belongs to the trigonal space group $R\bar{3}$ with cell dimensions $a = b = 21.671$ (6) Å, $c = 16.639$ (2) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6557$ (3) Å^3, and $D_{\text{calcd}} = 1.167$ Mg/m^3 ($Z = 9$), while *all-trans*-**1b** crystallizes in the monoclinic space group $P2_1/a$ with cell dimensions $a = 18.308$ (6) Å, $b = 11.339$ (3) Å, $c = 15.352$ (4) Å, $\alpha = \gamma = 90°$, $\beta = 94.50$ (2)°, $V = 3186$ (2) Å^3, and $D_{\text{calcd}} = 1.106$ Mg/m^3 ($Z = 4$). The experimental conditions, crystal data, and summaries of structural refinements for the two compounds are listed in Table I. The crystal structures of both compounds were solved by MULTAN[11] and refined by the block-diagonal least-squares method.[12] Four large reflections of *cis–trans*-**1b**, (3,-2,2), (5,-3,-1), (7,-5,3), and (7,-5,6), affected seriously by extinction or absorption were excluded from the refinement. The final fractional coordinates and

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[10] X-ray crystallographic analysis of 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne has been reported; see ref 7.

[11] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 369.

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Table I. Crystal Data, Experimental Conditions and Summaries of Structural Refinement for *cis–trans*-1b and *all-trans*-1b

	cis–trans-**1b**	*all-trans*-**1b**
mol formula	$Si_4C_{32}H_{32}$	$Si_4C_{32}H_{32}$
mol wt	528.95	528.95
space group	$R\bar{3}$	$P2_1/a$
cell dimens		
a, Å	21.671 (6)	18.308 (6)
b, Å	21.671 (6)	11.339 (3)
c, Å	16.639 (2)	15.352 (4)
α, deg	90.0	90.0
β, deg	90.0	94.50 (2)
γ, deg	120.0	90.0
V, Å^3	6557 (3)	3186 (2)
D_{calcd}, Mg/m^3	1.167	1.106
cryst size, mm	0.2 × 0.2 × 0.5	0.5 × 0.5 × 0.6
cryst habit	prismatic	prismatic
cryst color	colorless	colorless
μ, mm^{-1}	1.98	0.20
diffractometer	Rigaku AFC5	Rigaku AFC4
temp, K	298	298
wavelength, Å	1.5418 (Cu Kα)	0.7107 (Mo Kα)
monochromator	graphite crystal	graphite crystal
scan type	θ–2θ	θ–2θ
scan speed, deg/min	8	8
scan width, deg	$4 < 2\theta < 120$	$3 < 2\theta < 45$
diffraction geometry	symmetrical A	symmetrical A
range of h,k,l		
h	$0 < h < 14^a$	$0 < h < 19$
k	$0 < k < 14^a$	$0 < k < 12$
l	$-14 < l < 14^a$	$-16 < l < 16$
no. of unique reflns	2265	4430
no. of obsd reflns	1904 ($F_o > 3\sigma(F_o)$)	2691 ($F_o > 3\sigma(F_o)$)
R_{sym}	0.055	0.017
$F(000)$	140	280
R	0.079	0.064
R_w^{b}	0.103	0.071
S	1.84	1.94
max $\Delta\rho$, e/Å^3	0.58	0.17
min $\Delta\rho$, e/Å^3	–0.42	–0.17

[a] Indices are given in rhombohedral reciprocal lattice. [b] Weighting schemes for *cis–trans*-**1b** and *all-trans*-**1b** are $(\sigma(F_o) + 0.09724F_o + 0.00070F_o^2)^{-1}$ and $(\sigma(F_o) + 0.07800F_o + 0.00001F_o^2)^{-1}$, respectively.

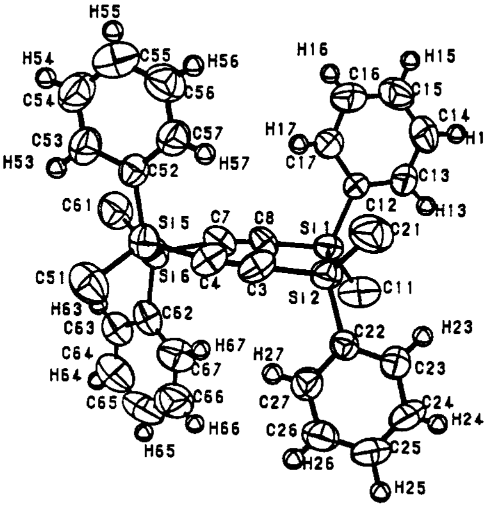

Figure 2. Molecular structure of *all-trans*-**1b** with the atomic numbering system drawn as Figure 1.

equivalent isotropic thermal parameters for non-hydrogen atoms of *cis–trans*-**1b** and *all-trans*–**1b** are listed in Tables II and III, respectively. Perspective views of the molecular structures of *cis–trans*-**1b** and *all-trans*-**1b** with their atomic numbering schemes are shown in Figures 1 and 2. Bond distances and angles for both compounds are given in Tables IV and V.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) with Esd's in Parentheses for *cis–trans*-1b

atom	x	y	z	B_{eq}/B_{iso}^{a}
Si(6)	0.20037 (6)	0.12143 (6)	0.21459 (7)	4.04 (2)
Si(1)	0.42290 (6)	0.29199 (6)	0.09711 (7)	4.03 (2)
C(7)	0.2776 (2)	0.2011 (2)	0.1720 (2)	4.5 (1)
C(8)	0.3335 (2)	0.2439 (2)	0.1424 (2)	4.4 (1)
C(61)	0.1237 (2)	0.0838 (2)	0.1420 (3)	5.6 (1)
C(62)	0.1738 (2)	0.1472 (2)	0.3107 (2)	4.2 (1)
C(63)	0.1049 (2)	0.1077 (2)	0.3402 (2)	5.1 (1)
C(64)	0.0834 (2)	0.1266 (3)	0.4094 (2)	5.9 (2)
C(65)	0.1301 (3)	0.1858 (3)	0.4506 (2)	6.1 (2)
C(66)	0.1989 (3)	0.2258 (2)	0.4241 (3)	6.4 (2)
C(67)	0.2206 (2)	0.2074 (2)	0.3539 (2)	5.4 (1)
C(11)	0.4174 (2)	0.3104 (3)	–0.0113 (2)	6.3 (2)
C(12)	0.4780 (2)	0.3771 (2)	0.1533 (2)	4.3 (1)
C(13)	0.5169 (2)	0.4419 (2)	0.1134 (2)	5.1 (1)
C(14)	0.5591 (2)	0.5043 (2)	0.1562 (3)	6.4 (2)
C(15)	0.5627 (3)	0.5045 (3)	0.2377 (3)	6.9 (2)
C(16)	0.5250 (3)	0.4421 (3)	0.2782 (3)	6.9 (2)
C(17)	0.4821 (2)	0.3784 (2)	0.2366 (2)	5.9 (2)
H(61a)	0.087 (3)	0.037 (2)	0.165 (3)	4 (1)
H(61b)	0.132 (4)	0.061 (3)	0.088 (4)	9 (2)
H(61c)	0.108 (4)	0.123 (4)	0.141 (4)	8 (2)
H(11a)	0.383 (2)	0.271 (2)	–0.037 (2)	3 (1)
H(11b)	0.460 (3)	0.324 (3)	–0.033 (3)	6 (1)
H(11c)	0.397 (4)	0.340 (4)	–0.009 (4)	9 (2)
H(63)	0.067 (2)	0.065 (2)	0.307 (3)	3 (1)
H(64)	0.034 (3)	0.098 (3)	0.423 (3)	7 (2)
H(65)	0.118 (2)	0.198 (2)	0.501 (3)	4 (1)
H(66)	0.234 (3)	0.268 (3)	0.449 (3)	4 (1)
H(67)	0.269 (3)	0.233 (3)	0.339 (3)	4 (1)
H(13)	0.514 (2)	0.446 (3)	0.056 (3)	4 (1)
H(14)	0.582 (3)	0.546 (3)	0.140 (3)	6 (1)
H(15)	0.596 (3)	0.550 (3)	0.269 (3)	6 (1)
H(16)	0.531 (3)	0.439 (3)	0.334 (3)	6 (1)
H(17)	0.456 (3)	0.332 (3)	0.265 (3)	5 (1)

[a] $B_{eq} = (4/3)(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + abB_{12}\cos\gamma)$.

The molecular structure of *cis–trans*-**1b** shown stereoscopically in Figure 3a,b has a center of symmetry and a quasi $2/m$ symmetry. Four phenyl groups are displaced from equivalent positions of the $2/m$ symmetry by rotation about the respective Si–Ph bonds. The eight-membered rings are in a plane within +0.05 Å. Phenyl groups are located in trans position to each other at each Si–Si bond, and in cis position at each Si—C≡C—Si group. The molecule *all-trans*-**1b** shown by stereoscopic pairs in Figure 4a,b exhibits roughly 222 symmetry. The phenyl groups on the Si—Si and Si—C≡C—Si moieties are all trans to each other. Four phenyl groups are displaced from the equivalent positions of the 222 symmetry as those of *cis–trans*-**1b**. The eight-membered ring is twisted and its maximum deviation from a least-squares plane is as large as 0.27 Å.

Anionic Polymerization. The anionic polymerization of **1b**–**5b** was carried out using *n*-butyllithium as a catalyst in a degassed sealed tube. Thus, after a THF solution of *cis–trans*-**1b** in the presence of 0.3 mol % of *n*-butyllithium was stirred at room temperature for 64 h, precipitation of the resulting mixture from ethanol afforded poly[(1,2-dimethyldiphenyldisilanylene)ethynylene] (**1c**) whose molecular weight was determined to be 80 800 (M_w/M_n = 4.08) in 14% yield, after twice reprecipitation from benzene–ethanol. Similar treatment of *all-trans*-**1b** also gave the polymer **1c** with a molecular weight of 77 900 (M_w/M_n = 2.78) in 32% yield. Interestingly, ^{1}H and ^{13}C NMR spectra for the polymer obtained from *cis–trans*-**1b** were identical with those of the polymer prepared by anionic polymerization of *all-trrans*-**1b** (see below).

The polymer of **1c** was prepared by a different synthetic route in order to compare spectral data to **1c** prepared

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Esd's in Parentheses for *all-trans*-1b

atom	x	y	z	B_{eq}/B_{iso}
Si(1)	0.2221 (1)	0.2821 (1)	0.4036 (1)	4.9 (1)
Si(2)	0.1763 (1)	0.4214 (1)	0.2975 (1)	5.1 (1)
Si(5)	0.2039 (1)	0.1352 (1)	0.0774 (1)	5.4 (1)
Si(6)	0.1958 (1)	−0.0123 (1)	0.1846 (1)	5.3 (1)
C(3)	0.1797 (3)	0.3422 (5)	0.1935 (3)	5.6 (1)
C(4)	0.1837 (3)	0.2693 (5)	0.1364 (3)	5.6 (1)
C(7)	0.2218 (2)	0.0702 (5)	0.2853 (3)	5.2 (1)
C(8)	0.2249 (2)	0.1451 (5)	0.3411 (3)	5.0 (1)
C(11)	0.1613 (3)	0.2660 (7)	0.4945 (5)	8.4 (2)
C(12)	0.3173 (2)	0.3164 (4)	0.4465 (3)	4.4 (1)
C(13)	0.3331 (3)	0.3775 (6)	0.5225 (4)	7.2 (2)
C(14)	0.4045 (3)	0.4009 (7)	0.5548 (4)	8.6 (2)
C(15)	0.4614 (3)	0.3629 (6)	0.5122 (4)	7.8 (2)
C(16)	0.4480 (3)	0.3016 (7)	0.4357 (5)	8.7 (2)
C(17)	0.3763 (3)	0.2786 (6)	0.4046 (4)	7.2 (2)
C(21)	0.2347 (4)	0.5561 (6)	0.2990 (5)	9.1 (2)
C(22)	0.0788 (2)	0.4626 (4)	0.3096 (3)	4.5 (1)
C(23)	0.0596 (3)	0.5337 (5)	0.3777 (4)	6.4 (2)
C(24)	−0.0132 (3)	0.5613 (6)	0.3860 (4)	7.3 (2)
C(25)	−0.0682 (3)	0.5207 (6)	0.3292 (4)	7.0 (2)
C(26)	−0.0501 (3)	0.4527 (5)	0.2617 (4)	6.5 (2)
C(27)	0.0219 (3)	0.4216 (5)	0.2523 (3)	5.5 (1)
C(51)	0.1390 (3)	0.1100 (7)	−0.0203 (4)	8.3 (2)
C(52)	0.3000 (3)	0.1493 (4)	0.0469 (3)	4.9 (1)
C(53)	0.3291 (3)	0.0653 (5)	−0.0063 (4)	7.0 (2)
C(54)	0.4008 (4)	0.0730 (6)	−0.0281 (4)	8.4 (2)
C(55)	0.4466 (3)	0.1615 (7)	0.0031 (4)	8.4 (2)
C(56)	0.4179 (3)	0.2459 (6)	0.0549 (5)	8.0 (2)
C(57)	0.3462 (3)	0.2389 (5)	0.0769 (4)	6.3 (2)
C(61)	0.2579 (3)	−0.1387 (5)	0.1683 (4)	7.6 (2)
C(62)	0.0991 (3)	−0.0592 (5)	0.1967 (3)	5.6 (1)
C(63)	0.0787 (3)	−0.1775 (5)	0.1953 (4)	7.2 (2)
C(64)	0.0100 (4)	−0.2118 (7)	0.2113 (5)	9.2 (2)
C(65)	−0.0410 (3)	−0.1317 (7)	0.2304 (4)	9.2 (2)
C(66)	−0.0239 (3)	−0.0140 (8)	0.2321 (4)	9.0 (2)
C(67)	0.0457 (3)	0.0222 (6)	0.2153 (4)	7.7 (2)
H(11a)	0.119 (3)	0.241 (5)	0.472 (4)	6 (2)
H(11b)	0.159 (3)	0.342 (6)	0.517 (4)	7 (2)
H(11c)	0.185 (3)	0.213 (5)	0.537 (4)	5 (2)
H(21a)	0.283 (3)	0.539 (6)	0.302 (4)	7 (2)
H(21b)	0.225 (3)	0.594 (6)	0.242 (4)	7 (2)
H(21c)	0.223 (3)	0.612 (6)	0.349 (4)	7 (2)
H(51a)	0.091 (3)	0.070 (5)	−0.004 (3)	5 (1)
H(51b)	0.154 (3)	0.040 (6)	−0.057 (4)	7 (2)
H(51c)	0.137 (4)	0.178 (6)	−0.050 (4)	8 (2)
H(61a)	0.258 (3)	−0.194 (4)	0.217 (3)	4 (1)
H(61b)	0.308 (3)	−0.102 (6)	0.171 (4)	7 (2)
H(61c)	0.245 (4)	−0.174 (6)	0.119 (4)	8 (2)
H(13)	0.295 (3)	0.405 (5)	0.559 (3)	4 (1)
H(14)	0.414 (3)	0.446 (6)	0.609 (4)	7 (2)
H(15)	0.516 (3)	0.381 (5)	0.535 (3)	5 (1)
H(16)	0.484 (3)	0.280 (6)	0.400 (4)	8 (2)
H(17)	0.370 (3)	0.240 (4)	0.353 (3)	4 (1)
H(23)	0.100 (3)	0.563 (4)	0.422 (3)	4 (1)
H(24)	−0.023 (3)	0.603 (5)	0.436 (3)	5 (2)
H(25)	−0.124 (3)	0.540 (5)	0.341 (3)	5 (1)
H(26)	−0.088 (3)	0.424 (4)	0.219 (3)	4 (1)
H(27)	0.034 (2)	0.372 (4)	0.206 (3)	2 (1)
H(53)	0.295 (3)	−0.004 (4)	−0.028 (3)	4 (1)
H(54)	0.420 (4)	0.014 (6)	−0.067 (4)	9 (2)
H(55)	0.496 (4)	0.172 (7)	−0.010 (5)	10 (2)
H(56)	0.445 (3)	0.310 (6)	0.079 (4)	7 (2)
H(57)	0.325 (2)	0.298 (4)	0.115 (3)	2 (1)
H(63)	0.117 (3)	−0.232 (5)	0.184 (4)	6 (2)
H(64)	−0.004 (3)	−0.291 (6)	0.209 (4)	7 (2)
H(65)	−0.089 (3)	−0.153 (6)	0.247 (4)	7 (2)
H(66)	−0.062 (3)	0.045 (5)	0.246 (4)	6 (2)
H(67)	0.058 (2)	0.108 (4)	0.222 (3)	3 (1)

[a] $B_{eq} = (4/3)(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)$.

Table IV. Bond Lengths (Å) and Bond Angles (deg) with Their Esd's in Parentheses for *cis–trans*-1b

Si(6)–C(7)	1.843 (5)	Si(6)–C(61)	1.879 (6)
Si(6)–C(62)	1.875 (5)	Si(1)–C(8)	1.841 (5)
Si(1)–C(11)	1.864 (7)	Si(1)–C(12)	1.871 (5)
C(7)–C(8)	1.201 (7)	C(62)–C(63)	1.388 (7)
C(62)–C(67)	1.387 (8)	C(63)–C(64)	1.379 (9)
C(64)–C(65)	1.359 (9)	C(65)–C(66)	1.370 (9)
C(66)–C(67)	1.390 (9)	C(12)–C(13)	1.393 (7)
C(12)–C(17)	1.388 (8)	C(13)–C(14)	1.391 (8)
C(14)–C(15)	1.359 (9)	C(15)–C(16)	1.358 (10)
C(16)–C(17)	1.402 (10)	C(61)–H(61a)	1.00 (6)
C(61)–H(61b)	1.08 (8)	C(61)–H(61c)	1.05 (8)
C(11)–H(11a)	0.92 (5)	C(11)–H(11b)	0.90 (7)
C(11)–H(11c)	0.95 (8)	C(63)–H(63)	1.04 (5)
C(64)–H(64)	0.96 (8)	C(65)–H(65)	0.95 (5)
C(66)–H(66)	0.94 (6)	C(67)–H(67)	0.94 (6)
C(13)–H(13)	0.97 (6)	C(14)–H(14)	0.83 (7)
C(15)–H(15)	1.03 (7)	C(16)–H(16)	0.95 (7)
C(17)–H(17)	0.99 (6)	Si(6)–Si(5)	2.380 (2)

C(7)–Si(6)–C(61)	110.6 (2)	C(7)–Si(6)–C(62)	108.6 (2)
C(61)–Si(6)–C(62)	109.9 (2)	C(8)–Si(1)–C(11)	110.8 (3)
C(8)–Si(1)–C(12)	109.0 (2)	C(11)–Si(1)–C(12)	110.5 (3)
Si(6)–C(7)–C(8)	166.7 (5)	Si(1)–C(8)–C(7)	166.7 (5)
Si(6)–C(62)–C(63)	120.9 (4)	Si(6)–C(62)–C(67)	122.2 (4)
C(63)–C(62)–C(67)	116.9 (5)	C(62)–C(63)–C(64)	122.1 (5)
C(63)–C(64)–C(65)	119.9 (6)	C(64)–C(65)–C(66)	119.8 (6)
C(65)–C(66)–C(67)	120.5 (6)	C(62)–C(67)–C(66)	120.8 (5)
Si(1)–C(12)–C(13)	121.4 (4)	Si(1)–C(12)–C(17)	121.4 (4)
C(13)–C(12)–C(17)	117.1 (5)	C(12)–C(13)–C(14)	120.5 (5)
C(13)–C(14)–C(15)	121.6 (6)	C(14)–C(15)–C(16)	119.1 (7)
C(15)–C(16)–C(17)	120.6 (7)	C(12)–C(17)–C(16)	121.1 (6)
Si(6)–C(61)–H(61a)	106 (3)	Si(6)–C(61)–H(61b)	115 (4)
Si(6)–C(61)–H(61c)	103 (4)	H(61a)–C(61)–H(61b)	96 (5)
H(61a)–C(61)–H(61c)	113 (5)	H(61b)–C(61)–H(61c)	123 (6)
C(62)–C(63)–H(63)	120 (3)	C(63)–C(64)–H(64)	116 (5)
C(65)–C(64)–H(64)	124 (5)	C(64)–C(65)–H(65)	122 (3)
C(66)–C(65)–H(65)	119 (3)	C(65)–C(66)–H(66)	125 (4)
C(67)–C(66)–H(66)	115 (4)	C(62)–C(67)–H(67)	119 (4)
C(66)–C(67)–H(67)	119 (4)	Si(1)–C(11)–H(11a)	112 (3)
Si(1)–C(11)–H(11b)	107 (4)	Si(1)–C(11)–H(11c)	102 (5)
H(11a)–C(11)–H(11b)	110 (6)	H(11a)–C(11)–H(11c)	102 (6)
H(11b)–C(11)–H(11c)	123 (7)	C(14)–C(13)–H(13)	118 (3)
C(13)–C(14)–H(14)	129 (5)	C(15)–C(14)–H(14)	109 (5)
C(14)–C(15)–H(15)	121 (4)	C(16)–C(15)–H(15)	119 (4)
C(15)–C(16)–H(16)	122 (4)	C(17)–C(16)–H(16)	118 (4)
C(16)–C(17)–H(17)	122 (4)	Si(5)–Si(6)–C(6)	103.7 (2)

from anionic ring-opening polymerization. The reaction of bis(chloromethylphenylsilyl)acetylene with sodium dispersion in refluxing toluene gave a yellow solid polymer with molecular weight of $M_w = 16000$ ($M_w/M_n = 2.91$) in 33% yield.[13] In contrast to the ^{1}H NMR spectrum of **1c**, which shows narrow resonances, the polymer obtained from the sodium condensation reveals broad signals along with a sharp signal in the methylsilyl region, as shown in Figure 5. The ^{13}C NMR spectrum of **1c** shows two sharp resonances at δ −4.02 and −3.95 ppm due to methylsilyl carbons and at δ 114.4 ppm attributed to ethynylene carbons, while the polymer obtained from the sodium condensation displays multiple resonances in the region of both methylsilyl carbons and acetylene carbons. These results indicate that the ring-opening polymerization proceeds with stereospecificity.

The reaction of *cis–trans*-**1b** and *all-trans*-**1b** with a catalytic amount of *n*-butyllithium afforded the polymers only in low yields. However, 1,2,5,6-tetrasilacycloocta-3,7-diynes that have no phenyl groups on silicon atoms, such as **2b–5b**, undergo the ring-opening polymerization under the same conditions to give (disilanylene)ethynylene polymers in high yields. Thus, treatment of **2b** with a catalytic amount of *n*-butyllithium gave poly[(1,2-diethyldimethyldisilanylene)ethynylene] (**2c**) with a high molecular weight in 88% yield. Eight-membered cyclic compounds having long-chain alkyl groups as substituents on silicon atoms, **3b** and **4b**, also undergo polymerization

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(13) Recently, poly[(disilanylene)ethynylenes] have been synthesized by the reaction of 1,2-dichlorodisilanes and dilithium reagents of 1,2-diethynyldisilanes; see ref 14.

(14) Iwahara, T.; Hayase, S.; West, R. *Macromolecules* **1990**, *23*, 1298.

Table V. Bond Lengths (Å) and Bond Angles (deg) with Their Esd's in Parentheses for *all-trans*-1b

Si(1)–Si(2)	2.375 (3)	Si(1)–C(8)	1.828 (6)	C(63)–C(64)	1.357 (11)	C(64)–C(65)	1.351 (12)
Si(1)–C(11)	1.862 (9)	Si(1)–C(12)	1.855 (6)	C(65)–C(66)	1.370 (13)	C(66)–C(67)	1.382 (12)
Si(2)–C(3)	1.836 (6)	Si(2)–C(21)	1.863 (9)	C(11)–H(11a)	0.87 (6)	C(11)–H(11b)	0.93 (6)
Si(2)–C(22)	1.868 (6)	Si(5)–Si(6)	2.360 (3)	C(11)–H(11c)	0.97 (6)	C(13)–H(13)	0.98 (5)
Si(5)–C(4)	1.823 (6)	Si(5)–C(51)	1.859 (8)	C(14)–H(14)	0.98 (7)	C(15)–H(15)	1.06 (6)
Si(5)–C(52)	1.864 (6)	Si(6)–C(7)	1.837 (6)	C(16)–H(16)	0.92 (7)	C(17)–H(17)	0.90 (5)
Si(6)–C(61)	1.859 (8)	Si(6)–C(62)	1.872 (6)	C(21)–H(21a)	0.91 (7)	C(21)–H(21b)	0.98 (7)
C(3)–C(4)	1.212 (8)	C(7)–C(8)	1.205 (8)	C(21)–H(21c)	1.03 (6)	C(23)–H(23)	1.02 (5)
C(12)–C(13)	1.369 (9)	C(12)–C(17)	1.368 (9)	C(24)–H(24)	0.93 (6)	C(25)–H(25)	1.08 (6)
C(13)–C(14)	1.386 (11)	C(14)–C(15)	1.344 (11)	C(26)–H(26)	0.98 (5)	C(27)–H(27)	0.94 (4)
C(15)–C(16)	1.370 (12)	C(16)–C(17)	1.385 (12)	C(51)–H(51a)	0.97 (6)	C(51)–H(51b)	1.02 (7)
C(22)–C(23)	1.388 (9)	C(22)–C(27)	1.389 (8)	C(51)–H(51c)	0.90 (7)	C(53)–H(53)	1.04 (5)
C(23)–C(24)	1.384 (10)	C(24)–C(25)	1.360 (10)	C(54)–H(54)	0.99 (7)	C(55)–H(55)	0.94 (8)
C(25)–C(26)	1.354 (10)	C(26)–C(27)	1.382 (9)	C(56)–H(56)	0.94 (6)	C(57)–H(57)	0.99 (5)
C(52)–C(53)	1.388 (9)	C(52)–C(57)	1.379 (9)	C(61)–H(61a)	0.97 (5)	C(61)–H(61b)	1.00 (7)
C(53)–C(54)	1.382 (10)	C(54)–C(55)	1.369 (11)	C(61)–H(61c)	0.87 (7)	C(63)–H(63)	0.97 (6)
C(55)–C(56)	1.375 (11)	C(56)–C(57)	1.382 (10)	C(64)–H(64)	0.93 (7)	C(65)–H(65)	0.96 (6)
C(62)–C(63)	1.392 (9)	C(62)–C(67)	1.390 (9)	C(66)–H(66)	1.00 (6)	C(67)–H(67)	1.00 (5)

Si(2)–Si(1)–C(8)	103.2 (2)	Si(2)–Si(1)–C(11)	112.3 (3)	Si(1)–C(11)–H(11c)	107 (3)	H(11a)–C(11)–H(11b)	112 (6)
Si(2)–Si(1)–C(12)	112.0 (2)	C(8)–Si(1)–C(11)	110.7 (3)	H(11a)–C(11)–H(11c)	114 (5)	H(11b)–C(11)–H(11c)	112 (5)
C(8)–Si(1)–C(12)	107.5 (3)	C(11)–Si(1)–C(12)	110.8 (3)	C(12)–C(13)–H(13)	122 (3)	C(14)–C(13)–H(13)	116 (3)
Si(1)–Si(2)–C(3)	103.7 (2)	Si(1)–Si(2)–C(21)	111.4 (3)	C(13)–C(14)–H(14)	120 (4)	C(15)–C(14)–H(14)	119 (4)
Si(1)–Si(2)–C(22)	112.7 (2)	C(3)–Si(2)–C(21)	110.7 (4)	C(14)–C(15)–H(15)	122 (3)	C(16)–C(15)–H(15)	119 (3)
C(3)–Si(2)–C(22)	107.8 (3)	C(21)–Si(2)–C(22)	110.2 (3)	C(15)–C(16)–H(16)	124 (4)	C(17)–C(16)–H(16)	117 (4)
Si(6)–Si(5)–C(4)	102.6 (2)	Si(6)–Si(5)–C(51)	112.5 (3)	C(12)–C(17)–H(17)	121 (3)	C(16)–C(17)–H(17)	117 (3)
Si(6)–Si(5)–C(52)	110.4 (2)	C(4)–Si(5)–C(51)	112.8 (3)	Si(2)–C(21)–H(21a)	113 (4)	Si(2)–C(21)–H(21b)	106 (4)
C(4)–Si(5)–C(52)	106.6 (3)	C(51)–Si(5)–C(52)	111.5 (3)	Si(2)–C(21)–H(21c)	111 (4)	H(21a)–C(21)–H(21b)	105 (6)
Si(5)–Si(6)–C(7)	101.6 (2)	Si(5)–Si(6)–C(61)	112.3 (3)	H(21a)–C(21)–H(21c)	111 (5)	H(21b)–C(21)–H(21c)	111 (5)
Si(5)–Si(6)–C(62)	112.4 (2)	C(7)–Si(6)–C(61)	112.7 (3)	C(22)–C(23)–H(23)	119 (3)	C(24)–C(23)–H(23)	121 (3)
C(7)–Si(6)–C(62)	104.3 (3)	C(61)–Si(6)–C(62)	112.8 (3)	C(23)–C(24)–H(24)	116 (4)	C(25)–C(24)–H(24)	122 (4)
Si(2)–C(3)–C(4)	166.1 (6)	Si(5)–C(4)–C(3)	162.8 (6)	C(24)–C(25)–H(25)	119 (3)	C(26)–C(25)–H(25)	123 (3)
Si(6)–C(7)–C(8)	162.2 (5)	Si(1)–C(8)–C(7)	166.1 (5)	C(25)–C(26)–H(26)	121 (3)	C(27)–C(26)–H(26)	118 (3)
Si(1)–C(12)–C(13)	122.6 (5)	Si(1)–C(12)–C(17)	121.5 (5)	C(22)–C(27)–H(27)	117 (3)	C(26)–C(27)–H(27)	121 (3)
C(13)–C(12)–C(17)	116.0 (6)	C(12)–C(13)–C(14)	122.1 (7)	Si(5)–C(51)–H(51a)	111 (3)	Si(5)–C(51)–H(51b)	112 (4)
C(13)–C(14)–C(15)	120.7 (8)	C(14)–C(15)–C(16)	119.0 (8)	Si(5)–C(51)–H(51c)	107 (4)	H(51a)–C(51)–H(51b)	105 (5)
C(15)–C(16)–C(17)	119.5 (8)	C(12)–C(17)–C(16)	122.7 (7)	H(51a)–C(51)–H(51c)	109 (5)	H(51b)–C(51)–H(51c)	113 (6)
Si(2)–C(22)–C(23)	121.4 (4)	Si(2)–C(22)–C(27)	121.9 (4)	C(52)–C(53)–H(53)	118 (3)	C(54)–C(53)–H(53)	121 (3)
C(23)–C(22)–C(27)	116.7 (5)	C(22)–C(23)–C(24)	120.2 (6)	C(53)–C(54)–H(54)	120 (4)	C(55)–C(54)–H(54)	119 (4)
C(23)–C(24)–C(25)	122.3 (7)	C(24)–C(25)–C(26)	118.0 (7)	C(54)–C(55)–H(55)	126 (5)	C(56)–C(55)–H(55)	117 (5)
C(25)–C(26)–C(27)	121.2 (6)	C(22)–C(27)–C(26)	121.5 (6)	C(55)–C(56)–H(56)	124 (4)	C(57)–C(56)–H(56)	115 (4)
Si(5)–C(52)–C(53)	120.2 (5)	Si(5)–C(52)–C(57)	123.1 (5)	C(52)–C(57)–H(57)	116 (3)	C(56)–C(57)–H(57)	122 (3)
C(53)–C(52)–C(57)	116.7 (6)	C(52)–C(53)–C(54)	121.0 (6)	Si(6)–C(61)–H(61a)	111 (3)	Si(6)–C(61)–H(61b)	104 (4)
C(53)–C(54)–C(55)	121.9 (7)	C(54)–C(55)–C(56)	117.4 (7)	Si(6)–C(61)–H(61c)	110 (4)	H(61a)–C(61)–H(61b)	107 (5)
C(55)–C(56)–C(57)	121.0 (7)	C(52)–C(57)–C(56)	122.0 (6)	H(61a)–C(61)–H(61c)	111 (5)	H(61b)–C(61)–H(61c)	115 (6)
Si(6)–C(62)–C(63)	121.8 (5)	Si(6)–C(62)–C(67)	121.1 (5)	C(62)–C(63)–H(63)	115 (4)	C(64)–C(63)–H(63)	124 (4)
C(63)–C(62)–C(67)	116.8 (6)	C(62)–C(63)–C(64)	121.6 (7)	C(63)–C(64)–H(64)	122 (4)	C(65)–C(64)–H(64)	118 (4)
C(63)–C(64)–C(65)	120.8 (8)	C(64)–C(65)–C(66)	119.9 (8)	C(64)–C(65)–H(65)	123 (4)	C(66)–C(65)–H(65)	117 (4)
C(65)–C(66)–C(67)	119.9 (8)	C(62)–C(67)–C(66)	121.0 (7)	C(65)–C(66)–H(66)	120 (4)	C(67)–C(66)–H(66)	121 (4)
Si(1)–C(11)–H(11a)	108 (4)	Si(1)–C(11)–H(11b)	104 (4)	C(62)–C(67)–H(67)	121 (3)	C(66)–C(67)–H(67)	118 (3)

under the same conditions to give the corresponding polymers **3c** and **4c** in 94 and 75% yields. The molecular weights were determined to be 30 900 for **3c** and 65 400 for **4c**, relative to polystyrene standards. Similarly, perethyl cyclic compound **5b** gave poly[(tetraethyldisilanylene)ethynylene] (**5c**) with a high molecular weight in 90% yield. The polymers **1c**, **2c**, and **5c** are solids, melt without decomposition, and are soluble in common organic solvents. The polymers that have long-chain alkyl groups on the silicon atoms, **3c** and **4c**, are viscous liquids.

All (disilanylene)ethynylene polymers prepared by the anionic polymerization exhibit very sharp resonances in the ^{1}H and ^{13}C NMR spectra. The ^{1}H and ^{13}C NMR spectra for **2c** are shown in Figures 6 and 7 as typical examples. Some properties of the polymers **1c**–**5c** are shown in Table VI.

Table VI. Properties of Polymers 1c–5c

polymer	M_w	M_w/M_n	UV λ_{max}, nm (ϵ/SiSiC≡C) in THF	UV λ_{max}, nm (ϵ/SiSiC≡C) film	mp, °C
1c	80 800	4.08	239 (22 000)	249	60–85
2c	121 000	3.78	241 (13 000)	245	140–145
3c	30 900	2.03	244 (16 000)	253	oil
4c	65 400	2.11	243 (17 000)	255	oil
5c	72 800	2.16	243 (13 000)	243	156–158

Mechanism of Polymerization. In order to learn more about the ring-opening polymerization, we carried out the stoichiometric reaction of eight-membered cyclic compound **5b** with alkyllithium. Thus, the reaction of **5b** with 1 equiv of methyllithium in THF at room temperature, followed by hydrolysis of the resulting solution afforded 3,4,4,7,7,8,8-heptaethyl-3-methyl-3,4,7,8-tetrasiladeca-5,9-diyne (**6**) in quantitative yield. Similar treatment of **5b** with methyllithium and then with methyl iodide gave 3,4,4,7,7,8,8-heptaethyl-3-methyl-3,4,7,8-tetrasilaundeca-5,9-diyne (**7**) in almost quantitative yield (Scheme II).

These results indicate that the first step in the reaction of the eight-membered cyclic compounds with alkyllithium involves nucleophilic attack of the carbanion at the silicon atom to give the ring-opened ethynyl carbanion. The reaction of the resulting ethynyl carbanion with the starting cyclic compound would be involved in chain-propagating steps (Scheme III).

Recently, Bortolin, Brown, and Parbhoo have reported that homo- and copolymers composed of an alternating silyl group and diethynyl unit undergo a redistribution reaction in the presence of a catalytic amount of a di-

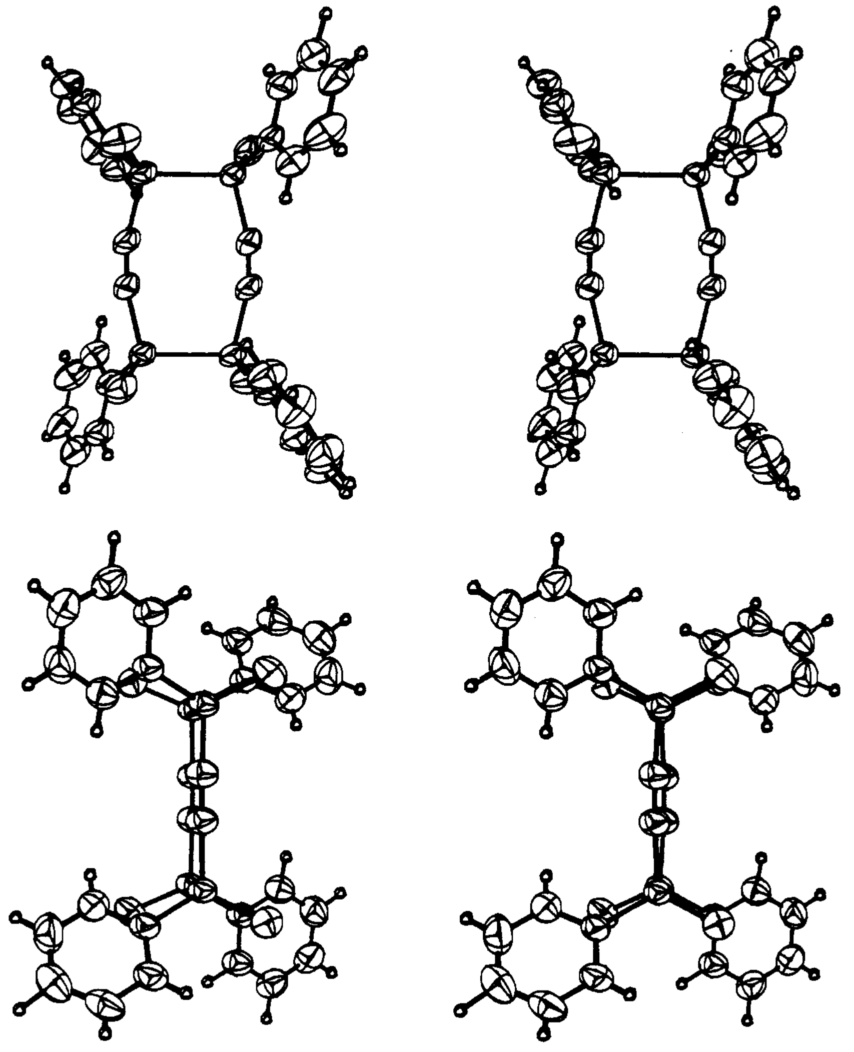
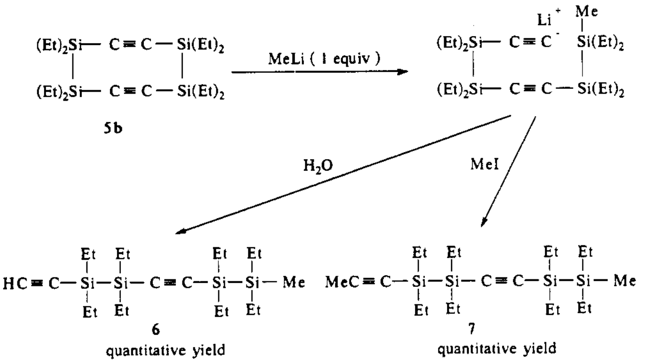
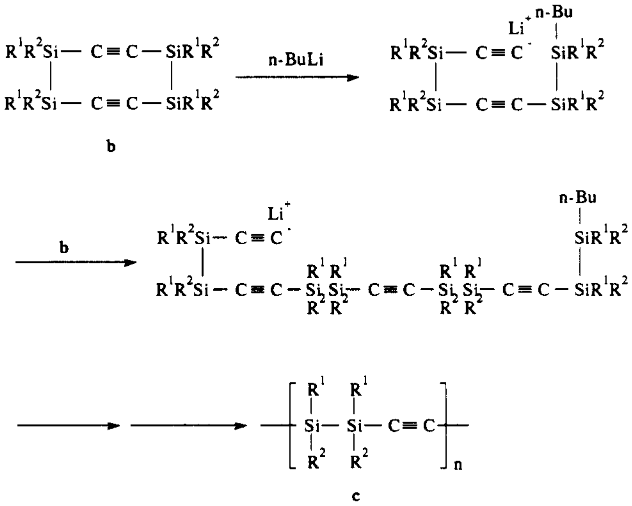


Figure 3. Stereoviews of *cis–trans*-**1b**: (a, top) projected along the normal of the eight-membered ring; (b, bottom) projected along the plane of the eight-membered ring.

Scheme II



Scheme III



lithium derivative of diethynyldiphenylsilane, leading to the random exchange of silylethynyl units.[15,16] In order to check this possibility in the present system, we treated polymer **1c** with a molecular weight of 77 900 with a catalytic amount of *n*-butyllithium in THF at room temperature for 64 h. To our surprise, polymer **1c** was completely transformed into oligomers whose molecular weight was determined to be $M_w = 1500$. No starting polymer **1c** was detected by GPC. Presumably, disilanylene–ethynylene bonds are cleaved and anionic depolymerization takes place to give the oligomers, like the well-known catalytic degradation of linear polysiloxanes. The low yield of **1c** in the ring-opening polymerization of *cis–trans-* and *all-trans*-**1b** is responsible for such depolymerization of some of the polymers once formed.

In contrast to the phenyl-substituted polymer **1c**, the reaction of alkyl-substituted polymer **5c** with a catalytic

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(15) Bortolin, R.; Parbhoo, B.; Brown, S. S. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1079.

(16) Bortolin, R.; Brown, S. S. D.; Parbhoo, B. *Macromolecules* **1990**, *23*, 2465.

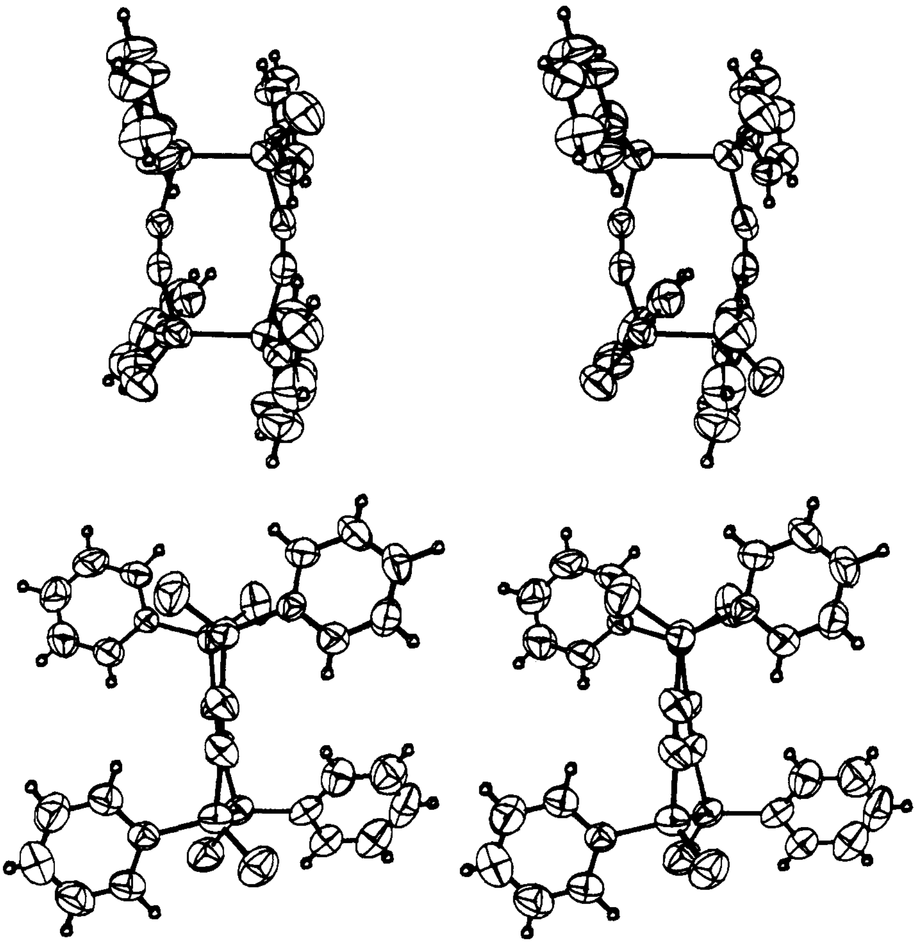

Figure 4. Stereoviews of *all-trans*-**1b**: (a, top) projected along the normal of the eight-membered ring; (b, bottom) projected along a quasi 2-fold axis of the molecule.

amount of *n*-butyllithium under the same conditions produced no oligomers with low molecular weights, but the molecular weight distribution of **5c** became much broader, as shown in Figure 8, indicating that the redistribution reaction also took place in this system. In spite of the living polymerization, the rather broad molecular weight distribution observed in the present system is responsible for the redistribution reaction. The narrow molecular weight distribution for the polymers bearing long-chain alkyl groups may be ascribed to the fact that the rate of the redistribution reaction is slow. Indeed, only a small change was observed when polymer **4c** was treated with a catalytic amount of *n*-butyllithium under the same conditions as shown in Figure 9.

Ultraviolet Spectra. The (disilanylene)ethynylene polymers exhibit strong absorption bands usually falling in the region from 243 to 255 nm in a THF solution, which are lower in energy than those of 1,2-diethynyldisilanes. The absorption maxima and the extinction coefficients per (disilanylene)ethynylene unit are given in Table VI. The λ_{max} values of the films of **1c**–**5c** are observed at 243–255 nm, longer wavelengths than those in the solution. The UV absorption band of **1c** in a THF solution shows λ_{max} at 239 nm, the shortest wavelength and the broadest absorption among the polymes **1c**–**5c**, while (tetraalkyldisilanylene)ethynylene polymers **2c**–**5c** exhibit absorptions at 241–244 nm. The profile of UV spectra for **1c**, **3c**, and **5c** are shown in Figure 10, as typical examples. The absorption at 239 nm for **1c** is probably not attributed to a (disilanylene)ethynylene group, but due to a phenyldisilanyl group, because the absorption maximum of 1,2-diethynyl-1,2-dimethyldiphenyldisilane **1a** appears at 236 nm,[17] while those of **3a** and **5a** appear at 216 and 218 nm, respectively. Presumably, the absorption due to the (disilanylene)ethynylene skeleton for **1c** appears at a longer wavelength, and therefore, the absorption band of this polymer becomes much broader.

The electronic transition is ascribed to excitations involving electrons in the silicon–silicon σ bonds. In fact, both of the highest occupied crystal orbital and the lowest unoccupied crystal orbital calculated by the SCF CO method for poly[(disilanylene)ethynylene] (**8**) are σ type

$$\left[H_2SiSiH_2C \equiv C \right]_n$$

8

orbitals.[18] Furthermore, the polymer that has no silicon–silicon bonds in the polymer backbone, polymer **9** composed of an alternating disiloxanylene group and ethynylene unit, shows absorptions at 216 nm, a shorter wavelength than that of **5c** (243 nm).

The polymer **9** could be readily obtained by the reaction of the polymer **5c** with 1 equiv of trimethylamine oxide in refluxing benzene in high yield.

$$5c \ + \ Me_3NO \longrightarrow \left[Et_2SiOSiEt_2C \equiv C \right]_n$$

9

Photochemical Properties. As expected, polymers **1c**–**5c** are highly photoactive. Irradiation of thin films of

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[17] 1,2-Diphenyltetramethyldisilane exhibits absorption at 236 nm, see: Gilman, H.; Atwell, W. H.; Schwebke, G. L. *J. Organomet. Chem.* **1964**, *2*, 369.

[18] Tanaka, K.; Nakajima, K.; Okada, M.; Yamabe, T.; Ishikawa, M. *Organometallics* **1991**, *10*, 2679.

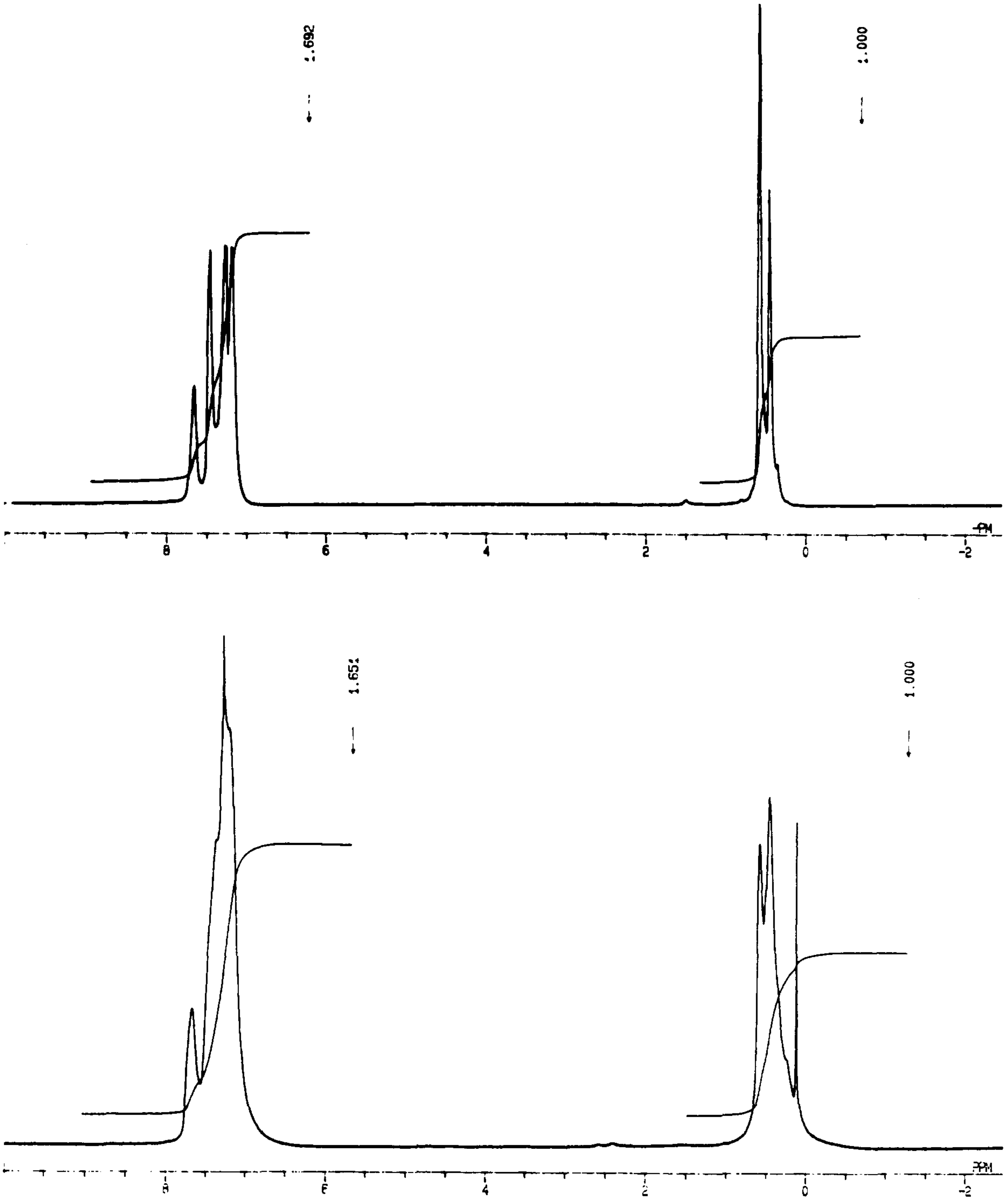

Figure 5. ^{1}H NMR spectra of poly[(1,2-dimethyldiphenyldisilanylene)ethynylene]: (a, top) polymer **1c**; (b, bottom) polymer prepared from sodium condensation of bis(chloromethylphenylsilyl)acetylene.

1c–**5c** with a low-pressure mercury lamp in air causes a rapid decrease of absorptions near 245 nm, indicating that homolytic scission of silicon–silicon bonds in the polymer backbone occurs, as observed in the photolysis of poly[*p*-(disilanylene)phenylene].[2] Profiles of the ultraviolet spectra obtained from irradiation of the film prepared from polymer **1c** are shown in Figure 11, as a typical example. All other polymers **2c**–**5c** showed spectra similar to those of **1c** when their thin films were irradiated with a low-pressure mercury lamp in the air. IR spectra of all of the resulting films show strong absorptions due to the stretching frequencies of Si–OH and Si–O–Si bonds. The formation of the Si–OH and Si–O–Si bonds can best be explained by the reaction of the silyl radicals generated by photolytic scission of silicon–silicon bonds in the polymer backbone with oxygen in the air, as reported previously.[2]

When benzene solutions of the polymers **1c**–**5c** were photolyzed with a low-pressure mercury lamp, soluble photodegradation products were obtained in all cases. In order to learn the influence of irradiation time on the molecular weight of the photodegradation products, we followed molecular weight changes of the products produced in the photolysis by GPC. As can be seen in Figures 12–14, in all cases, the molecular weights of the photoproducts decreased rapidly with increasing irradiation time and remained unchanged after ca. 5 h of irradiation.

We also carried out the photolysis of **1c** and **5c** in the presence of methanol to trap the intermediate which would be produced. In both cases, the photodegradation products

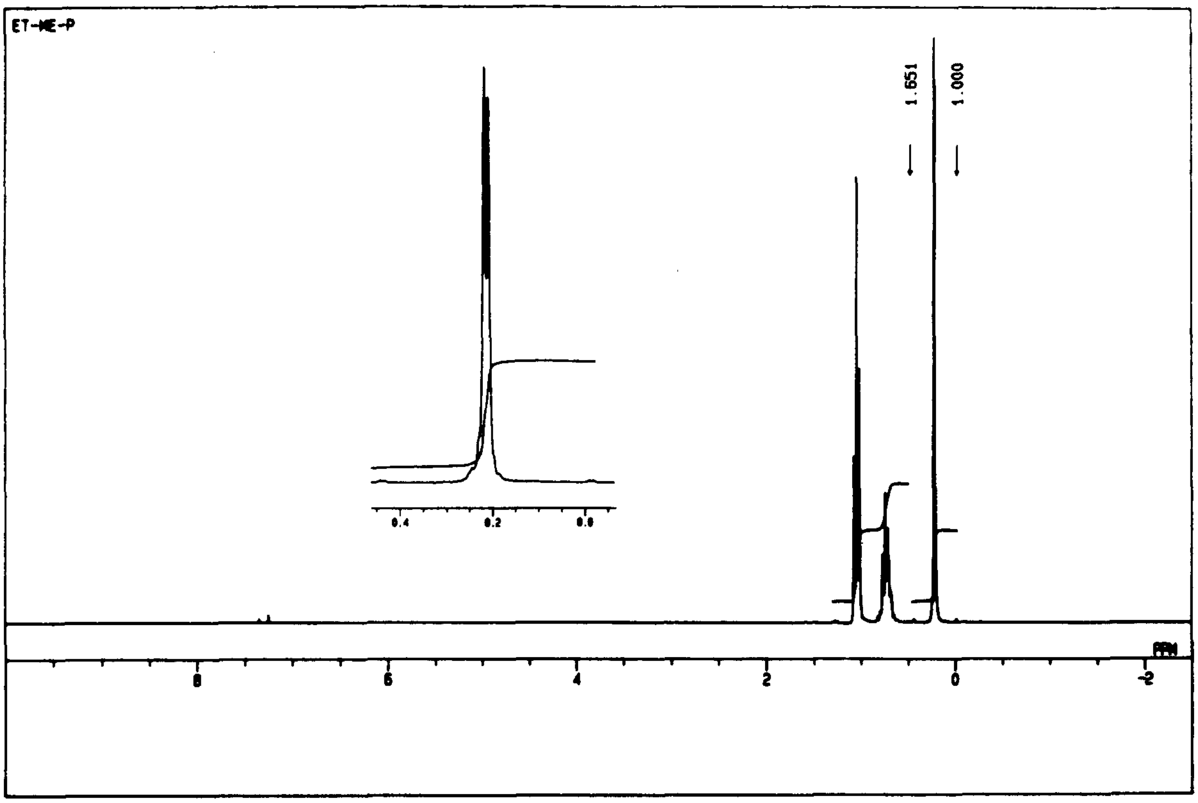

Figure 6. ^{1}H NMR spectrum of **2c**.

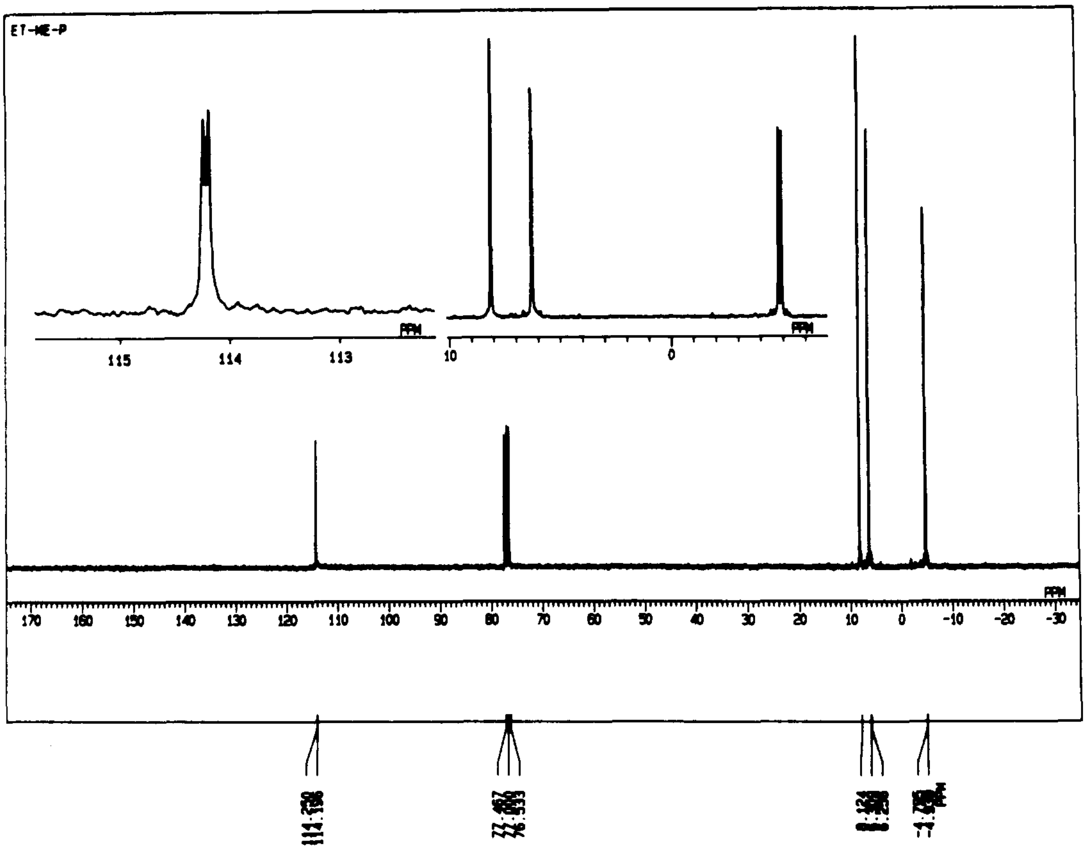

Figure 7. ^{13}C NMR spectrum of **2c**.

whose molecular weights were determined to be lower than those of the products produced from the photolysis in the absence of methanol were obtained, as shown in Figures 12 and 13. ^{1}H NMR spectra of the resulting photoproducts display signals due to methoxy protons and hydrosilyl protons, respectively. IR spectra of both products also show strong absorptions at 2100 cm^{-1}, attributed to Si–H stretching frequencies. These results clearly indicate the formation of silenes which would be produced by homolytic scission of a silicon–silicon bond, followed, by dispropor-

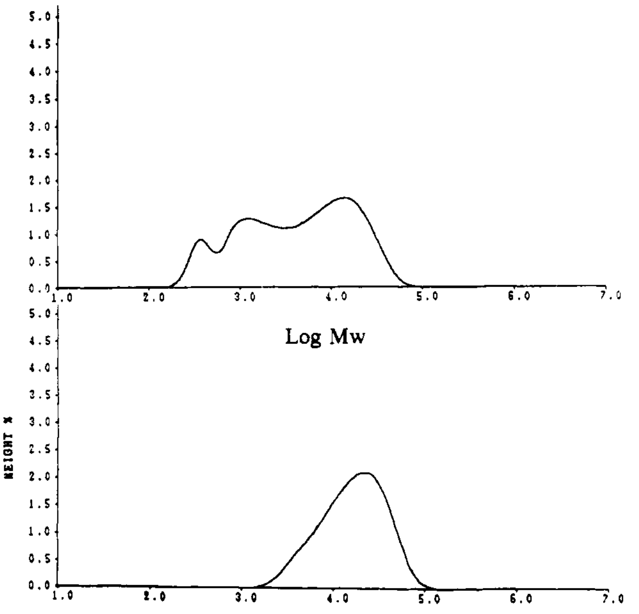

Figure 8. GPC profile of **5c**: (a, bottom) before the redistribution reaction; (b, top) after treatment of **5c** with a catalytic amount of BuLi in THF at room temperature for 64 h.

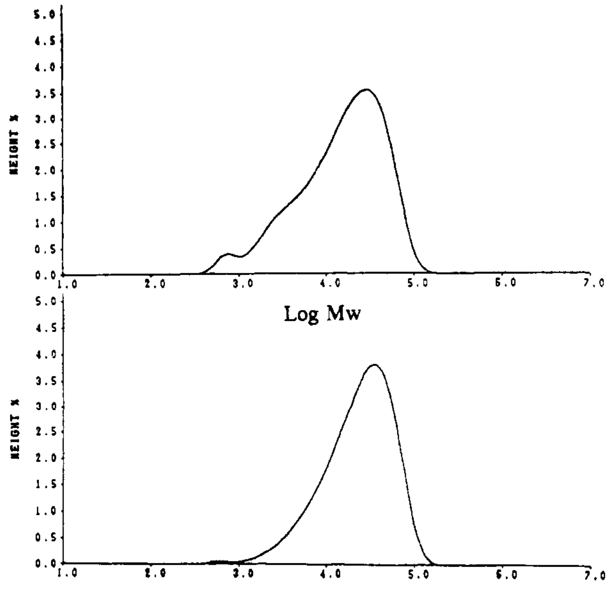

Figure 9. GPC profile of **4c**: (a, bottom) before redistribution reaction; (b, top) after treatment of **4c** with a catalytic amount of BuLi in THF at room temperature for 64 h.

tionation of the resulting silyl radicals as reported previously in the photolysis of poly[(disilanylene)phenylenes].[2]

In marked contrast to the photochemical behavior of **1c–5c**, the photolysis of polymer **9** afforded insoluble polymers. Thus, irradiation of a benzene solution of **9** under the same conditions and evaporation of the resulting solution gave solid substances which are insoluble in common organic solvents. Presumably, in this case, the cross-linking reaction took place.

Conducting Properties. The poly[(disilanylene)ethynylenes] are insulators, like other polymers composed of an alternating disilanylene unit and a π-electron system. However, on treatment of the polymers with an oxidizing agent, antimony pentafluoride, they become conducting. Thus, when thin films of **1c**, **2c**, and **5c**, which are prepared by spin-coating on a quartz plate, were treated with a stream of antimony pentafluoride vapor diluted with nitrogen gas at atmospheric pressure and the films were exposed in air, highly conducting films were obtained. The conductivities determined by the four-probe method are shown in Table VII. The conductivities of the polymers **1c**, **2c**, and **5c** measured in vacuo, however, were shown to be lower than those obtained in the air. Thus, the

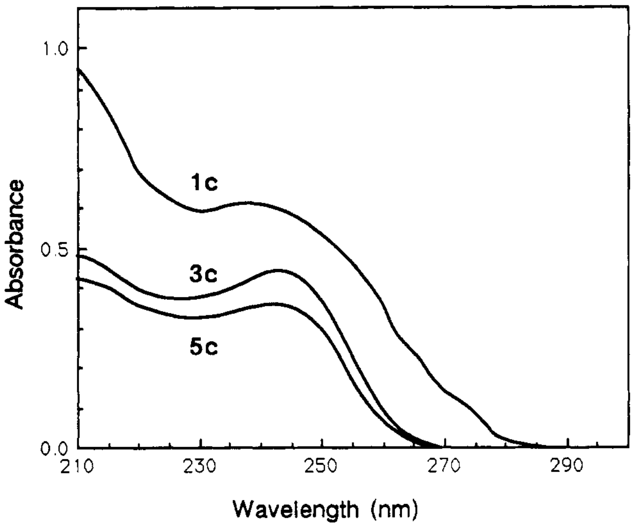

Figure 10. UV spectra of **1c**, **3c**, and **5c**.

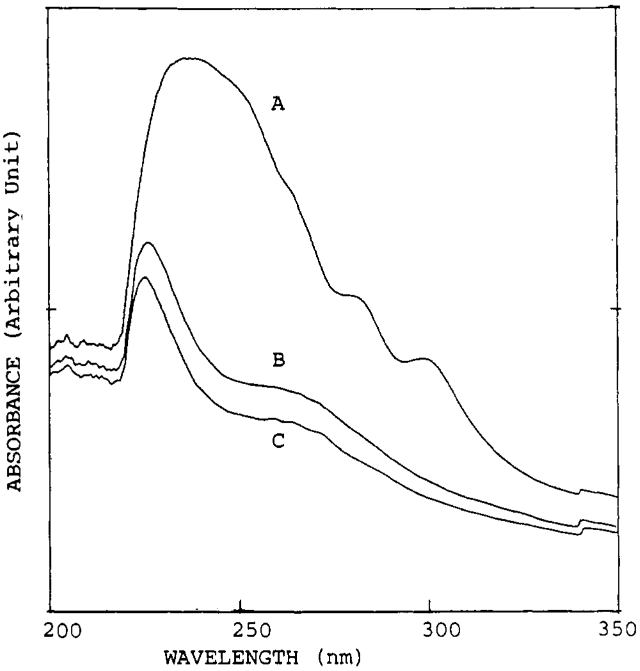

Figure 11. UV spectra of a thin solid film of **1c**: (A) before irradiation; (B) after irradiation for 15 min; (C) after irradiation for 30 min.

Table VII. Conductivities of Polymers 1c, 2c, 5c, and 9 Doped with Antimony Pentafluoride Vapor

	conductivity, S·cm^{-1}		
polymer	in air (μm)[a]	in vacuo (μm)[a]	after 7 days in SbF$_5$ vapor
1c	4×10^{-1} (130)	7×10^{-4} (0.5)	1×10^{-7}
2c	2 (38)	3×10^{-3} (0.5)	2×10^{-7}
5c	8×10^{-1} (17)	1×10^{-3} (0.5)	3×10^{-7}
9	less than 10^{-8} (ca. 25)		

[a] Thickness of a film.

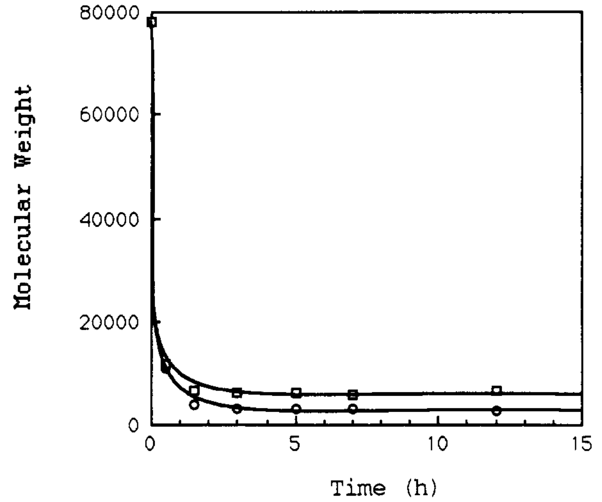

Figure 12. Plot of molecular weights of products vs irradiation time for the photolysis of **1c**: (□) irradiation in benzene; (○) irradiation in the presence of methanol in benzene.

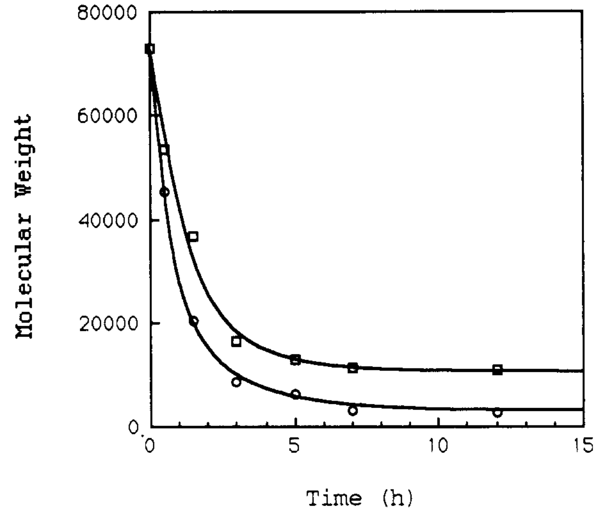

Figure 13. Plot of molecular weights of products vs irradiation time for the photolysis of **5c**: (□) irradiation in benzene; (○) irradiation in the presence of methanol in benzene.

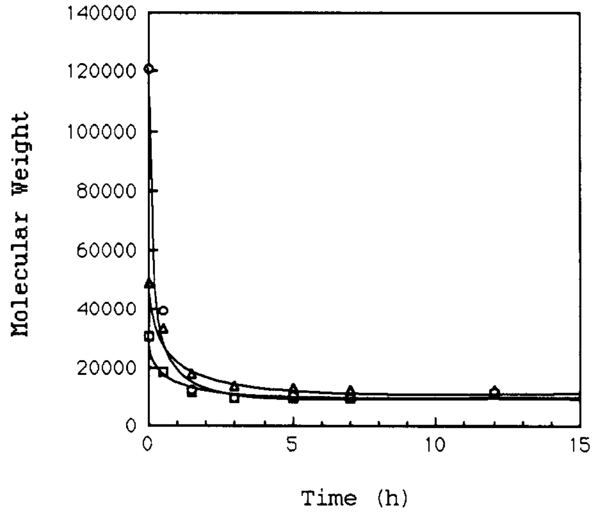

Figure 14. Plot of molecular weights of products vs irradiation time in the photolysis of (○) **2c**, (□) **3c**, and (△) **4c** in benzene.

conductivities increased rapidly at the beginning of doping and were 10^{-4}–10^{-3} S·cm^{-1} during doping for 10 h. The maximum conductivities (σ_{max}) obtained during doping in vacuo are shown in Table VII. When the doped films were allowed to stand in an atmosphere of antimony pentafluoride vapor, the conductivities gradually decreased and finally reached constant values (10^{-7} S·cm^{-1}) after 7 days. Interestingly, when the films which reached the constant value were exposed in air, the conductivities suddenly increased more than 3 or 4 orders of magnitude. For example, when the doped film of **2c** whose conductivity was 2×10^{-7} S·cm^{-1}, after 7 days of standing in an atmosphere of antimony pentafluoride vapor, was exposed in air, its conductivity increased rapidly and reached 1×10^{-2} S·cm^{-1} after about 6 h. This value remained constant in air at least for 2 h. The film of polymer **5c** showed behavior similar to that of **2c**. The conductivity which was 3×10^{-7} S·cm^{-1} in an atmosphere of antimony pentafluoride vapor became 2×10^{-2} S·cm^{-1} after exposure to air for 6 h.[19] The reason for high conductivity of the films observed in air is still unknown, but a trace of moisture in air might be responsible for such high conductivity.

Interestingly, the conductivity of polymer **9** that has no silicon–silicon bonds in the polymer chain was measured to be less than 10^{-8} S·cm^{-1} in air, after similar treatment with antimony pentafluoride vapor. This result clearly indicates that the silicon–silicon bonds play an important role in conducting properties. At present, we believe that the mechanism of conductivity involves transfer of an electron from a silicon–silicon bonding orbital to a dopant molecule and delocalization of this electron hole through the π-electron system and the silicon–silicon σ system.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran used as solvent for ring-opening polymerization was dried over sodium–potassium alloy and distilled under reduced pressure using vacuum line techniques. Other solvents were dried over sodium in the presence of benzophenone.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL Model JNM-EX 270 spectrometer. UV spectra were determined with a Hitachi U-3210 spectrophotometer. IR spectra were measured on a Perkin-Elmer 1600-FT infrared spectrometer. Molecular weights of polymers were determined with two Shodex columns, using THF as the eluent and are relative to polystyrene standards.

Preparation of 1,2-Diethyl-1,2-dimethyldiphenyldisilane. Into a 500-mL three-necked flask was placed ethylmagnesium bromide prepared from 25 mL (0.35 mol) of ethyl bromide and 8.4 g (0.35 mol) of magnesium in 150 mL of dry THF. To this was added 49.8 g (0.16 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane[20] dissolved in 40 mL of dry THF. The mixture was stirred for 2 h at room temperature and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated and distilled under reduced pressure to give 42.4 g (89% yield) of 1,2-diethyl-1,2-dimethyldiphenyldisilane: bp 111–113 °C (1 mmHg); MS *m/e* 298 (M$^+$); IR 1427, 1248, 1106 cm^{-1}; ^{1}H NMR (δ, in CDCl$_3$) 0.34 (6 H, s, MeSi), 0.91 (10 H, br s, EtSi), 6.73–6.99 (10 H, m, phenyl ring protons); ^{13}C NMR (δ, in CDCl$_3$) −6.37, −6.26 (MeSi), 5.44, 5.55, 7.93 (EtSi), 127.7, 128.3, 134.2, 137.2 (phenyl ring carbons). Anal. Calcd for C$_{18}$H$_{26}$Si$_2$: C, 72.41; H, 8.78. Found: C, 72.31; H, 8.65.

Preparation of 1,2-Di-*n*-butyl-1,2-dimethyldiphenyldisilane. This compound was prepared from *n*-butylmagnesium bromide (0.33 mol) and 48.0 g (0.15 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane in 77% yield in the same manner as above: bp 145–147 °C (0.5 mmHg); MS *m/e* 354 (M$^+$); IR 1426, 1246, 1105 cm^{-1}; ^{1}H NMR (δ, in CDCl$_3$) 0.38, 0.39 (6 H, s, MeSi), 0.86–1.33 (18 H, m, *n*-BuSi), 7.32–7.41 (10 H, m, phenyl ring

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(19) When the doped film of **1c** was exposed in air, its conductivity increased up to 4 S·cm^{-1} after 2 h but did not show a constant value.

(20) Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* 1971, *31*, 17.

protons); ^{13}C NMR (δ, in $CDCl_3$) −5.93, −5.78 (MeSi), 13.16, 13.70, 26.56, 26.63 (*n*-BuSi), 127.6, 128.3, 134.2, 138.3 (phenyl ring carbons). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.35; H, 9.63.

Preparation of 1,2-Di-*n*-hexyl-1,2-dimethyldiphenyldisilane. This compound was prepared from *n*-hexylmagnesium bromide (0.4 mol) and 59.1 g (0.19 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane in 86% yield: bp 165–180 °C (2 mmHg); MS *m*/*e* 410 (M^+); IR 1427, 1247, 1105 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.36, 0.37 (6 H, s, MeSi), 0.86–0.91 (10 H, m, *n*-HexSi), 1.25–1.30 (16 H, m, *n*-HexSi), 7.30–7.41 (10 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −5.93, −5.77 (MeSi), 13.52, 13.61, 14.11, 22.57, 24.30, 31.45, 33.37 (*n*-HexSi), 127.6, 128.3, 134.1, 138.4 (phenyl ring carbons). Anal. Calcd for $C_{26}H_{42}Si_2$: C, 76.06; H, 10.31. Found: C, 76.00; H, 10.31.

Preparation of 1,2-Diphenyltetraethyldisilane. A solution of diethylphenylsilyllithium prepared from 66.14 g (0.33 mol) of chlorodiethylphenylsilane and 6.4 g (1 mol) of lithium in 200 mL of THF was added to 68.8 g (0.35 mol) of chlorodiethylphenylsilane. The salt was filtered off and washed with dry hexane. After evaporation of the solvents, the residue was distilled under reduced pressure to give 92.7 g (86% yield) of 1,2-diphenyltetraethyldisilane: bp 127–129 °C (1 mmHg); MS *m*/*e* 326 (M^+) 297 ($M^+ -$ Et); IR 1427, 1102, 1006 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.99 (20 H, br s, EtSi), 7.29 (10 H, br s, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 3.76, 8.09 (EtSi), 127.6, 128.2, 134.5, 137.2 (phenyl ring carbons). Anal. Calcd for $C_{20}H_{30}Si_2$: C, 73.54; H, 9.26. Found: C, 73.64; H, 9.23.

Preparation of 1,2-Dichloro-1,2-diethyl-1,2-dimethyldisilane. Into a 300-mL three-necked flask was placed a mixture of 42.3 g (0.14 mol) of 1,2-diethyl-1,2-dimethyldiphenyldisilane and 0.5 g (3.7 mmol) of anhydrous aluminum chloride in 150 mL of dry benzene. Dry hydrogen chloride gas was passed into the stirred mixture at room temperature. The progress of the reaction was monitored by GLC. After completion of the reaction, 5 mL of dry acetone was added to the mixture. Distillation under reduced pressure gave 25.5 g (84% yield) of 1,2-dichloro-1,2-diethyl-1,2-dimethyldisilane: bp 75–77 °C (14 mmHg); MS *m*/*e* 214 (M^+); IR 1459, 1408, 1252, 1059 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.57 (6 H, s, MeSi), 1.00–1.14 (10 H, m, EtSi); ^{13}C NMR (δ, in $CDCl_3$) −0.57, −0.41 (MeSi), 6.63, 9.99 (EtSi). Anal. Calcd for $C_6H_{16}Si_2Cl_2$: C, 33.48; H, 7.49. Found: C, 33.53; H, 7.39.

Preparation of 1,2-Dichloro-1,2-di-*n*-butyl-1,2-dimethyldisilane. This compound was prepared by the reaction of 41.6 g (0.12 mol) of 1,2-di-*n*-butyl-1,2-dimethyldiphenyldisilane with hydrogen chloride gas in the presence of 0.5 g (3.7 mmol) of anhydrous aluminum chloride in 100 mL of dry benzene in the same manner as above. Distillation under reduced pressure gave 17.6 g (55% yield) of 1,2-dichloro-1,2-di-*n*-butyl-1,2-dimethyldisilane: bp 141–143 °C (27 mmHg); MS *m*/*e* 213 ($M^+ - n$-Bu); IR 1464, 1252, 1081 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.53_8, 0.54_2 (6 H, s, MeSi), 0.76–1.47 (18 H, m, *n*-BuSi); ^{13}C NMR (δ, in $CDCl_3$) −0.12, 0.00 (MeSi), 13.62, 17.40, 25.20, 26.02 (*n*-BuSi). Anal. Calcd for $C_{10}H_{24}Si_2Cl_2$: C, 44.26; H, 8.91. Found: C, 44.25; H, 8.89.

Preparation of 1,2-Dichloro-1,2-di-*n*-hexyl-1,2-dimethyldisilane. This compound was prepared by the reaction of 67.9 g (0.17 mol) of 1,2-di-*n*-hexyl-1,2-dimethyldiphenyldisilane with hydrogen chloride gas in the presence of 0.5 g (3.7 mmol) of anhydrous aluminum chloride in 180 mL of dry benzene in 79% yield: bp 116–118 °C (2 mmHg); MS *m*/*e* 241 ($M^+ - n$-Hex); IR 1466, 1251, 1101 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.57 (6 H, s, MeSi), 0.77–1.64 (26 H, m, *n*-HexSi); ^{13}C NMR (δ, in $CDCl_3$) 0.08, 0.09 (MeSi), 14.05, 17.79, 22.56, 23.04, 31.39, 32.69 (*n*-HexSi). Anal. Calcd for $C_{14}H_{32}Si_2Cl_2$: C, 51.35; H, 9.85. Found: C, 51.56; H, 9.83.

Preparation of 1,2-Dichlorotetraethyldisilane. This compound was prepared from 92.7 g (0.28 mol) of tetraethyl-1,2-diphenyldisilane and hydrogen chloride gas in the presence of 0.5 g (3.7 mmol) of anhydrous aluminum chloride in 85% yield: bp 118–124 °C (27 mmHg); MS *m*/*e* 242 (M^+); IR 1462, 1411, 1005 cm^{-1}; ^1H NMR (δ, in $CDCl_3$), 0.99–1.07 (20 H, m, EtSi); ^{13}C NMR (δ, in $CDCl_3$) 6.85, 8.58 (EtSi). Anal. Calcd for $C_8H_{20}Si_2Cl_2$: C, 39.49; H, 8.29. Found: C, 39.22; H, 8.24.

Preparation of 1a. Compound **1a** (a mixture of *dl* and meso) was prepared by the ethynylmagnesium bromide with 1,2-dichloro-1,2-dimethyldiphenyldisilane in 82% yield. All spectral data were identical with those reported previously.[9b]

Preparation of 2a. Into a 2-L three-necked flask was placed a solution of ethynylmagnesium bromide prepared from 320 mL (0.3 mol) of ethylmagnesium bromide and acetylene gas in 400 mL of dry THF. To this was added 14.0 g (0.065 mol) of 1,2-dichloro-1,2-diethyldimethyldisilane at room temperature. The mixture was stirred for 10 h at room temperature and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated and distilled under reduced pressure to give 11.0 g (87% yield) of **2a**: bp 77–80 °C (20 mmHg); MS *m*/*e* 194 (M^+); IR 3287 ($\equiv$CH), 2027 (C$\equiv$C) cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.31 (6 H, s, MeSi), 0.61–1.27 (10 H, m, EtSi), 2.51 (2 H, s, acetylene protons); ^{13}C NMR (δ, in $CDCl_3$) −5.18 (MeSi), 5.98, 7.93 (EtSi), 87.0, 96.0 (C$\equiv$C). Anal. Calcd for $C_{10}H_{18}Si_2$: C, 61.78; H, 9.33. Found: C, 61.59; H, 9.23.

Preparation of 3a.[8] Compound **3a** was synthesized from the reaction of ethynylmagnesium bromide (0.18 mol) prepared from ethylmagnesium bromide and acetylene gas with 17.6 g (0.065 mol) of 1,2-dichloro-1,2-di-*n*-butyldimethyldisilane in 83% yield in the same manner as above; bp 135–138 °C (27 mmHg); MS *m*/*e* 235 ($M^+ -$ Me), 193 ($M^+ - n$-Bu); IR 3291 ($\equiv$CH), 2028 (C$\equiv$C) cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.266, 0.270 (6 H, s, MeSi), 0.71–1.48 (18 H, m, *n*-BuSi), 2.47 (2 H, s, acetylene protons); ^{13}C NMR (δ, in $CDCl_3$) −4.80, −4.72 (MeSi), 13.44, 13.70, 26.27, 26.60 (*n*-BuSi), 87.4, 95.9 (C$\equiv$C). Anal. Calcd for $C_{14}H_{26}Si_2$: C, 67.12; H, 10.46. Found: C, 66.96; H, 10.32.

Preparation of 4a. Compound **4a** was prepared from ethynylmagnesium bromide (0.20 mol) and 25.3 g (0.077 mol) of 1,2-dichloro-1,2-di-*n*-hexyldimethyldisilane in 48% yield; bp 101–103 °C (2 mmHg); MS *m*/*e* 221 ($M^+ - n$-Hex); IR 3292 ($\equiv$CH), 2028 (C$\equiv$C) cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.30 (6 H, s, MeSi), 0.67–1.60 (26 H, m, *n*-HexSi), 2.47 (2 H, s, acetylene protons); ^{13}C NMR (δ, in $CDCl_3$) −4.75 (MeSi), 13.84, 14.11, 22.56, 24.40, 31.49, 32.96 (*n*-HexSi), 87.4, 95.6 (C$\equiv$C). Anal. Calcd for $C_{18}H_{34}Si_2$: C, 70.51; H, 11.18. Found: C, 70.48; H, 11.17.

Preparation of 5a. Compound **5a** was prepared from ethynylmagnesium bromide (0.26 mol) and 19.4 g (0.08 mol) of 1,2-dichlorotetraethyldisilane in 84% yield: bp 113–118 °C (27 mmHg); MS *m*/*e* 222 (M^+); IR 3289 ($\equiv$CH), 2027 (C$\equiv$C) cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.44–1.37 (20 H, m, EtSi), 2.47 (2 H, s, acetylene protons); ^{13}C NMR (δ, in $CDCl_3$) 4.57, 8.15 (EtSi), 86.4, 96.4 (C$\equiv$C). High-resolution mass spectrum. Calcd for $C_{12}H_{22}Si_2$: 222.1254. Found: 222.1252.

Preparation of *cis*–*trans*-1b and *all*-*trans*-1b. Into a 500-mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed isopropylmagnesium chloride prepared from 5 mL (0.055 mol) of isopropyl chloride and 1.34 g (0.055 mol) of magnesium in 15 mL of dry THF. To this was added 7.26 g (0.025 mol) of **1a** in 100 mL of dry THF at room temperature over a period of 15 min. The mixture was stirred at room temperature for 1 h. To this was added 7.79 g (0.025 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane in 90 mL of dry THF over a period of 2 h at room temperature. The mixture was stirred for 15 h at room temperature and then hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined and washed with water and then dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was chromatographed on silica gel using benzene as the eluent. Evaporation of benzene gave white solids, and the resulting solids were fractionally recrystallized from benzene to give 2.65 g (20% yield) of *r*-1,*t*-2,*t*-5,*c*-6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (*cis*–*trans*-**1b**). The solid obtained from evaporation of the mother liquid was recrystallized from mixed solvent consisting of benzene–hexane in a ratio of 1:1 to give 2.17 g (17% yield) of *r*-1,*t*-2,*c*-5,*t*-6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (*all*-*trans*-**1b**). For *cis*–*trans*-**1b**: mp 202–203 °C; MS *m*/*e* 528 (M^+); IR 1428, 1249, 1008 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.42 (12 H, s, MeSi), 7.36–7.76 (20 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −4.4 (MeSi), 119.8 (C$\equiv$C), 128.2, 129.5, 133.9, 134.2 (phenyl ring carbons). Anal. Calcd for $C_{32}H_{32}Si_4$: C, 72.61; H, 6.08. Found: C, 72.66; H, 6.10. For *all*-*trans*-**1b**: mp 155–156 °C; MS *m*/*e* 528 (M^+); IR 1428, 1248, 1007 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.42 (12 H, s, MeSi), 7.38–7.75 (20 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −4.5 (MeSi), 119.9 (C≡C), 128.1, 129.5, 133.7, 134.3 (phenyl ring carbons). Anal. Calcd for $C_{32}H_{32}Si_4$: C, 72.61; H, 6.08. Found: C, 72.58; H, 6.13.

Preparation of 2b.[9a] Compound **2b** was prepared from isopropylmagnesium chloride (0.055 mol) and 5.38 g (0.025 mol) of 1,2-dichloro-1,2-dimethyldiethyldisilane in 50% yield: bp 128–130 °C (2 mmHg); mp 30–32 °C; MS *m/e* 336 (M^+); IR 1248, 1008, 955 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.22 (12 H, s, MeSi), 0.76–1.16 (20 H, m, EtSi); ^{13}C NMR (δ, in $CDCl_3$) −4.99 (MeSi), 6.17, 8.25 (EtSi), 119.6 (C≡C). Anal. Calcd for $C_{16}H_{32}Si_4$: C, 57.06; H, 9.58. Found: C, 57.27; H, 9.47.

Preparation of 3b.[8] Compound **3b** was prepared from the di-Grignard reagent of **3a** (0.014 mol) and 4.00 g (0.014 mol) of 1,2-dichloro-1,2-di-*n*-butyldimethyldisilane in 54% yield; bp 150–154 °C (1 mmHg); MS *m/e* 448 (M^+), 391 (M^+ − *n*-Bu); IR 1464, 1249, 1081 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.22 (12 H, s, MeSi), 0.72–0.77 (8 H, m, *n*-BuSi), 0.89–0.91 (12 H, m, *n*-BuSi), 1.32–1.38 (16 H, m, *n*-BuSi); ^{13}C NMR (δ, in $CDCl_3$) −4.49 (MeSi), 13.73, 26.29, 26.90 (*n*-BuSi), 119.8 (C≡C). Anal. Calcd for $C_{24}H_{48}Si_4$: C, 64.20; H, 10.78. Found: C, 64.16; H, 10.73.

Preparation of 4b. Compound **4b** was prepared from the reaction of the di-Grignard reagent of **4a** (0.01 mol) with 3.80 g (0.01 mol) of 1,2-dichloro-1,2-di-*n*-hexyldimethyldisilane in 52% yield: MS *m/e* 560 (M^+); IR 1466, 1247, 1100 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.21 (12 H, s, MeSi), 0.71–0.74 (8 H, m, *n*-HexSi), 0.85–0.90 (12 H, m, *n*-HexSi), 1.27–1.36 (32 H, m, *n*-HexSi); ^{13}C NMR (δ, in $CDCl_3$) −4.47 (MeSi), 14.11, 22.59, 24.68, 31.51, 33.02 (*n*-HexSi), 119.7 (C≡C). Anal. Calcd for $C_{32}H_{64}Si_4$: C, 68.49; H, 11.50. Found: C, 68.27; H, 11.45.

Preparation of 5b. Compound **5b** was prepared from the reaction of the di-Grignard reagent of **5a** (0.025 mol) with 6.08 g (0.025 mol) of 1,2-dichlorotetraethyldisilane in 50% yield: bp 125–127 °C (5 mmHg); MS *m/e* 392 (M^+); IR 1459, 1230, 1006 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.69–0.78 (16 H, m, EtSi), 1.01–1.07 (24 H, m, EtSi); ^{13}C NMR (δ, in $CDCl_3$) 4.53, 8.45 (EtSi), 119.6 (C≡C). Anal. Calcd for $C_{20}H_{40}Si_4$: C, 61.14; H, 10.26. Found: C, 61.05; H, 10.22.

Polymerization of *cis–trans*-1b. A mixture of 0.694 g (1.31 mmol) of *cis-trans*-**1b** and 0.0195 mmol (1.49 mol %) of *n*-butyllithium in 4 mL of THF was stirred in a sealed tube at room temperature for 64 h. After addition of two or three drops of a benzene solution of hydrogen chloride, the mixture was poured into ethanol. The resulting solid was reprecipitated from benzene–ethanol and dried under reduced pressure to give 0.10 g (14% yield) of **1c**: mp 60–85 °C; M_w = 80 800, M_n = 19 800 (M_w/M_n = 4.08); IR 1428, 1248, 1108 cm^{-1}; UV λ_{max} (thin solid film) 249 nm; ^1H NMR (δ, in $CDCl_3$) 0.45, 0.58 (6 H, broad s, MeSi), 7.17–7.66 (10 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −3.93 (MeSi), 114.4 (C≡C), 127.8, 129.2, 133.5, 134.5 (phenyl ring carbons).[21] Anal. Calcd for $(C_{16}H_{16}Si_2)_n$: C, 72.61; H, 6.08. Found: C, 72.47; H, 6.12.

Polymerization of *all-trans*-1b. A mixture of 2.93 g (5.56 mmol) of *all-trans*-**1b** and 0.0315 mmol (0.57 mol %) of *n*-butyllithium in 10 mL of THF was stirred in a sealed tube at room temperature for 64 h. After addition of two or three drops of a benzene solution of hydrogen chloride to the reaction mixture, the mixture was poured into ethanol. The resulting solid was reprecipitated first from benzene–ethanol and then benzene–isopropyl alcohol and dried under reduced pressure to give 0.937 g (32% yield) of **1c**: mp 60–78 °C; M_w = 77 900, M_n = 27 800 (M_w/M_n = 2.78); IR 1428, 1248, 1107 cm^{-1}; UV λ_{max} (thin solid film) 249 nm; ^1H NMR (δ, in $CDCl_3$) 0.42, 0.45, 0.57, 0.58 (6 H, s, MeSi), 7.17–7.67 (10 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −4.02, −3.95 (MeSi), 114.4 (C≡C), 127.8, 129.2, 133.5, 134.5 (phenyl ring carbons). Anal. Calcd for $(C_{16}H_{16}Si_2)_n$: C, 72.61; H, 6.08. Found: C, 72.53; H, 5.92.

Polymerization of 2b. A mixture of 2.96 g (8.81 mmol) of **2b** and 0.0315 mmol (0.36 mol %) of *n*-butyllithium in 15 mL of THF was stirred in a sealed tube at room temperature for 64 h. The resulting solid was reprecipitated from benzene–isopropyl alcohol and dried under reduced pressure to give 2.61 g (88% yield) of **2c**:[22] mp 140–145 °C; M_w = 121 000, M_n = 31 900 (M_w/M_n = 3.80); IR 1248, 1011, 957 cm^{-1}; UV λ_{max} (thin solid film) 245 nm; ^1H NMR (δ, in $CDCl_3$) 0.22, 0.23 (6 H, s, MeSi), 0.70–1.08 (10 H, m, EtSi); ^{13}C NMR (δ, in $CDCl_3$) −4.96, −4.81 (MeSi), 6.25, 6.29, 8.12 (EtSi), 114.19, 114.23 (C≡C). Anal. Calcd for $(C_8H_{16}Si_2)_n$: C, 57.06; H, 9.58. Found: C, 44.02; H, 9.33.

Polymerization of 3b. A mixture of 2.14 g (4.78 mmol) of **3b** and 0.0315 mmol (0.66 mol %) of *n*-butyllithium in 10 mL of THF was stirred in a sealed tube at room temperature for 64 h. The resulting viscous oil was washed with ethanol twice and dried under reduced pressure to give 2.02 g (94% yield) of **3c**: colorless viscous liquid; M_w = 30 900, M_n = 15 200, (M_w/M_n = 2.03); IR 1464, 1246, 1080 cm^{-1}; UV λ_{max} (thin liquid film) 253 nm; ^1H NMR (δ, in $CDCl_3$) 0.21, 0.22 (6 H, s, MeSi), 0.70–0.79 (4 H, m, *n*-BuSi), 0.89–0.91 (6 H, m, *n*-BuSi), 1.32–1.46 (8 H, m, *n*-BuSi); ^{13}C NMR (δ, in $CDCl_3$) −4.56, −4.38 (MeSi), 13.77, 26.29, 26.79 (*n*-BuSi), 114.50, 114.56 (C≡C). Anal. Calcd for $(C_{12}H_{24}Si_2)_n$: C, 64.20; H, 10.78. Found: C, 64.20; H, 10.61.

Polymerization of 4b. A mixture of 2.46 g (4.39 mmol) of **4b** and 0.0252 mmol (0.57 mol %) of *n*-butyllithium in 10 mL of THF was stirred in a sealed tube at room temperature for 64 h. The resulting oil was washed with ethanol twice and dried under reduced pressure to give 1.85 g (75% yield) of **4c**: colorless viscous liquid; M_w = 65 400, M_n = 31 000 (M_w/M_n = 2.11); IR 1466, 1246, 1100 cm^{-1}; UV λ_{max} (thin liquid film) 255 nm; ^1H NMR (δ, in $CDCl_3$) 0.20_6, 0.21_2 (6 H, s, MeSi), 0.70–0.90 (10 H, m, *n*-HexSi), 1.21–1.42 (16 H, m, *n*-HexSi); ^{13}C NMR (δ, in $CDCl_3$) −4.56, −4.38 (MeSi), 14.13, 22.64, 24.55, 31.61, 33.10 (*n*-HexSi), 114.50, 114.56 (C≡C). Anal. Calcd for $(C_{16}H_{32}Si_2)_n$: C, 68.49; H, 11.50. Found: C, 68.58; H, 11.40.

Polymerization of 5b. A mixture of 3.76 g (9.59 mmol) of **5b** and 0.0378 mmol (0.39 mol %) of *n*-butyllithium in 10 mL of THF was stirred in a sealed tube at room temperature for 64 h. The resulting solid was reprecipitated from benzene–ethanol and dried under reduced pressure to give 3.36 g (90% yield) of **5c**: mp 156–158 °C; M_w = 72 800, M_n = 33 000 (M_w/M_n = 2.16); IR 1458, 1231, 1007 cm^{-1}; UV λ_{max} (thin solid film) 243 nm; ^1H NMR (δ, in $CDCl_3$) 0.72–0.77 (8 H, m, EtSi), 1.04–1.07 (12 H, m, EtSi); ^{13}C NMR (δ, in $CDCl_3$) 4.86, 8.29 (EtSi), 113.9 (C≡C). Anal. Calcd for $(C_{10}H_{20}Si_2)_n$: C, 61.14; H, 10.26. Found: C, 59.78; H, 10.92.

Preparation of Bis(methylphenylsilyl)acetylene. Into a 2-L three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed a di-Grignard reagent of acetylene prepared from 340 mL (0.50 mol) of ethylmagnesium bromide and acetylene gas. To this was added 74.9 g (0.48 mol) of chloromethylphenylsilane in 100 mL of diethyl ether over a period of 1.5 h at room temperature. The mixture was stirred for 12 h at room temperature and then heated to reflux for 1 h. The mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of ether, the residue was distilled under reduced pressure to give 46.7 g (73% yield) of bis(methylphenylsilyl)acetylene; bp 120–122 °C (0.5 mmHg); MS *m/e* 266 (M^+); IR 2145 cm^{-1} (HSi); ^1H NMR (δ, in $CDCl_3$) 0.54 (6 H, d, MeSi), 4.61 (2 H, q, HSi), 6.94–7.67 (10 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −3.88 (MeSi), 112.2 (C≡C), 128.0, 129.9, 132.9, 134.4 (phenyl ring carbons). Anal. Calcd for $C_{16}H_{18}Si_2$: C, 72.11; H, 6.81. Found: C, 72.06; H, 6.77.

Preparation of Bis(chloromethylphenylsilyl)acetylene. Into a 500-mL three-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 46.2 g (0.17 mol) of bis(methylphenylsilyl)acetylene and a catalytic amount of palladium chloride in 250 mL of dry CCl_4. The mixture was heated to reflux for 20 h. After evaporation of the solvent, the residue was distilled under reduced pressure to give 41.0 g (71% yield) of bis(chloromethylphenylsilyl)acetylene; bp 139–142 °C (1 mmHg); MS *m/e* 334 (M^+); IR 1430, 1258, 1118 cm^{-1}; ^1H NMR (δ, in $CDCl_3$) 0.87 (6 H, s, MeSi), 7.20–7.77 (10 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 2.51 (MeSi), 111.0 (C≡C), 128.3, 131.2, 132.8, 133.6

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[21] In the ^{13}C NMR spectrum of this polymer, the resonance at −4.02 ppm determined for the polymer prepared from *all-trans*-**1b** was observed as a shoulder at −3.93 ppm.

[22] Combustion analysis of carbon of this polymer always showed a smaller value than the theoretical one. In contrast to the other polymers described here, the color of the ash remaining after combustion analysis is black. Presumably, some silicon carbides are formed in addition to SiO_2.

(phenyl ring carbons). Anal. Calcd for $C_{16}H_{16}Si_2Cl_2$: C, 57.30; H, 4.81. Found: C, 57.29; H, 4.76.

Polymerization of Bis(chloromethylphenylsilyl)acetylene. Into a 100-mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 1.04 g (45 mmol) of sodium and 30 mL of dry toluene. The contents of the flask were heated to reflux under nitrogen atmosphere and then stirred vigorously to prepare the sodium dispersion. To this was added a solution of 6.76 g (20 mmol) of bis(chloromethylphenylsilyl)acetylene dissolved in 25 mL of dry toluene over a period of 1.5 h at 90–100 °C. After the mixture was heated to reflux for 20 h, the remaining sodium was decomposed with a 1:1 mixture of ethanol and acetic acid. The mixture was then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with benzene. The organic layer and extracts were combined and washed with water and then dried over anhydrous magnesium sulfate. The solvents were evaporated to give a solid polymer. The crude polymer was purified three times by reprecipitation from benzene–ethanol to give 1.72 g (33% yield) of yellow polymer: mp 70–82 °C; $M_w = 16\,000$, $M_n = 5500$, ($M_w/M_n = 2.91$); IR 1428, 1250, 1108 cm^{-1}; UV λ_{max} (thin solid film) 247 nm; ^{1}H NMR (δ, in $CDCl_3$) 0.11$_2$, 0.11$_6$, 0.46, 0.58 (6 H, s, MeSi), 6.80–7.70 (10 H, m, phenyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) −3.97, −3.20, −0.18, 1.01 (MeSi), 108.6–116.5 ($C\equiv C$), 127.7, 127.9, 129.2, 134.4, 134.5, 134.8 (phenyl ring carbons).

Reaction of 5b with 1 Equiv of MeLi Followed by Hydrolysis. Into a 30-mL three-necked flask fitted with a stirrer and reflux condenser was placed 0.588 g (1.5 mmol) of **5b** in 5 mL of dry THF. To this was added 1 mL of methyllithium–ether solution (1.50 mmol) with stirring at −78 °C. The mixture was stirred for 0.5 h at room temperature and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water and then dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was distilled under reduced pressure to give 0.433 g (71% yield) of **6**: bp 170 °C (1 mmHg); MS *m/e* 408 (M$^+$); IR 3293 ($\equiv CH$), 2027 ($C\equiv C$) cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.09 (3 H, s, MeSi), 0.58–1.15 (40 H, m, EtSi), 2.35 (1 H, s, acetylene protons); ^{13}C NMR (δ, in $CDCl_3$) −6.28 (MeSi), 4.75, 4.89, 5.43, 8.11, 8.21, 8.45 (EtSi), 86.7, 96.1, 112.8, 115.4 ($C\equiv C$). Anal. Calcd for $C_{21}H_{44}Si_4$: C, 61.68; H, 10.85. Found: C, 61.38; H, 10.89.

Reaction of 5b with 1 Equiv of MeLi Followed by Treatment with Methyl Iodide. Into a 30-mL three-necked flask fitted with a stirrer and reflux condenser was placed 0.538 g (1.37 mmol) of **5b** in 5 mL of dry THF. To this was added 1 mL of a methyllithium–ether solution (1.5 mmol) with stirring at −78 °C. The mixture was stirred for 0.5 h at room temperature and quenched with 0.5 mL of methyl iodide. The mixture was hydrolyzed, and the organic layer was separated and concentrated. The residue was distilled under reduced pressure to give 0.368 g (64% yield) of **7**: bp 170 °C (1 mmHg); MS *m/e* 422 (M$^+$); IR 2178 ($C\equiv C$) cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.11 (3 H, s, MeSi), 0.54–1.43 (40 H, m, EtSi), 1.87 (3 H, s, $C\equiv CMe$); ^{13}C NMR (δ, in $CDCl_3$) −6.26 (MeSi) 4.95, 5.17, 5.44, 8.15, 8.31, 8.42 (EtSi), 79.9, 105.8, 113.6, 114.8 ($C\equiv C$). Anal. Calcd for $C_{22}H_{46}Si_4$: C, 62.48; H, 10.96. Found: C, 62.48; H, 11.04.

Reaction of 5c with Trimethylamine Oxide. Into a 30-mL three-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.200 g (1.0 mmol, $M_w = 62\,800$, $M_n = 22\,000$) of **5c** and 0.107 g (0.96 mmol) of trimethylamine oxide in 6 mL of dry benzene. The mixture was heated to reflux for 15 h. After evaporation of the solvent, the residue was reprecipitated twice from benzene–ethanol to give 0.165 g (78% yield) of (siloxanylene)ethynylene polymer **9**: M_w 50 500; IR 1074 cm^{-1} (OSi); UV λ_{max} (thin liquid film) 223 nm; ^{1}H NMR (δ, in $CDCl_3$) 0.65 (8 H, q, EtSi), 1.01 (12 H, t, EtSi); ^{13}C NMR (δ, in $CDCl_3$) 6.44, 7.93 (EtSi) 110.8 ($C\equiv C$). Anal. Calcd for $(C_{10}H_{20}Si_2O)_n$: C, 56.54; H, 9.49. Found: C, 56.27; H, 9.64.

Reaction of 1c with *n*-Butyllithium. A mixture of 0.50 g (1.89 mmol) of **1c** ($M_w = 77\,900$, $M_w/M_n = 2.78$) and 0.0183 mmol (1 mol %) of *n*-butyllithium in 8 mL of THF (dried over sodium–potassium alloy) was stirred in a sealed tube at room temperature for 64 h. GPC analysis showed that all starting polymer **1c** was transformed into oligomers with a molecular weight of $M_w = 1\,500$ ($M_w/M_n = 2.10$).

Reaction of 4c with *n*-Butyllithium. A mixture of 0.764 g (2.83 mmol) of **4c** ($M_w = 48\,900$, $M_w/M_n = 2.41$) and 0.026 mmol (0.92 mol %) of *n*-butyllithium in 5 mL of THF was stirred in a sealed tube at room temperature for 64 h. Molecular weight of the resulting product was determined to be $M_w = 39\,000$ ($M_w/M_n = 3.20$) (see Figure 9).

Reaction of 5c with *n*-Butyllithium. A mixture of 0.945 g (4.82 mmol) of **5c** ($M_w = 33\,900$, M_w/M_n 2.39) and 0.0315 mmol (0.65 mol %) of *n*-butyllithium in 10 mL of THF was stirred at room temperature for 64 h. Molecular weight of the resulting product was determined to be $M_w = 15\,900$ ($M_w/M_n = 8.31$) (see Figure 8).

Photolysis of 1c in Solution. A solution of 53 mg (0.201 mmol) of **1c** ($M_w = 77\,900$, $M_w/M_n = 2.78$) in 20 mL of dry benzene was irradiated with a low-pressure mercury lamp at room temperature under a nitrogen atmosphere. Molecular weights of the reaction mixture were monitored for a definite time by GPC. After 12 h of reaction, the molecular weight of the photodegradation product was determined to be $M_w = 6710$ ($M_w/M_n = 2.35$). The results are shown in Figure 12.

Photolysis of 1c in the Presence of Methanol. A solution of 50 mg (0.189 mmol) of **1c** ($M_w = 77\,900$, $M_w/M_n = 2.78$) and 139 mg (4.34 mmol) of methanol in 20 mL of dry benzene was irradiated with a low-pressure mercury lamp at room temperature. The molecular weight of the resulting product was determined to be $M_w = 2820$ ($M_w/M_n = 2.29$), after 12 h of irradiation.

Photolysis of 2c in Solution. A solution of 65 mg (0.386 mmol) of **2c** ($M_w = 121\,000$, $M_w/M_n = 3.80$) in 20 mL of dry benzene was irradiated with a low-pressure mercury lamp at room temperature. The molecular weight of the photoproduct was determined to be $M_w = 14\,400$ ($M_w/M_n = 4.99$), after 12 h of irradiation.

Photolysis of 3c in Solution. A solution of 83 mg (0.371 mmol) of **3c** ($M_w = 30\,900$, $M_w/M_n = 2.03$) in 20 mL of dry benzene was irradiated at room temperature. The molecular weight of the product was determined to be $M_w = 11\,100$ ($M_w/M_n = 2.71$).

Photolysis of 4c in Solution. A solution of 102 mg (0.364 mmol) of **4c** ($M_w = 48\,900$, $M_w/M_n = 2.41$) in 54 mL of dry benzene was irradiated at room temperature. The molecular weight of the product was determined to be $M_w = 4910$ ($M_w/M_n = 2.62$).

Photolysis of 5c in Solution. A solution of 208 mg (1.06 mmol) of **5c** ($M_w = 72\,800$, $M_w/M_n = 2.16$) in 55 mL of dry benzene was irradiated with a low-pressure mercury lamp at room temperature. The molecular weight of the product was determined to be $M_w = 10\,900$ ($M_w/M_n = 2.42$), after 12 h of irradiation.

Photolysis of 5c in the Presence of Methanol. A solution of 196 mg (1 mmol) of **5c** ($M_w = 72\,800$, $M_w/M_n = 2.16$) and 662 mg (20.7 mmol) of methanol in 60 mL of dry benzene was irradiated with a low-pressure mercury lamp at room temperature. Molecular weights of the reaction mixture were monitored for a definite time by GPC (see Figure 13). After 12 h of irradiation, the molecular weight of the photoproduct was determined to be $M_w = 2900$ ($M_w/M_n = 4.13$).

Measurement of Conductivity in Air. A methylene dichloride solution (ca. 10%) of the poly[(disilanylene)ethynylenes] **1c**, **2c**, and **5c** was spin-coated on a quartz plate by a spinner (2000 rpm) and baked at 70 °C for 2 h under reduced pressure. The thickness of the resulting film was determined by the mechanical probe method (Dektak 3030). The film was then treated with a stream of SbF_5 vapor diluted by dry nitrogen (0.2 mL of SbF_5–0.9 L of N_2/min) for 2 h. An excess of SbF_5 vapor was removed under reduced pressure (1 mmHg) for 30 m. After the resulting film was allowed to stand in air for 2 h, the conductivity of the film was measured by the four-probe method. The results are shown in Table VII.

Measurement of Conductivity in Vacuo. A 10% THF solution of the polymers **1c**, **2c**, and **5c** was spin-coated on a silicon wafer by a spinner (2000 rpm). The thickness of the film was measured by an Okazaki Mfg. Co., Ltd. Model D-10SS instrument. The film was placed in a glass vessel connected to a conductivity measuring instrument. The glass vessel was also connected with a container containing liquid SbF_5, which was degassed prior to use. After the vessel was evacuated with a pump (1 mmHg), SbF_5 vapor was introduced into the vessel from liquid SbF_5 at room temperature. The conductivity of the film was determined simultaneously with doping by the four-probe method. The maximum conductivity (σ_{max}) observed during doping for 5 h was shown in Table VII. The film was allowed to stand in an atmosphere of SbF_5 vapor for 7 days to reach a constant value. Then, a supply of SbF_5 vapor was stopped, the excess of SbF_5 vapor was removed by a pump, and the film was exposed to air. The conductivity was immediately measured by the four-probe method.

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Registry No. *dl*-**1a**, 139102-54-8; *meso*-**1a**, 139102-59-3; *dl*-**2a**, 139102-55-9; *meso*-**2a**, 139102-60-6; *dl*-**3a**, 139102-56-0; *meso*-**3a**, 139102-61-7; *dl*-**4a**, 139130-62-4; *meso*-**4a**, 139102-62-8; **5a**, 139102-57-1; *cis–trans*-**1b**, 139236-44-5; (±)-*all-trans*-**1b**, 139236-45-6; *cis–trans*-**1b** (homopolymer), 139341-69-8; (±)-*all-trans*-**1b** (homopolymer), 139341-70-1; *cis–trans*-**2b**, 139236-46-7; (±)-*all-trans*-**2b**, 139236-48-9; *cis–trans*-**2b** (homopolymer), 139341-71-2; (±)-*all-trans*-**2b** (homopolymer), 139341-73-4; *cis–trans*-**3b**, 139102-58-2; (±)-*all-trans*-**3b**, 139236-49-0; *cis–trans*-**3b** (homopolymer), 139236-51-4; (±)-*all-trans*-**3b** (homopolymer), 139341-74-5; *cis–trans*-**4b**, 139236-47-8; (±)-*all-trans*-**4b**, 139236-50-3; *cis–trans*-**4b** (homopolymer), 139341-72-3; (±)-*all-trans*-**4b** (homopolymer), 139341-75-6; **5b**, 135020-33-6; **5b** (homopolymer), 135020-34-7; $Et(SiPhMe)_2Et$, 139102-48-0; $Cl(SiPhMe)_2Cl$, 29442-41-9; $Bu(SiPhMe)_2Bu$, 139102-49-1; $H(CH_2)_6(SiPhMe)_2(CH_2)_6H$, 139102-50-4; $Ph(SiEt_2)_2Ph$, 18586-57-7; $Et_2SiPhLi$, 139102-51-5; $ClEt_2SiPh$, 17876-59-4; $Cl(SiMeEt)_2Cl$, 111230-98-9; $Cl(SiBuMe)_2Cl$, 139102-52-6; $H(CH_2)_6(SiMeCl)_2(CH_2)_6H$, 139102-53-7; $Cl_2(SiEt_2)_2$, 85590-06-3; $(SiHMePh)_2C{\equiv}C$, 17964-73-7; ClSiHPhMe, 1631-82-9; $(ClMeSiPh)_2C{\equiv}C$, 17937-56-3; $(ClMeSiPh)_2C{\equiv}C$ (homopolymer), 139102-63-9; *n*-BuLi, 109-72-8; SbF_5, 7783-70-2.

Supplementary Material Available: Tables of fractional coordinates and isotropic temperature factors of all atoms, including hydrogen atoms, bond distances and angles, and anisotropic temperature factors of all the non-hydrogen atoms for *cis–trans*-**1b** and *all-trans*-**1b** (8 pages); listings of observed and calculated structure factors for *cis–trans*-**1b** and *all-trans*-**1b** (14 pages). Ordering information is given on any current masthead page.

Ruthenium-Catalyzed Arbuzov Rearrangement of (Allyloxy)phosphines: Isolation and X-ray Structure Analysis of an Intermediate Leading to Mechanistic Conclusions

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The $[CpRu(CH_3CN)_3]PF_6$-catalyzed classical Arbuzov rearrangement of (allyloxy)phosphines $Ph_nP(OC_3H_5)_{3-n}$ ($n = 0–2$) at room temperature in neat (allyloxy)phosphine proceeds to completion in a short time period and gives only the classical Arbuzov rearrangement products, $Ph_nP(O)(C_3H_5)(OC_3H_5)_{2-n}$ ($n = 0–2$). The reaction mechanism was studied in acetonitrile solution by $^{31}P\{^1H\}$ NMR spectroscopy and supported by isolation and characterization of intermediates and final products. In addition to the classical Arbuzov product, with $Ph_2P(OC_3H_5)$, the mono-chelation product $[CpRu(CH_3CN)\{\eta^3\text{-}Ph_2P(OC_3H_5)]PF_6$ (**6**) was isolated and characterized; with $PhP(OC_3H_5)_2$, the bis-chelation products $[CpRu\{\eta^5\text{-}PhP(OC_3H_5)_2\}]PF_6$ (**5a,b**) were isolated and characterized; with $P(OC_3H_5)_3$, the intermediate phosphite complex $[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]PF_6$ (**2**), the final product of dealkylation $[CpRu\{\eta^5\text{-}P(O)(OC_3H_5)_2\}]$ (**4**), the alkylation product $[CpRu(\eta^3\text{-}C_3H_5)(CH_3CN)_2][PF_6]_2$ (**1**), and the hydrolysis product $[CpRu\{\eta^5\text{-}P(OH)(OC_3H_5)_2\}]PF_6$ (**3**) have been isolated and characterized by elemental analysis, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The structure of **2** was confirmed by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions $a = 7.603$ (5) Å, $b = 20.507$ (3) Å, $c = 12.054$ (2) Å, $\beta = 97.45$ (2)°, and $\rho_{calcd} = 1.829$ g cm^{-3} with $Z = 4$. Refinement converged to $R = 0.041$ and 1892 independent observed ($I/\sigma(I) \geq 3.0$) reflections. The two coordinated alkene moieties are inequivalent having different dihedral angles between the planes of the C_5H_5 rings and the C–C axes (4.8, 36.10°) and slightly different average Ru–C bond distances of 2.213 (8) and 2.239 (9) Å. The P–OH and P=O complexes, **3** and **4**, are interconvertible via simple acid–base reactions.

Introduction

The well-known Arbuzov rearrangement has been widely employed for the synthesis of phosphonate and phosphinic acid esters and phosphine oxides.[2] Arbuzov-like dealkylation reactions of transition metal phosphite complexes have also been reviewed,[3] and the rearrangement mechanisms, thoroughly discussed. However, metal-catalyzed rearrangements of allylic phosphites were not included in either review although thermal rearrangement of allylic

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