Polymeric Organosilicon Systems. 15. Thermal and Radical-Induced Polymerization of 1,2,5,6-Tetrasilacycloocta-3,7-diynes

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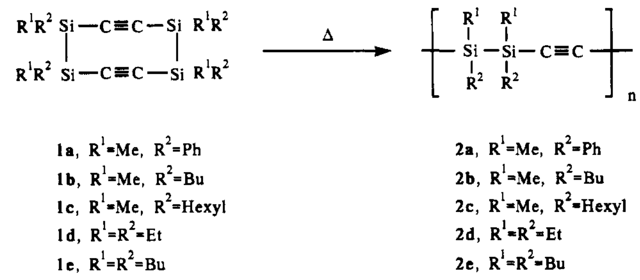
Treatment of 1,2,5,6-tetramethyl-1,2,5,6-tetraphenyl-, 1,2,5,6-tetrabutyl-1,2,5,6-tetramethyl-, 1,2,5,6-tetrahexyl-1,2,5,6-tetramethyl-, 1,1,2,2,5,5,6,6-octaethyl-, and 1,1,2,2,5,5,6,6-octabutyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**1a**–**1e**) in a degassed tube at 230 °C afforded the respective ring-opened polymers, poly[(disilanylene)ethynylenes] (**2a**–**2e**) with high molecular weights in high yields. In the presence of a catalytic amount of di-*tert*-butyl peroxide (DTBP), the tetrasilacyclooctadiynes also undergo polymerization to give the ring-opened polymers at a lower temperature than the thermal ring-opening polymerization. Heating **1a** with 5 mol % of DTBP at 150 °C for 5 h gave **2a** whose molecular weight was determined to be 25 000 in 60% yield, while **1d** afforded **2d** with a molecular weight of 159 000 in 63% yield. Similar treatment of **1b** and **1e** at 180 °C produced polymers **2b** and **2e** with molecular weights of 28 000 and 7000, respectively. The reaction of tetrasilacyclooctadiynes with a catalytic amount of DTBP in the presence of a hydrosilane afforded ring-opened polymers in yields higher than those of polymers obtained in the absence of the hydrosilane. Treatment of **2d**, whose molecular weight was determined to be 157 000, with 6 mol % DTBP and 19 mol % methyldiphenylsilane at 150 °C for 5 h resulted in depolymerization of the starting polymer to give the polymer with a molecular weight of 12 000 in quantitative yield.

Introduction

We have designed and synthesized the polymers which have the regular alternating arrangement of a disilanyl unit and π-electron system in the polymer backbone. The alternating polymers composed of the disilanylene unit and a phenylene,[1,2] ethenylene,[3] butenyne,[4] ethynylene,[5,6] and diethynylene[7-9] group are photoactive and show conducting properties when the polymers are doped by oxidating agents such as antimony pentafluoride. Recently, we have found that the reaction of 1,2,5,6-tetrasilacycloocta-3,7-diynes with a catalytic amount of *n*-butyllithium in THF at room temperature proceeds with ring-opening polymerization to give poly[(disilanylene)ethynylenes] with high molecular weights.[5a] Later, however, it was found that there are some limitations to this method. For example, the anionic polymerization of 1,2,5,6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne affords poly[(1,2-dimethyl-1,2-diphenyldisilanylene)ethynylene] only in low yield. Moreover, gel permeation chromatography of the poly[(disilanylene)ethynylenes] obtained by this method shows a rather broad molecular weight distribution, owing to the redistribution reaction[10] involved in this system.[5] In an attempt to develop a method that gives the copolymers in high yields, we discovered that 1,2,5,6-tetrasilacycloocta-3,7-diynes undergo thermal ring-opening polymerization to give poly[(disilanylene)ethynylenes] in high yields.[11] In this paper we report thermal and radical-induced ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes.

Scheme I



Results and Discussion

The starting *cis–trans*-1,2,5,6-tetramethyl-1,2,5,6-tetraphenyl-, 1,2,5,6-tetrabutyl-1,2,5,6-tetramethyl-, 1,2,5,6-tetrahexyl-1,2,5,6-tetramethyl-, and 1,1,2,2,5,5,6,6-octaethyl-1,2,5,6-tetrasilacycloocta-3,7-diynes (**1a**–**1d**) were prepared by the method reported previously.[5b] 1,1,2,2,5,5,6,6-Octabutyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**1e**) was synthesized by the reaction of the di-Grignard reagent of

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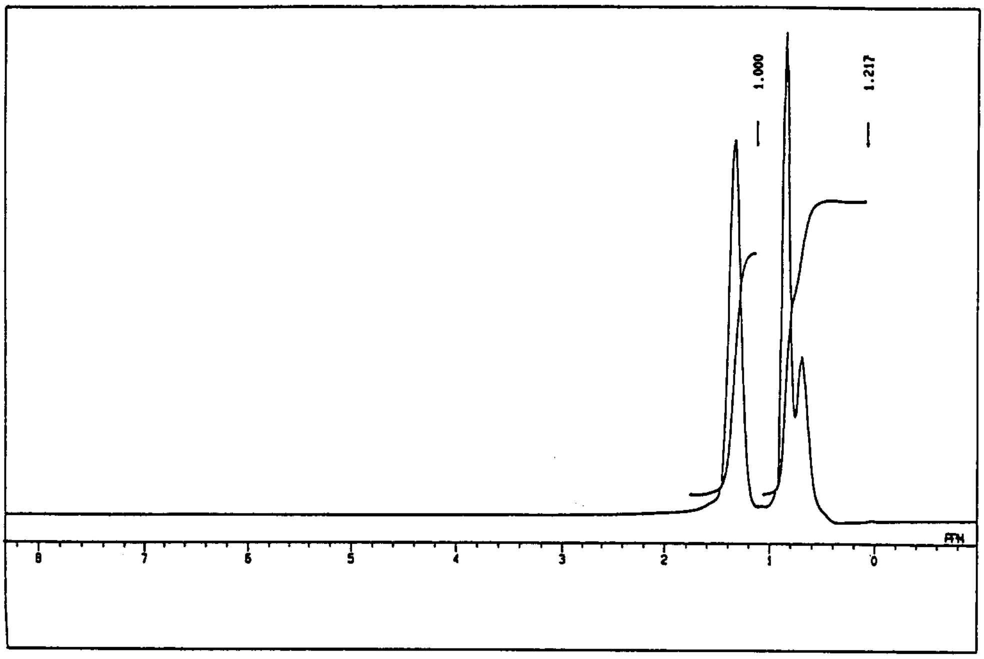

Figure 1. ^{1}H NMR spectrum for **2e**.

tetrabutyl-1,2-diethynyldisilane[6] with tetrabutyl-1,2-dichlorodisilane.

Thermal Ring-Opening Polymerization. When compound **1a** was heated in a degassed sealed tube at 230 °C for 24 h and the resulting polymer was reprecipitated twice from ethanol–benzene, poly[(1,2-dimethyl-1,2-diphenyldisilanylene)ethynylene] (**2a**) whose molecular weight was determined to be 220 000 was obtained in 87% yield (Scheme I). In contrast to the polymer synthesized from the anionic ring-opening polymerization of **1a**, which is a colorless solid, polymer **2a** thus obtained shows light yellow color. However, ^{1}H and ^{13}C NMR chemical shifts and the UV spectrum for **2a** prepared from thermal ring-opening polymerization were very similar to those of the polymer from the anionic polymerization of **1a**.[5b]

The thermal ring-opening polymerization is remarkably general for 1,2,5,6-tetrasilacycloocta-3,7-diynes and cleanly affords ring-opened polymers with high molecular weights in high yields. Thus, heating **1b** under the same conditions for 24 h produced poly[(1,2-dibutyl-1,2-dimethyldisilanylene)ethynylene] (**2b**) in 20% yield. In this reaction 70% of the starting compound **1b** was recovered unchanged. When **1b** was heated at 260 °C for 24 h, **2b** was obtained in 59% yield, after twice reprecipitated from ethanol–benzene. GLC analysis of the solvent used for reprecipitation showed the presence of 27% of the unchanged starting compound **1b**. Treatment of **1c** at 260 °C for 24 h produced poly[(1,2-dihexyl-1,2-dimethyldisilanylene)ethynylene] (**2c**) in 50% yield, in addition to 26% of the unchanged compound **1c**. Similar treatment of **1d** at 230 °C for 24 h gave poly[(tetraethyldisilanylene)ethynylene] (**2d**) in 34% yield, along with 46% of the starting compound **1d**. Prolonged heating of **1d** under the same conditions gave polymer **2d** in 52% yield. Again, 48% of **1d** was recovered unchanged. Heating **1e** at 230 °C for 24 h, however, afforded poly[(tetrabutyldisilanylene)ethynylene][6] (**2e**) in a trace amount, while reaction at 260 °C for 24 h gave **2e** in 21% yield, in addition to 74% of the unchanged starting compound **1e**. All spectral data obtained for polymers **2b**–**2d** were very similar to those obtained from the anionic ring-opening polymerization, indicating that the polymers obtained from thermal ring-opening polymerization must have the regular alternating arrangement of a disilanylene group and ethynylene unit. ^{1}H and ^{13}C NMR spectra for **2e**, which are consistent with those of the polymer prepared by West et al. using a different method,[6] are shown in Figures 1 and 2. The thermal ring-opening polymerization is an extremely clean reaction. Even in the synthesis of **2c** and **2e** at 260 °C, only polymers and the starting compounds are detected. No decomposition products are detected in the reaction mixture by either GLC or GPC analysis. The reaction conditions and some properties of the resulting polymers are shown in Table I.

Molecular Weight Determination. The molecular weights of the polymers shown in Tables I and II were determined by GPC, rerative to polystyrene standards. In order to learn more about the real molecular weight of the present polymers, we carried out the molecular weight determination of **2a**–**2d** by osmometry. Interestingly, M_n values measured by GPC, relative to polystyrene standard were in good agreement with those obtained from osmometry. Thus, when polymer **2a** whose molecular weight was determined to be M_n = 16 900 (M_w = 71 000) by GPC was measured by osmometry, its molecular weight was shown to be 15 400. Similarly, polymer **2a** with M_n = 7300 (M_w = 30 200) was determined to be 7000 by osmometry. Polymer **2b** which was determined to be M_n = 18 000 (M_w = 29 900) by GPC was calculated to be 17 500 by osmometry, while polymer **2c** and **2d** with M_n = 33 700 (M_w = 64 000) and M_n = 54 100 (M_w = 171 000), respectively, were shown to be 30 500 and 53 600.

Radical-Induced Polymerization. In order to learn more about the mechanism for the thermal ring-opening polymerization, we carried out the ring-opening reaction of 1,2,5,6-tetrasilacycloocta-3,7-diynes in the presence of radical initiators. Thus, heating **1a** and **1d** with a catalytic amount of benzoyl peroxide in benzene in a sealed glass tube at 100 °C for 4 h gave no polymeric products, but starting compounds **1a** and **1d** were recovered unchanged. The reaction of **1a** and **1d** with a catalytic amount of AIBN in refluxing toluene gave no ring-opened products. Again,

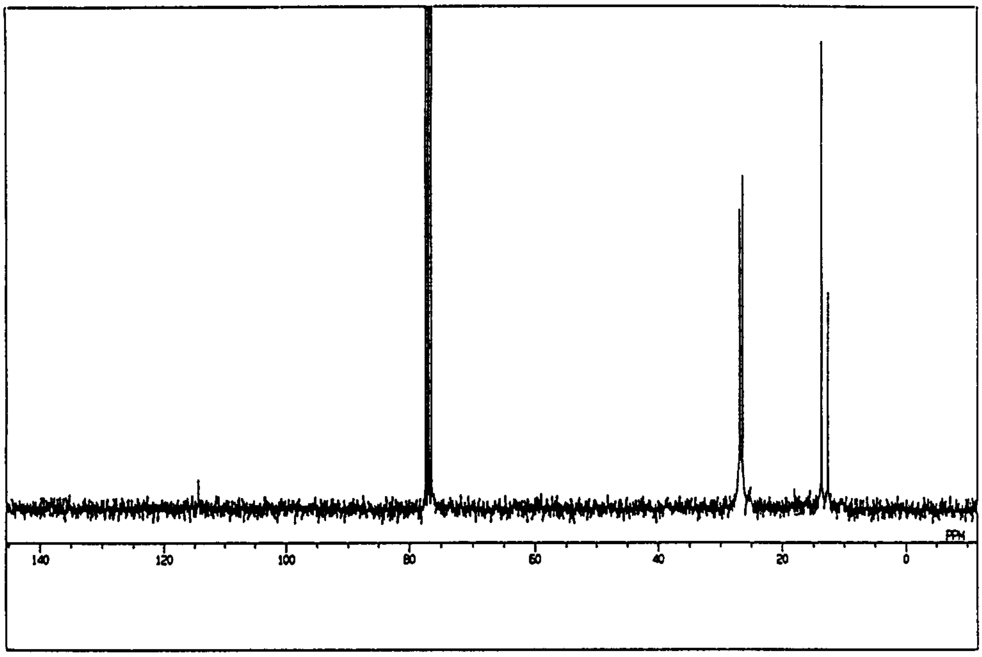

Figure 2. ^{13}C NMR spectrum for **2e**.

Table I. Thermal Ring-Opening Polymerization of 1a–1e

polymer	temp (°C)	time (h)	M_w	M_w/M_n	yield (%)
2a, R^1 = Ph, R^2 = Me	230	24	220 000	4.0	87
2b, R^1 = Bu, R^2 = Me	230	24	47 000	2.2	20 (70)[a]
	260	24	100 000	3.2	59 (27)[a]
2c, R^1 = Hex, R^2 = Me	260	24	98 000	3.6	50 (26)[a]
2d, R^1 = R^2 = Et	230	24	183 000	4.0	34 (46)[a]
	230	48	384 000	4.3	52 (48)[a]
2e, R^1 = R^2 = Bu	230	24			trace
	260	24	24 000	2.1	21 (74)[a]

[a] Yield of recovered starting compound.

the starting cyclic compounds **1a** and **1d** were recovered unchanged quantitatively. When **1d** was heated with 5 mol % BPO at 150 °C for 5 h in benzene, **2d** was obtained in 4% yield, in addition to 74% of the starting compound **1d**. This result shows that the radical-induced ring-opening polymerization occurs at higher temperature. We used di-*tert*-butyl peroxide (DTBP) as a radical initiator and found that this peroxide is more effective than BPO for the ring-opening polymerization of the tetrasilacyclooctadiynes. Thus, heating **1a** with 5 mol % DTBP in benzene at 150 °C for 1 h in a sealed glass tube yielded polymer **2a** with a molecular weight of 26 000 (M_w) in 26% yield, after two reprecipitations from methanol–benzene. Treatment of **1a** for 3 h under the same conditions gave **2a** with a molecular weight of 44 000 (M_w) in 53% yield, while on heating for 5 h, **1a** afforded **2a** with a molecular weight of 25 000 (M_w) in 60% yield. The prolonged reaction results in formation of **2a** in a higher yield but results in the decrease of the molecular weight of the polymer. This may be ascribed to the radical-induced redistribution reaction which is involved in this system (see below). Tetrasilacyclooctadiynes that have the long alkyl group, such as a butyl or hexyl group, on the silicon atoms also undergo radical-induced ring-opening polymerization to give the polymers. However, the yields of the polymers thus obtained are quite low. Thus, treatment of **1b** with a catalytic amount of DTBP at 180 °C for 8 h in benzene produced **2b** in 16% yield, while **1e** at 180 °C for 5 h produced **2e** only in 5% yield. On the contrary, **1d** at 150 °C for 5 h afforded **2d** in 63% yield. The results obtained from radical-induced ring-opening polymerization are shown in Table II. All spectral data for **2a**, **2b**, **2d**, and **2e** obtained by radical-induced ring-opening polymerization were consistent with those of the polymers prepared from thermal ring-opening polymerization.

Polymers **2a**–**2e** prepared from anionic ring-opening polymerization and also thermal ring-opening polymerization can be stored without decomposition. These polymers are soluble in common organic solvents such as benzene, THF, and chloroform and show good solubility in these solvents after storage for several months. Polymers **2a**, **2b**, and **2e** prepared by radical-induced polymerization exhibit the same behavior as those obtained from other methods, but curiously enough, **2d** prepared by radical-induced polymerization becomes insoluble during storage of 1 or 2 days. Even the polymer purified by several reprecipitations shows such behavior. Although, at present, we cannot find out the reason for the formation of such an insoluble polymer, the cross-linking reaction presumably takes place in this case.[12]

It seems likely that the silyl radicals play an important role for both thermal and radical-induced ring-opening polymerization. To confirm this, we carried out the radical-induced reaction of **1a** in the presence of a hydrosilane in benzene. Thus, heating **1a** with a mixture of 5 mol % DTBP and 12 mol % methyldiphenylsilane in benzene at 150 °C for 5 h produced **2a** in 84% yield, while treatment of **1b** gave **2b** in 25% yield, along with 72% of the unchanged starting compound **1b**. All attempts to prepare **2b** in higher yield were unsuccessful and always afforded **2b** in low yields. Similar treatment of **1d** with a mixture of DTBP and methyldiphenylsilane gave **2d** in high yield.

It has been reported that thermal decomposition of DTBP in the presence of hydrosilanes produces silyl radicals.[13,14] In the present system, the methyldiphenylsilyl radical is probably produced initially, and the resulting

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[12] The esr spectrum of polymer **2d** prepared by radical-induced polymerization showed no esr signals due to free radicals.

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Table II. Radical-Induced Ring-Opening Polymerization of 1a, 1b, 1d, and 1e

polymer	temp (°C)	time (h)	amt of DTBP (mol %)	amt of $MePh_2SiH$ (mol %)	M_w	M_w/M_n	yield (%)
2a, $R^1 = Ph$, $R^2 = Me$	150	5	5		25 000	1.7	60 (13)[a]
2a	150	5	5	12	19 000	2.2	84 (6)[a]
2b, $R^1 = Bu$, $R^2 = Me$	180	8	5		28 000	1.9	16 (77)[a]
2b	180	8	7	34	13 000	2.5	25 (72)[a]
2d, $R^1 = R^2 = Et$	150	5	7		159 000	8.8	63 (26)[a]
2d	150	5	5	12	96 000	7.9	82
2e, $R^1 = R^2 = Bu$	180	5	9		7 000	1.6	5 (89)[a]

[a] Yield of recovered starting compound.

Scheme II

$$\mathbf{1d} + (t\text{-BuO})_2 + Me_2PhSiH \longrightarrow$$

$$Me_2PhSi{-}C{\equiv}C({-}SiEt_2SiEt_2C{\equiv}C{-})_nSiEt_2SiEt_2H$$

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silyl radical would attack the ethynyl carbon of the tetrasilacyclooctadiyne ring to give the ring-opened silyl radical in the initial step.

As can be seen in Table II, the radical-induced polymerization in the presence of the hydrosilane always gives the polymers in yields higher than those of polymers obtained in the absence of the hydrosilane. In the presence of the hydrosilane, the silyl radical would be produced effectively and therefore would result in higher yields of the polymers.

In marked contrast to **2d** obtained from DTBP-induced polymerization, which is transformed into insoluble substances during storage, the polymer obtained from silyl radical induced polymerization can be stored without decomposition. No insoluble polymers were produced after storage for several months.

In order to get more information concerning the terminal group of the polymers, we attempted to prepare the polymer with a low molecular weight. Thus, treatment of **1d** with 0.57 equiv of DTBP and 3.4 equiv of dimethylphenylsilane at 120 °C for 20 h gave the mixture of oligomers, which showed trimodal molecular weight distribution (Scheme II). No starting compound **1d** was detected in the reaction mixture by GLC analysis. Oligomer **3** that has the highest molecular weight distribution was isolated in 38% yield as a liquid by reprecipitation from methanol. The ^1H NMR spectrum of this oligomer shows resonances at δ 0.40, 3.49 and 3.55–3.61, and 7.34–7.65 ppm, attributed to Me–Si, H–Si, and Ph–Si protons, respectively, in addition to Et–Si protons. The ^{13}C NMR spectrum reveals signals at δ 1.98, 4.85 and 8.29, and 113.86 ppm, due to Me–Si, Et–Si, and ethynyl carbons, as well as Ph–Si carbons. These results indicate that a hydrosilyl group and dimethylphenylsilyl group are attached to both terminal ends of the oligomer.

Next, we investigated the reaction of bis(tetramethyl-1-phenyldisilanyl)acetylene (**4**) with the methyldiphenylsilyl radical to confirm which site, ethynyl carbon or silicon, the silyl radical attacks in the tetrasilacyclooctadiyne ring. Thus, when compound 4 was heated with 1.1 equiv of DTBP and 3.5 equiv of methyldiphenylsilane in a sealed glass tube at 120 °C for 20 h, three products, (tetramethyl-1-phenyldisilanyl)(methyldiphenylsilyl)acetylene (**5**), bis(methyldiphenylsilyl)acetylene (**6**), and 1,2,2,2-tetramethyl-1-phenyldisilane (**7**), were obtained in 20, 21, and 43% yields, respectively, in addition to 24% of the unreacted starting compound 4 (Scheme III). This model reaction clearly shows that the silyl radical attacks the ethynyl carbon in the tetrasilacyclooctadiyne ring, but not the silicon atom.

Scheme III

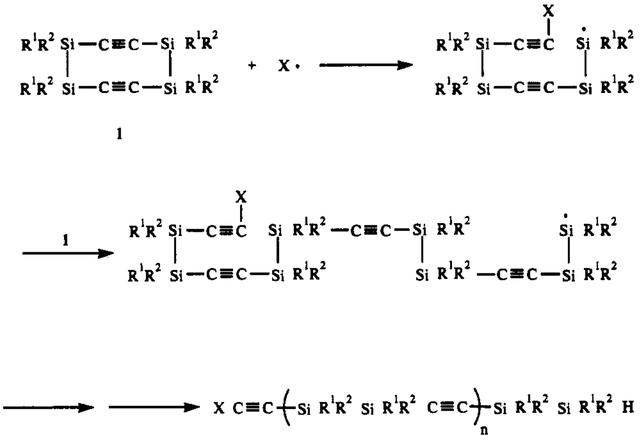
$$(t\text{-BuO})_2 \xrightarrow{\Delta} t\text{-BuO}^{\bullet} \xrightarrow{MePh_2SiH} MePh_2Si^{\bullet}$$

$$\underset{\mathbf{4}}{Me_3SiSiMePhC{\equiv}CSiMePhSiMe_3} + MePh_2Si^{\bullet} \longrightarrow \underset{\mathbf{5}}{Me_3SiSiMePhC{\equiv}CSiPh_2Me} + Me_3SiSi^{\bullet}MePh$$

$$\mathbf{5} + MePh_2Si^{\bullet} \longrightarrow \underset{\mathbf{6}}{MePh_2SiC{\equiv}CSiPh_2Me} + Me_3SiSi^{\bullet}MePh$$

$$Me_3SiSi^{\bullet}MePh \xrightarrow{\text{H abstraction}} \underset{\mathbf{7}}{Me_3SiSiMePhH}$$

Scheme IV



Products **5** and **6** were separated by medium pressure liquid chromatography, while **7** was isolated by GLC. The structures of these compounds were confirmed by spectroscopic analysis.

On the basis of the model reaction, the radical-induced ring-opening polymerization involves the attack of the radical on the ethynyl carbon atom, giving the ring-opened silyl radical in the initial step, and the resulting silyl radical attacks the ethynyl carbon of the starting tetrasilacyclooctadiyne to form a dimeric silyl radical; finally poly[(disilanylene)ethynylene] is produced as shown in Scheme IV.

The thermal ring-opening polymerization presumably involves homolytic scission of an ethynyl–silicon bond in the tetrasilacyclooctadiyne ring to give a diradical. The silyl radical thus formed attacks the ethynyl carbon of the tetrasilacyclooctadiyne to give dimeric species as mentioned above.

The silyl radical induced ring-opening polymerization always affords the polymers which have molecular weights lower than those of polymers obtained from thermal polymerization. This may be ascribed to the depolymerization reaction of the polymer once formed with the silyl radical. In fact, treatment of polymer **2d** whose molecular weight was determined to be 157 000 with 6 mol % DTBP and 19 mol % methyldiphenylsilane in benzene at 150 °C for 5 h led to depolymerization to give the polymer with a molecular weight of 12 000 in quantitative yield, while treatment of **2d** with the same molecular weight with 7 mol % DTBP in the absence of methyldiphenylsilane under the same reaction conditions resulted in the polymer whose molecular weight was determined to be 81 000, a molecular weight higher than that of the polymer obtained from the redistribution reaction in the presence of methyldiphenylsilane. These results are consistent with the fact that the molecular weights of the polymers obtained from silyl radical induced ring-opening polymerization are always lower than those of the polymers from DTBP-induced polymerization (see Table II). Such a redistribution reaction in the presence of a radical catalyst is a general model for poly[(disilanylene)ethynylenes]. Thus, the reaction of **2c** (M_w = 64 000) with a mixture of 9 mol % DTBP and 38 mol % methyldiphenylsilane under the same conditions produced a polymer with a molecular weight of 9700 in almost quantitative yield.

Experimental Section

General Procedures. All reactions used for the preparation of the starting compounds were carried out under an atmosphere of dry nitrogen. Benzene used as solvent for ring-opening polymerization was dried over lithium aluminum hydride and distilled before use. Tetrahydrofuran was dried over sodium in the presence of benzophenone and distilled before use.

^1H 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 1,1,2,2-Tetra-*n*-butyl-1,2-diphenylsilane.[6] Into a 500-mL three-necked flask was placed (dibutylphenylsilyl)-lithium prepared from 82.5 g (0.32 mol) of di-*n*-butylchlorophenylsilane and 6.4 g (1.0 mol) of lithium in 150 mL of dry THF. To this was added 79.4 g (0.31 mol) of di-*n*-butylchlorophenylsilane dissolved in 40 mL of dry THF. The mixture was stirred for 30 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, washed with water, and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 97.9 g (71% yield) of 1,1,2,2-tetra-*n*-butyl-1,2-diphenyldisilane: bp 180–185 °C (1 mmHg); MS *m/e* 438 (M^+); IR 2956, 2922, 2871, 1463, 1456, 1427, 1376, 1102, 1079, 868, 734, 698 cm^{-1}; ^1H NMR (δ in $CDCl_3$) 0.83–0.95 (20H, m, *n*-BuSi), 1.23–1.36 (16H, m, *n*-BuSi), 7.27–7.36 (10H, m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) 11.79, 13.66, 26.67, 26.79 (*n*-BuSi), 127.53, 128.12, 134.45, 137.77 (phenyl ring carbons). Anal. Calcd for $C_{28}H_{46}Si_2$: C, 76.63; H, 10.57. Found: C, 76.56; H, 10.46.

Preparation of 1,1,2,2-Tetra-*n*-butyl-1,2-dichlorodisilane.[6] Into a 300-mL three-necked flask was placed a mixture of 95.6 g (0.22 mol) of 1,1,2,2-tetra-*n*-butyl-1,2-diphenyldisilane 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, in order to deactivate the catalytic effect of aluminum chloride. The mixture was then distilled under reduced pressure to give 66.9 g (85% yield) of 1,1,2,2-tetra-*n*-butyl-1,2-dichlorodisilane; bp 124–128 °C (1 mmHg); MS *m/e* 354 (M^+); IR 2958, 2926, 2872, 1464, 1192, 1081, 883, 699 cm^{-1}; ^1H NMR (δ in $CDCl_3$) 0.67–1.75 (36H, m, *n*-BuSi); ^{13}C NMR (δ in $CDCl_3$) 13.57, 16.54, 25.37, 26.13 (*n*-BuSi). Anal. Calcd for $C_{16}H_{36}Si_2Cl_2$: C, 54.05; H, 10.21. Found: C, 54.01; H, 10.21.

Preparation of 1,1,2,2-Tetra-*n*-butyl-1,2-diethynyldisilane.[6] Into a 2-L three-necked flask was placed 220 mL (0.2 mol) of THF solution of ethynylmagnesium bromide prepared from ethylmagnesium bromide and acetylene gas in THF. To this was added 34.0 g (0.096 mol) of 1,1,2,2-tetra-*n*-butyl-1,2-dichlorodisilane 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 the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water. The solvent was concentrated, and the residue was distilled under reduced pressure to give 26.3 g (82% yield) of 1,1,2,2-tetra-*n*-butyl-1,2-diethynyldisilane; bp 111–113 °C (1 mmHg); MS *m/e* 277 (M^+ – *n*-Bu); IR 3292, 2027 cm^{-1}; ^1H NMR (δ in $CDCl_3$) 0.62–1.79 (36H, m, *n*-BuSi), 2.52 (2H, s, acetylene protons); ^{13}C NMR (δ in $CDCl_3$) 12.54, 13.67, 26.38, 26.40 (*n*-BuSi), 86.97, 96.29 ($C{\equiv}C$). Anal. Calcd for $C_{20}H_{38}Si_2$: C, 71.77; H, 11.44. Found: C, 71.66; H, 11.42.

Preparation of 1e. 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 8.4 g (0.025 mol) of 1,1,2,2-tetra-*n*-butyl-1,2-diethynyldisilane in 80 mL of dry THF at room temperature. The mixture was stirred at room temperature for 1 h, and then 8.9 g (0.025 mol) of 1,1,2,2-tetra-*n*-butyl-1,2-dichlorodisilane in 80 mL of dry THF was added to the resulting di-Grignard reagent over a period of 2 h at room temperature. The mixture was stirred for 12 h at room temperature and then hydrolyzed with dilute aqueous hydrochloric acid. 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 solvent, the residue was distilled under reduced pressure to give 8.8 g (56% yield) of **1e**; bp 174–176 °C (0.25 mmHg); MS *m/e* 616 (M^+); IR 2956, 2923, 2872, 2857, 1464, 1408, 1376, 1080, 999, 961, 883, 789, 691 cm^{-1}; ^1H NMR (δ in $CDCl_3$) 0.54–1.70 (72H, m, *n*-BuSi); ^{13}C NMR (δ in $CDCl_3$) 12.64, 13.62, 26.40, 27.16 (*n*-BuSi), 119.80 ($C{\equiv}C$). Anal. Calcd for $C_{36}H_{72}Si_4$: C, 70.04; H, 11.76. Found: C, 70.03; H, 11.65.

Thermal Polymerization of 1a. In a 1.0- × 20-cm glass tube was placed 286 mg (0.54 mmol) of **1a**. The tube was sealed under reduced pressure and heated at 230 °C for 24 h. The reaction mixture was poured into methanol. The resulting solid was reprecipitated twice from ethanol–benzene and dried under reduced pressure to give 249 mg (87% yield) of **2a** (M_w = 220 000, M_w/M_n = 4.0); ^1H NMR (δ in $CDCl_3$) 0.44, 0.57 (6H, s, MeSi), 7.16–7.66 (10H, m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) –3.95 (MeSi), 114.4 ($C{\equiv}C$), 127.8, 129.2, 133.5, 134.5 (phenyl ring carbons). (Lit:[5b] M_w = 80 800; ^1H NMR (δ in $CDCl_3$) 0.45, 0.58, 7.17–7.66; ^{13}C NMR (δ in $CDCl_3$) –3.93, 114.4, 127.8, 129.2, 133.5, 134.5.)

Thermal Polymerization of 1b. Compound **1b** (140 mg, 0.31 mmol) was heated in a sealed tube at 260 °C for 24 h. The reaction mixture was poured into methanol. The resulting oily product was washed twice with 20 mL of ethanol and dried under reduced pressure to give 83 mg (59% yield) of **2b** (M_w = 100 000, M_w/M_n = 3.2), in addition to 27% yield of the starting compound **1b**. For **2b**: ^1H NMR (δ in $CDCl_3$) 0.21 (6H, broad s, MeSi), 0.62–0.79 (4H, m, *n*-BuSi), 0.82–0.97 (6H, m, *n*-BuSi), 1.37–1.43 (8H, m, *n*-BuSi); ^{13}C NMR (δ in $CDCl_3$) –4.56, –4.40 (MeSi), 13.77, 26.31, 26.76 (*n*-BuSi), 114.50, 114.56 ($C{\equiv}C$). (Lit:[5b] M_w = 30 900; ^1H NMR (δ in $CDCl_3$) 0.21, 0.22, 0.70–0.79, 0.89–0.91, 1.32–1.46; ^{13}C NMR (δ in $CDCl_3$) –4.56, –4.38, 13.77, 26.29, 26.79, 114.50, 114.56.)

Thermal Polymerization of 1c. Compound **1c** (94 mg, 0.17 mmol) was heated in a sealed tube at 260 °C for 24 h. The reaction mixture was poured into methanol. The resulting oily product was washed twice with ethanol and dried under reduced pressure to give 47 mg (50% yield) of **2c** (M_w = 98 000, M_w/M_n = 3.6), in addition to 26% yield of the starting compound **1c**. For **2c**: ^{1}H NMR (δ in CDCl$_3$) 0.21 (6H, broad s, MeSi), 0.60–0.95 (10H, m, *n*-HexSi), 1.10–1.50 (16H, m, *n*-HexSi); ^{13}C NMR (δ in CDCl$_3$) –4.54, –4.36 (MeSi), 14.14, 22.66, 24.55, 31.63, 33.12 (*n*-HexSi), 114.52 (C≡C). (Lit:[5b] M_w = 65 400; ^{1}H NMR (δ in CDCl$_3$) 0.20, 0.21, 0.70–0.90, 1.21–1.42; ^{13}C NMR (δ in CDCl$_3$) –4.56, –4.38, 14.13, 22.64, 24.55, 31.61, 33.10, 114.50, 114.56.)

Thermal Polymerization of 1d. Compound **1d** (476 mg, 1.21 mmol) was heated in a sealed tube at 230 °C for 24 h. The product was reprecipitated twice from methanol–benzene and dried under reduced pressure to give 160 mg (34% yield) of **2d** (M_w = 183 000, M_w/M_n = 4.0), in addition to a 46% yield of the starting compound **1d**. For **2d**: ^{1}H NMR (δ in CDCl$_3$) 0.72–0.78 (8H, m, EtSi), 1.02–1.08 (12H, m, EtSi); ^{13}C NMR (δ in CDCl$_3$) 4.84, 8.29 (EtSi), 113.9 (C≡C). (Lit:[5b] M_w = 72 800; ^{1}H NMR (δ in CDCl$_3$) 0.72–0.77, 1.04–1.07; ^{13}C NMR (δ in CDCl$_3$) 4.86, 8.29, 113.9.)

Thermal Polymerization of 1e. Compound **1e** (543 mg, 0.88 mmol) was heated in a sealed tube at 260 °C for 24 h. The resulting oily product was washed twice with ethanol and dried under reduced pressure to give 113 mg (21% yield) of **2e** (M_w = 24 000, M_w/M_n = 2.1), in addition to a 74% yield of the starting compound **1e**. For **2e**: IR 2958, 2925, 2872, 1464, 1081, 785 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.65–1.39 (36H, m, *n*-BuSi); ^{13}C NMR (δ in CDCl$_3$) 12.72, 13.75, 26.47, 26.97 (*n*-BuSi), 114.50 (C≡C). Anal. Calcd for $(C_{18}H_{36}Si_2)_n$: C, 70.04; H, 11.76. Found: C, 69.85; H, 11.75. (Lit:[6] M_w = 10 700; ^{1}H NMR (δ in CDCl$_3$) 0.60–0.78, 0.78–0.95, 1.20–1.51; ^{13}C NMR (δ in CDCl$_3$) 12.77, 13.60, 26.57, 27.02, 114.54.)

Radical-Induced Polymerization of 1a. Into a 1.0- × 20-cm glass tube was placed a mixture of 0.098 g (0.19 mmol) of **1a** and 0.009 mmol (5 mol %) of di-*tert*-butyl peroxide in 0.5 mL of benzene. The glass tube was sealed under reduced pressure and heated at 150 °C for 5 h. The resulting solid was reprecipitated twice from benzene–methanol and dried under reduced pressure to give 0.059 g (60% yield) of **2a** (M_w = 25 000, M_w/M_n = 1.7), in addition to a 13% yield of the starting compound **1a**.

Radical-Induced Polymerization of 1b. A mixture of 0.165 g (0.37 mmol) of **1b** and 0.02 mmol (5 mol %) of di-*tert*-butyl peroxide in 0.3 mL of benzene was heated in a sealed tube at 180 °C for 8 h. The resulting oily product was washed twice with ethanol and dried under reduced pressure to give 0.027 g (16% yield) of **2b** (M_w = 28 000, M_w/M_n = 1.9), in addition to a 77% yield of the starting compound **1b**.

Radical-Induced Polymerization of 1d. A mixture of 0.243 g (0.62 mmol) of **1d** and 0.04 mmol (7 mol %) of di-*tert*-butyl peroxide in 0.3 mL of benzene was heated in a sealed tube at 150 °C for 5 h. The resulting solid was reprecipitated from benzene–methanol and dried under reduced pressure to give 0.153 g (63% yield) of **2d** (M_w = 159 000, M_w/M_n = 8.8), in addition to a 26% yield of the starting compound **1d**.

Radical-Induced Polymerization of 1e. A mixture of 0.324 g (0.53 mmol) of **1e** and 0.05 mmol (9 mol %) of di-*tert*-butyl peroxide in 0.5 mL of benzene was heated in a sealed tube at 180 °C for 5 h. The resulting oily product was washed twice with ethanol and dried under reduced pressure to give 0.015 g (5% yield) of **2e** (M_w = 7000, M_w/M_n = 1.6), in addition to an 89% yield of the starting compound **1e**.

Radical-Induced Polymerization of 1a in the Presence of Hydrosilane. Into a 1.0- × 20-cm glass tube was placed a mixture of 0.605 g (1.15 mmol) of **1a**, 0.06 mmol (5 mol %) of di-*tert*-butyl peroxide, and 0.17 mmol (12 mol %) of methyldiphenylsilane in 0.5 mL of benzene. The mixture was heated at 150 °C for 5 h. The product was reprecipitated twice from methanol–benzene and then dried under reduced pressure to give 0.507 g (84% yield) of **2a** (M_w = 19 000, M_w/M_n = 2.2), in addition to a 6% yield of the starting compound **1a**.

Radical-Induced Polymerization of 1b in the Presence of Hydrosilane. A mixture of 0.273 g (0.61 mmol) of **1b**, 0.04 mmol (7 mol %) of di-*tert*-butyl peroxide, and 0.21 mmol (34 mol %) of methyldiphenylsilane in 0.5 mL of benzene was heated in a sealed tube at 180 °C for 8 h. The oily product was washed twice with ethanol and dried under reduced pressure to give 0.069 g (25% yield) of **2b** (M_w = 13 000, M_w/M_n = 2.5), in addition to a 72% yield of the starting compound **1b**.

Radical-Induced Polymerization of 1d in the Presence of Hydrosilane. A mixture of 0.478 g (1.22 mmol) of **1d**, 0.06 mmol (5 mol %) of di-*tert*-butyl peroxide, and 0.15 mmol (12 mol %) of methyldiphenylsilane in 0.3 mL of benzene was heated in a sealed tube at 150 °C for 5 h. The product was reprecipitated twice from methanol–benzene and then dried under reduced pressure to give 0.391 g (82% yield) of **2d** (M_w = 96 000, M_w/M_n = 7.9).

Reaction of 2c with DTBP in the Presence of Hydrosilane. A mixture of 71 mg (0.25 mmol) of **2c** (M_w = 64 000, M_w/M_n = 1.9), 0.02 mmol (9 mol %) of di-*tert*-butyl peroxide, and 0.10 mmol (38 mol %) of methyldiphenylsilane in 0.5 mL of benzene was heated in a sealed tube at 150 °C for 5 h. GPC analysis showed that all starting polymer **2c** was transformed into a polymer with a molecular weight of M_w = 9700 (M_w/M_n = 2.2).

Reaction of 2d with DTBP in the Presence of Hydrosilane. A mixture of 159 mg (0.81 mmol) of **2d** (M_w = 157 000, M_w/M_n = 3.6), 0.05 mmol (6 mol %) of di-*tert*-butyl peroxide, and 0.15 mmol (19 mol %) of methyldiphenylsilane in 0.5 mL of benzene was heated in a sealed tube at 150 °C for 5 h to give a polymer with a molecular weight of M_w = 12 000 (M_w/M_n = 2.2).

Reaction of 2d with DTBP. A mixture of 16.6 mg (0.085 mmol) of **2d** (M_w = 157 000, M_w/M_n = 3.6) and 0.006 mmol (7 mol %) of di-*tert*-butyl peroxide in 0.3 mL of benzene was heated in a sealed tube at 150 °C for 5 h to give a polymer with a molecular weight of M_w = 81 000 (M_w/M_n = 5.3).

Reaction of 4 with 1 Equiv of DTBP in the Presence of Methyldiphenylsilane. A mixture of 0.364 g (0.89 mmol) of **4**, 0.94 mmol (1.1 equiv) of di-*tert*-butyl peroxide, and 3.13 mmol (3.5 equiv) of methyldiphenylsilane was heated in a sealed tube at 120 °C for 20 h. GLC analysis of the reaction mixture indicated the presence of **5**–**7** in 20, 21, and 43% yields, in addition to 24% of the starting compound **4**. Products **5** and **6** were isolated by MPLC. Product **7** was isolated by GLC. For **5**: IR 3049, 2954, 2099 (C≡C), 1429, 1246, 1115, 860, 836, 799 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.16 (9H, s, Me$_3$Si), 0.52 (3H, s, MeSi), 0.73 (3H, s, MeSi), 7.34–7.72 (15H, m, phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) –4.40 (MeSi), –2.51 (Me$_3$Si), 0.73 (MeSi), 113.95, 114.75 (C≡C), 127.89, 128.91, 129.63, 134.16, 134.52, 135.27, 135.42 (phenyl ring carbons). Anal. Calcd for $C_{25}H_{30}Si_3$: C, 72.38; H, 7.30. Found: C, 72.38; H, 7.16. For **6**: IR 3069, 3021, 2962, 1428, 1254, 1111, 805 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.75 (6H, s, MeSi), 7.34–7.70 (20H, m, phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) –2.10 (MeSi), 113.71 (C≡C), 127.84, 127.94, 129.72, 134.54 (phenyl ring carbons). Anal. Calcd for $C_{28}H_{26}Si_2$: C, 80.32; H, 6.26. Found: C, 80.28; H, 6.21. For **7**: IR 2094 (Si—H); ^{1}H NMR (δ in CDCl$_3$) 0.13 (9H, s, Me$_3$Si), 0.40, 0.42 (3H, s, MeSi), 4.21–4.25 (1H, q, SiH), 7.31–7.50 (5H, m, phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) –8.20, –7.98 (MeSi), –1.95, –1.79 (Me$_3$Si), 127.71, 128.02, 128.43, 128.73, 134.52, 134.79, 136.00 (phenyl ring carbons). Exact mass calcd for $C_{10}H_{18}Si_2$: 194.0974. Found: 194.0953.

Reaction of 1d with 0.57 Equiv of DTBP in the Presence of Dimethylphenylsilane. A mixture of 0.165 g (0.42 mmol) of **1d**, 0.24 mmol (0.57 equiv) of di-*tert*-butyl peroxide, and 1.41 mmol (3.4 equiv) of dimethylphenylsilane was heated in a sealed tube at 120 °C for 20 h. GPC analysis of the reaction mixture showed trimodal molecular weight distribution. No starting compound **1d** was detected in the reaction mixture by GLC analysis. The resulting oily product was reprecipitated twice from methanol–benzene to give oligomer **3** that has the highest molecular weight distribution in 38% yield: M_w = 3000 (M_w/M_n = 1.3); IR 2084 cm^{-1} (Si—H); ^{1}H NMR (δ in CDCl$_3$) 0.40 (MeSi), 0.72–1.10 (EtSi), 3.49, 3.55–3.61 (HSi), 7.34–7.65 (phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) 1.98 (MeSi), 4.85, 8.29 (EtSi), 113.86 (C≡C), 127.60, 129.25, 133.69, 134.18 (phenyl ring carbons), and signals with low intensities at 4.71, 5.26, 9.80, 114.30; ^{29}Si NMR (δ in CDCl$_3$) –30.77, and signals with low intensities at –27.11, –28.95, –30.16.

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