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Polymeric Organosilicon Systems. 25. Preparation of Branched Polymers by Regiospecific Hydrosilylation of Poly[(silylene)diethynylenes] and Their Properties

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Regiospecific 1,2-hydrosilylation reactions of (dimethylsilylene)-, (methylphenylsilylene)-, and (diethylsilylene)diethynylene polymers with 1,4-bis(methylphenylsilyl)benzene in the presence of a catalytic amount of $Rh_6(CO)_{16}$ afforded the respective branched polymers with high molecular weights in high yields. The rate of the hydrosilylation and degree of branching were found to be affected by polarity of the solvent, amounts of the catalyst, reaction temperature, and concentration of the polymers. It was found that degradation of the resulting branched polymers and also starting polymers readily took place when they were treated with ethanol in the presence of triphenylphosphine. The reaction of poly[(tetramethyldisilanylene)diethynylene] with hydrosilanes in the presence of the rhodium(0) catalyst proceeded to give hydrosilylation products, but scission of the polymer chain was also observed. A mechanism for the degradation of polymers is discussed on the basis of the results obtained for model compounds.

Introduction

The alternating polymers composed of a silylene or disilanylene unit and π-electron system are of considerable interest because of their potential application in the areas of ceramic precursors,[1,2] photoresists,[3,4] and conducting materials.[5−7] Many papers concerning the synthesis and properties of these polymers have been published to date.[8] However, little interest has been shown in the synthesis of branched polymers that have an alternating arrangement of a silylene unit and π-electron system.

Recently, we have found that the regiospecific addition of 1,4-bis(methylphenylsilyl)benzene to poly[(silylene)diethynylenes][7,9,10] can be achieved with the use of a $Rh_6(CO)_{16}$ catalyst to give branched polymers composed of a silylene unit and enyne and phenylene π-systems.[11] Tanaka et al. have also reported that the reaction of poly[(methylphenylsilylene)diethynylenes] with 1,2,4,5-tetrakis(dimethylsilyl)benzene in the presence of a $Pt(CH_2{=}CH_2)(PMe_3)_2$ catalyst affords the polymer that has a cross-linked structure.[12] In this paper we report the results of a detailed study on the reactions of poly[(silylene)diethynylenes] with 1,4-bis(methylphenylsilyl)benzene in the presence of a catalytic amount of $Rh_6(CO)_{16}$. We also report depolymerization of the starting poly[(silylene)diethynylenes] and the branched polymers in the presence of a catalytic amount of triphenylphosphine in ethanol−benzene.

Results and Discussion

Hydrosilylation of Poly[(silylene)diethynylenes]. The starting poly[(dimethylsilylene)diethynylene] (**1a**), poly[(methylphenylsilylene)diethynylene] (**1b**), and poly[(diethylsilylene)diethynylene] (**1c**) were synthesized by the reaction of 1,4-dilithio-1,3-butadiyne obtained from hexachloro-1,3-butadiene and *n*-butyllithium, with the corresponding dichlorosilanes as shown in Scheme 1.[10]

We first investigated the reaction of polymer **1a**[7b,10] with triethylsilane in the presence of various catalysts, in order to find an effective catalyst for selective 1,2-hydrosilylation. The reaction of **1a** with 4 equiv of Et_3SiH in the presence of a catalytic amount of chloroplatinic acid at 50 °C for 36 h afforded the hydrosilylation product, but a depolymerization reaction also took place to give the product with a molecular weight lower than that of the starting polymer **1a**. The reaction with a

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(1) Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci. Part A, Polym. Chem. Ed.* **1990**, *28*, 955.

(2) Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Alain, J.; Mutin, P. H. *Organometallics* **1992**, *11*, 2507.

(3) Ishikawa, M.; Nate, K. *Inorganic and Organometallic Polymers*; Zerdin, M.; Wynne, K. J.; Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 16.

(4) Nate, K.; Inoue, T.; Sugiyama, H.; Ishikawa, M. *J. Appl. Polym. Sci.* **1987**, *34*, 2445.

(5) (a) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604. (b) Ohshita, J.; Matsuguchi, A.; Furumori, K.; Hong, R.-F.; Ishikawa, M.; Yamanaka, T.; Koike, T.; Shioya, J. *Macromolecules* **1992**, *25*, 2134.

(6) Barton, T. J.; Ijadi-Maghsoodi, S.; Pang, Y. *Macromolecules* **1991**, *24*, 1257.

(7) (a) Chicart, P.; Corriu, R. J. P.; Moreau, J. J. E.; Garnier, F.; Yassar, A. *Chem. Mater.* **1991**, *3*, 8. (b) Brefort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, T.; Garnier, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500.

(8) For example: (a) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106. (b) Hu, S.; Weber, W. P. *Polym. Bull.* **1989**, *22*, 133. (c) Iwahara, M.; Hayase, S. H.; West, R. *Macromolecules* **1990**, *23*, 1298. (d) Tanaka, K.; Nakajima, K.; Okada, M.; Yamabe, T.; Ishikawa, M. *Organometallics* **1991**, *10*, 2679. (e) Kotani, S.; Shiina, K.; Sonogashira, K. *Appl. Organomet. Chem.* **1991**, *5*, 417.

(9) Ishikawa, M.; Hasegawa, Y.; Kunai, A. *J. Organomet. Chem.* **1990**, *381*, C57.

(10) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485.

(11) Ishikawa, M.; Toyoda, E.; Horio, T.; Kunai, A. *Organometallics* **1994**, *13*, 26.

(12) Uchimaru, Y.; Brandl, P.; Tanaka, M.; Goto, M. *39th Symposium on Organometallic Chemistry*; Tokyo, Japan, Oct 23−24, 1992; Division of Organometallilc Chemistry; Kinki Chemical Society: Osaka, Japan, 1992; Abstracts pp 76−78.

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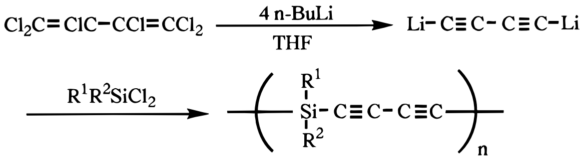
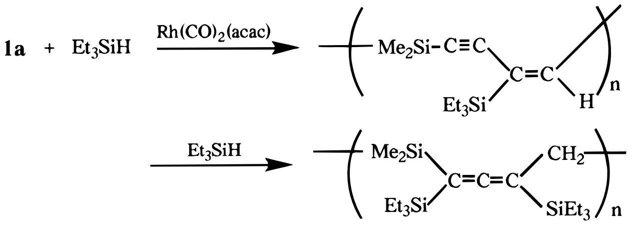
Scheme 1

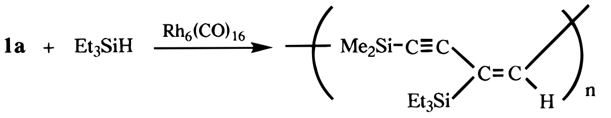


1a, R^1=R^2=Me
1b, R^1=Ph, R^2=Me
1c, R^1=R^2=Et

Scheme 2

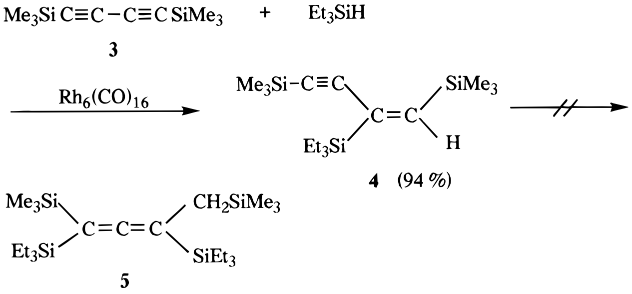


Scheme 3

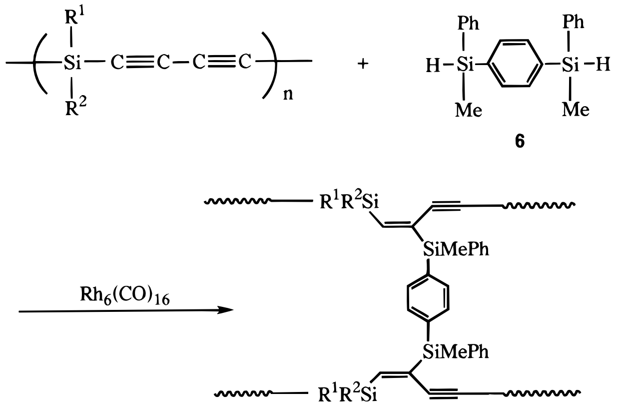


2a

Scheme 4



Scheme 5



7a, R^1=R^2=Me
7b, R^1=Ph, R^2=Me
7c, R^1=R^2=Et

$RhCl(PPh_3)_3$ catalyst under the same conditions gave a product only in low yield, while a $Rh(CO)_2(acac)$ catalyst readily afforded a hydrosilylation product. However, the IR spectrum of the resulting polymer indicates strong absorptions at 2129 and 1875 cm^{-1}, due to enyne and allenic bonds, respectively.[13] Its ^{13}C NMR spectrum shows resonances at 69−71, 74−75, and 209−210 ppm, attributed to terminal allenic carbons and internal allenic carbon, and resonances at 100−104, 108−109, 143−145, and 153−158 ppm, due to enyne carbons. The presence of the allenic bond clearly indicates that the reaction involves 1,4-addition of Et_3SiH into the initially formed enyne structure (Scheme 2).

We found that a $Rh_6(CO)_{16}$ catalyst[14] gives a 1,2-adduct with high regiospecificity. Thus, the reaction of **1a** with 4 equiv of Et_3SiH in the presence of $Rh_6(CO)_{16}$ at 40 °C for 24 h produced the only monohydrosilylation product, poly[(dimethylsilylene)[2-(triethylsilyl)but-1-en-3-yne-1,4-diyl]] (**2a**; Scheme 3). No allenic structure was detected in the polymer backbone by IR and ^{13}C NMR spectroscopic analysis. A similar reaction of **1b** with triethylsilane afforded the corresponding monohydrosilylation product, poly[(methylphenylsilylene)[2-(triethylsilyl)but-1-en-3-yne-1,4-diyl]] (**2b**).

In order to learn the location of a triethylsilyl group in an enyne group in the polymer backbone, we carried out the hydrosilylation of a model compound, 1,4-bis(trimethylsilyl)butadiyne (**3**), in the presence of the $Rh_6(CO)_{16}$ catalyst. Thus, the reaction of **3** with 5 equiv of triethylsilane in the presence of 0.9 mol % of $Rh_6(CO)_{16}$ in benzene at 70 °C for 10 min proceeded cleanly to give 2-(triethylsilyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (**4**) in 94% yield, with high regiospecificity (Scheme 4). No allenic compound was found in the reaction mixture, even after 11 h of reaction. In contrast to this, the reaction of **3** with triethylsilane in the presence of $Rh(CO)_2(acac)$ at 60 °C for 16 h produced a mixture of **4** and 1,3-bis(triethylsilyl)-1,4-bis(trimethylsilyl)buta-1,2-diene (**5**) in 67% and 6% yields, respectively. The similar reaction of **3** with triethylsilane in the presence of a $RhCl(PPh_3)_3$ catalyst at 80 °C for 48 h afforded **5** in 68% yield, in addition to a 13% yield of **4**.[13] On the basis of the results obtained from the hydrosilylation of **3** in the presence of the $Rh_6(CO)_{16}$ catalyst, the triethylsilyl group in polymer **2** is probably located at the C-2 position of an enyne group.

Next, we examined the reaction of poly[(silylene)diethynylenes] with 1,4-bis(methylphenylsilyl)benzene (**6**) using the $Rh_6(CO)_{16}$ catalyst in the hope of obtaining soluble branched polymers that have the alternating arrangement of a silylene unit and phenylene and enyne units as π-electron systems. Thus, the reaction of **1a** with M_w = 8300 with 0.3 equiv of **6** in the presence of 0.5 mol % of the $Rh_6(CO)_{16}$ catalyst in benzene at 80 °C for 9 h gave soluble polymer **7a**, whose molecular weight was determined to be M_w = 250 000 in 49 wt % yield, after reprecipitation of the resulting polymer from ethanol−benzene (Scheme 5).

Poly[(methylphenylsilylene)diethynylene] (**1b**) and poly[(diethylsilylene)diethynylene] (**1c**) also react with **6** in the presence of a catalytic amount of $Rh_6(CO)_{16}$ in a benzene or THF solution to give branched polymers **7b** and **7c** in high yields, respectively. Thus, the reaction of **1b** (M_w = 7800) with 0.5 equiv of **6** in the presence of 0.5 mol % of the rhodium(0) catalyst in benzene at 80 °C for 8 h afforded product **7b** with a high

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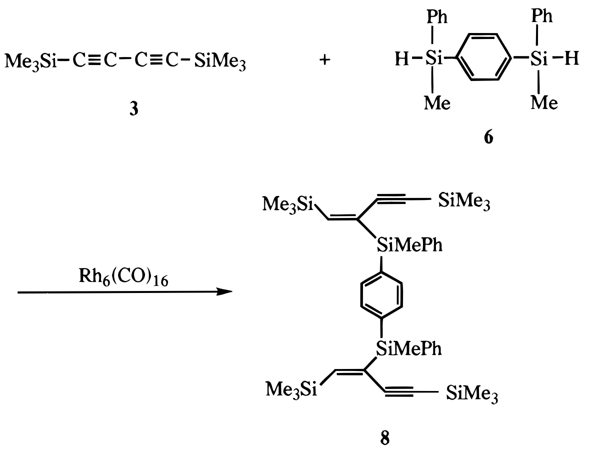
[13] The hydrosilylation of **3** with triethylsilane in the presence of $RhCl(PPh_3)_3$ or $Pt(PPh_3)_4$ has been reported to produce a mixture of enyne and allene derivatives; see: Kusumoto, T.; Hiyama, T. *Chem. Lett.* **1985**, 1405.

[14] James, B. R.; Rempel, G. L.; Teo, W. K. *Inorg. Synth.* **1976**, *16*, 49.

Scheme 6



molecular weight ($M_w = 939\,000$) in 70% yield, after reprecipitation of a crude polymer from ethanol−benzene. The similar reaction of **1c** ($M_w = 6000$) with 0.42 equiv of **6** in the presence of 0.6 mol % of $Rh_6(CO)_{16}$ in a benzene solution at 80 °C afforded polymer **7c** with a molecular weight of $M_w = 424\,000$ in 79% yield, after 21 h of reaction.

IR and ^1H and ^{13}C NMR spectra of polymers **7a**−**c** clearly indicate the presence of enyne, diyne, and phenylene groups, but not allenic bonds, in the polymer backbone. ^1H NMR spectra for **7a** and **7b** reveal a very weak resonance at 4.9 ppm due to an Si−H group, while polymer **7c** shows no resonance attributed to the Si−H proton. Polymers **7a**−**c** reveal very broad molecular weight distribution, and their UV spectra show broad absorptions tailing into 350 nm.[15] Polymers **7a**−**c** do not melt but are soluble in common organic solvents such as ethers, benzene, and chloroform.

In order to get more information about the structure of the branched polymers, we carried out the hydrosilylation reaction of **3** with the bis(silyl)benzene species **6**. Thus, treatment of **3** with 0.4 equiv of **6** in the presence of $Rh_6(CO)_{16}$ in benzene at 80 °C for 1 h produced (*E*)-1,4-bis[methylphenyl[1,4-bis(trimethylsilyl)but-1-en-3-yn-2-yl]silyl]benzene (**8**) in 92% yield as the sole product, indicating that Si−H adds across the triple bond in a cis fashion (Scheme 6). It seems likely that the reaction of **1a**−**c** with **6** proceeds in the same fashion as that of the model reaction. Consequently, the resulting branched polymers **7a**−**c** should have a partial structure similar to that of **8**.

In order to confirm this assumption, we prepared polymer **7c** with a relatively low molecular weight by the reaction of **1c** with 0.3 equiv of **6** and analyzed the resulting polymer **7c** ($M_w = 22\,500$, $M_w/M_n = 2.8$) by ^1H and ^{29}Si NMR. In the ^1H NMR spectra, the relative intensity of alkyl, hydrosilyl, vinyl, and phenyl protons is observed to be 1.0:0.01:0.04:0.34, which indicates that 0.29 equiv of hydrosilane **6** per original polymer unit reacts to give the cross-linked polymer.[16] It is also suggested that most of the bis(silyl) groups in **6** bridge across the main chain, but some remain as free Si−H.

In the ^{29}Si NMR spectra, the starting **1c** and **6** reveal a single resonance at −28.7 and −17.4 ppm, respectively, while polymer **7c** shows four resonances at −28.6 (br), −21.9, −17.7, and −11.0 (br) ppm. Of these, the broad signal at δ −28.6 is undoubtedly due to the $(C{\equiv}C)_2Et_2Si(C{\equiv}C)_2$ unit remaining in the polymer backbone and also due to a $(C{\equiv}C)_2Et_2\mathit{Si}C{\equiv}CC(Si){=}CH$ unit formed, while the signal at δ −17.7 may be ascribed to a residual hydrosilyl group. The signals at δ −21.9 and −11.0 can be assigned to a $(C{\equiv}C)_2Et_2SiCH{=}C{<}$ unit and a bridging −MePhSi− group, respectively, by comparing the chemical shifts with those for related compounds and by considering substituent effects on the chemical shifts of silicon atoms.[17] For examples, the ^{29}Si NMR signals for **1c** and **3** appear at −28.7 and −16.0 ppm, while those for poly[(dimethylsilylene)vinylene],[18] dimethyldivinylsilane,[17] and trimethylvinylsilane[17] have been reported to be −15.4, −13.7, and −6.8 ppm, respectively. Model compound **8** also reveals resonances at −18.7 ($Me_3SiC{\equiv}C$), −12.3 (−MePhSi−), and −8.0 ppm ($Me_3SiCH{=}C{<}$).

When polymer **7c** was treated with triphenylphosphine in the presence of ethanol, the ^{29}Si NMR signal at δ −28.6 disappeared, owing to preferential degradation at the bis(diethynyl)silyl moiety (see later discussion), but the other signals remained unchanged. In the ^1H NMR spectrum, the ratio of signal intensities for alkyl protons vs phenyl protons decreased from 3:1 for starting **7c** to 2:1 for the resulting polymer, presumably because intensities of diethylsilyl protons decrease on the degradation of the bis(diethynyl)silyl moiety. These results are wholly consistent with the structure proposed for **7c**.

We investigated the solvent effect on the rate of the hydrosilylation of **1b** with **6** in the presence of the $Rh_6(CO)_{16}$ catalyst under various conditions and found that the polarity of the solvents markedly influences the rate of the hydrosilylation in this system. When **1b** with $M_w = 11\,000$ was treated with **6** in the presence of the Rh(0) catalyst in benzene at 80 °C, the molecular weight of hydrosilylation product **7b** increased rapidly with increasing reaction time. For example, the molecular weight of **7b** was determined to be $M_w = 519\,000$ after 8 h of reaction, and it increased up to $M_w = 2\,040\,000$ after 24 h of reaction. In THF, however, the rate of addition of **6** to the same polymer **1b** is rather slow. The hydrosilylation product **7b** with $M_w = 130\,000$ was obtained after 23 h of reaction under the same conditions. After 70 h of reaction, polymer **7b**, whose molecular weight was determined to be $M_w = 282\,000$, was produced.

The rate of the reaction was considerably accelerated by increasing the amount of the catalyst and also raising the reaction temperature. In the presence of 0.2 mol % of the catalyst, the reaction of **1b** ($M_w = 7800$) with **6** in benzene at 80 °C for 25 h afforded polymer **7b** with a molecular weight of $M_w = 24\,900$, while the same reaction in the presence of 0.5 mol % of the catalyst for 5 h produced **7b** with a molecular weight of $M_w =$

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(15) The synthesis and some properties of soluble polysilane branched polymers have been reported: (a) Bianconi, P. A.; Schilling, F. C.; Weidmann, T. W. *Macromolecules* **1989**, *22*, 1697. (b) Furukawa, K.; Fujino, M.; Matsumoto, N. *Macromolecules* **1990**, *23*, 3423.

(16) Elemental analysis of this polymer showed somewhat lower values than the theoretical values (see Experimental Section), presumably due to the formation of ceramics such as silicon carbide. For example, see: Kunai, A.; Toyoda, E.; Horata, K.; Ishikawa, M. *Organometallics* **1995**, *14*, 714.

(17) Scholl, R. L.; Maciel, G. E.; Musker, W. K. *J. Am. Chem. Soc.* **1972**, *94*, 6376.

(18) Pang, Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671.

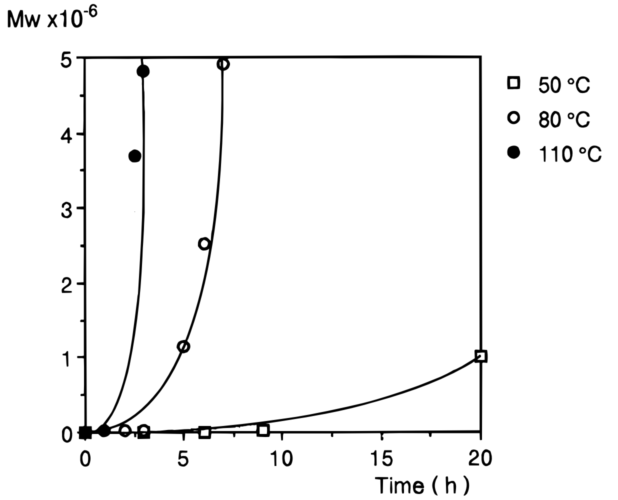


Figure 1. Plot of molecular weights of branched polymers produced at different reaction temperatures. Reactions were performed using a 0.2 M solution of **1b** and 0.3 equiv of **6** in the presence of 0.5 mol % of $Rh_6(CO)_{16}$ in benzene at 50 (□) and 80 °C (○), and in toluene at 110 °C (●).

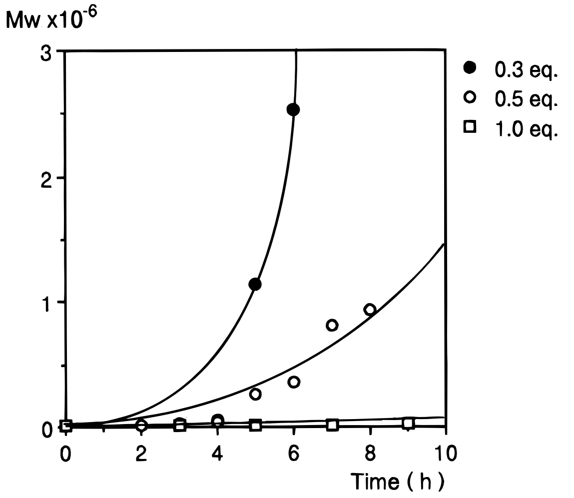


Figure 2. Plot of molecular weights of branched polymers produced with the use of different quantities of hydrosilanes. Reactions were performed using 0.2 M solutions of **1b** and 0.3 (●), 0.5 (○), and 1.0 equiv (□) of **6** in the presence of 0.5 mol % of $Rh_6(CO)_{16}$ in benzene at 80 °C.

1 136 000. Furthermore, the same reaction of **1b** with **6** in the presence of 1.0 mol % of the catalyst for 3 h produced **7b** with a molecular weight of 1 843 000. In the case of the reaction using 1.0 mol % of the catalyst, a GPC profile of the reaction mixture showed very broad molecular weight distribution, which goes up from M_w = 10 000 to over 1 900 000. The proportion of the polymer with a molecular weight higher than 1 000 000 to total polymer reached 30% after 5 h of reaction. After 7 h of reaction, however, insoluble polymers were formed in the reaction mixture.

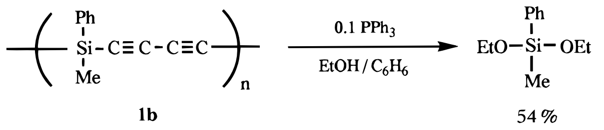
The hydrosilylation reaction was also accelerated by raising the reaction temperature as shown in Figure 1. Thus, treatment of polymer **1b** with $M_w = 7800$ with **6** in the presence of 0.5 mol % of $Rh_6(CO)_{16}$ in benzene at 50 °C for 20 h afforded **7b** with a molecular weight of M_w = 1 018 000, while the same reaction in refluxing toluene (110 °C) for 2.5 h produced **7b** with a molecular weight of M_w = 3 694 000. In this case, the proportion of the polymer with a molecular weight higher than 1 000 000 to the resulting branched polymer reached 48% after 4 h of reaction.

As expected, the hydrosilylation of **1b** with **6** proceeds rapidly in high concentration. The reaction of **1b** with $M_w = 7800$ with 0.3 equiv of **6** in the presence of 0.5 mol % of $Rh_6(CO)_{16}$ in a dilute benzene solution (0.05 M of **1b**) at 80 °C for 36 h produced **7b** with a molecular weight of $M_w = 9600$, while the same reaction of a solution involving a higher concentration of **1b** (0.3 M) for 3 h afforded the polymer with a molecular weight of M_w = 1 778 000. Furthermore, when a 0.5 M solution of **1b** was treated with 0.3 equiv of **6** under the same conditions, insoluble polymer was produced, and the molecular weight of the resulting branched polymer could not be determined.

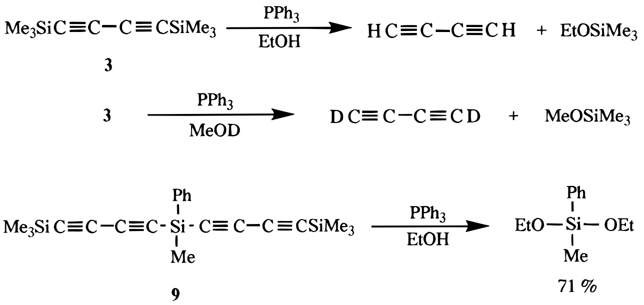
In contrast, the degree of the cross-linkage is suppressed when a high concentration of hydrosilane **6** is used. Thus, the reaction of **1b** with $M_w = 7800$ with 0.3 equiv of **6** in the presence of 0.5 mol % catalyst in benzene at 80 °C for 6 h afforded **7b** with a molecular weight of M_w = 2 533 000, while the same reaction of **1b** with 0.5 equiv of **6** for 6 h afforded **7b** with a molecular weight of M_w = 351 000. In these two cases, hydrosilane **6** used in the reaction was completely consumed. On the other hand, when the reaction of **1b** with $M_w = 7800$ was carried out using 1.0 equiv of **6**, the polymer with low molecular weight, M_w = 44 900, was obtained after 26 h of reaction (Figure 2). In this reaction, 11% of the hydrosilane was recovered unchanged. In ^{1}H NMR spectra of the polymers obtained from the reaction of high concentration of **6**, signals due to hydrosilyl protons were obviously observed at around 4.9 ppm. The result indicates that the rate of addition of an Si−H bond of **6** to the diyne moiety in **1b** is faster than that of the pendant Si−H bond in the polymer formed from hydrosilylation of **1b**. Presumably, at a high concentration of **6**, hydrosilylation of **1b** proceeds mostly with **6** to cause a significant decrease in quantity of the diyne units in the polymer chain, and this may prevent the cross-linking reaction between the diethynylene groups and the Si−H bonds of the polymer.

Degradation of Polymers. The branched polymers thus obtained become insoluble on standing for several days. This may be ascribed to the presence of a trace amount of the catalyst remaining in the polymers after reprecipitation. We attempted to deactivate this catalyst by chelating with a phosphine ligand. The reaction of **1b** ($M_w = 9000$) with **6** in the presence of 0.6 mol % of the Rh(0) catalyst in benzene at 80 °C for 44 h gave polymer **7b**, whose molecular weight was determined to be M_w = 869 000 by GPC. A small amount of triphenylphosphine was then added to the reaction mixture, and the mixture was stirred overnight at room temperature and filtered. Polymer **7b** was obtained in 72% yield after reprecipitation from ethanol. Surprisingly, it was found that the molecular weight of this polymer was much lower (M_w = 27 500) than that of the polymer obtained before treating with triphenylphosphine. The degradation of the polymer can be accelerated by addition of ethanol. Thus, when branched polymer **7b** with M_w = 1 467 300 was stirred with a small amount of PPh_3 in the presence of ethanol for 5 h, a degradation product whose molecular weight was determined to be M_w = 15 900 was produced. The IR spectrum of the resulting polymer still shows absorption bands due to an enyne unit, but absorptions attributed

Scheme 7



Scheme 8



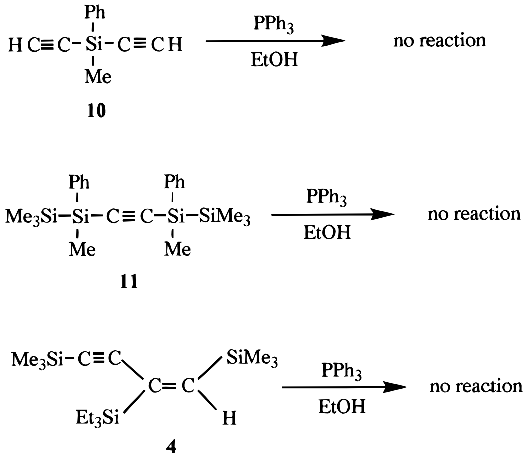
to a diyne unit almost disappeared, indicating that a C≡CC≡CSi bond in the polymer is cleaved by the action of the phosphine–ethanol mixture. The decrease in the molecular weight of the polymer by the action of the triphenylphosphine catalyst in the absence of ethanol may be ascribed to an O–H group which exists as a terminal group of the polymer.

We also examined the reaction of the starting linear polymers with PPh$_3$ under various conditions. When polymer **1b** (M_w = 8800) was treated with 1 equiv of PPh$_3$ in benzene at 80 °C for 10 h, an oligomer with a molecular weight of M_w = 3100 was produced. Treatment of **1b** (M_w = 8800) with 0.1 equiv of PPh$_3$ and 10 equiv of ethanol in benzene at 80 °C for 22 h afforded the oligomer with a molecular weight of M_w = 1300 in 57% yield, after reprecipitation from ethanol. Interestingly, diethoxymethylphenylsilane was isolated in 54% yield, by distillation of the solution used for reprecipitation of the polymer (Scheme 7). The reaction of polymer **1c** (M_w = 7400) in the presence of 0.1 equiv of PPh$_3$ and 20 equiv of ethanol at 80 °C for 30 h also gave a polymer with a molecular weight of M_w = 2000. On the other hand, heating **1b** in the presence of ethanol in benzene produced no degradation product, but the starting polymer was recovered unchanged, indicating that the presence of triphenylphosphine is necessary for the degradation.

Poly[(1,2-dimethyl-1,2-diphenyldisilanylene)diethynylene] (M_w = 7200) also underwent depolymerization under similar conditions, but the rate of the reaction was found to be slower than that for **1b**. In this reaction, the polymer with a molecular weight M_w = 4900 was obtained after 30 h of reaction. Such degradation is limited only to the polymers bearing a diethynylene moiety. The polymers poly[(1,2-dimethyl-1,2-diphenyldisilanylene)ethynylene], poly[(tetraethyldisilanylene)ethynylene], and poly[(1,2-dimethyl-1,2-diphenyldisilanylene)butenyne-1,4-diyl], which have no diethynylene group in the polymer backbone, afforded no degradation products when the polymers were treated with 1 equiv of PPh$_3$ in the presence of an excess of ethanol in refluxing benzene.

In order to obtain more information about the degradation reaction of the polymers, we examined the reaction with the use of model compounds (Scheme 8). When 1,4-bis(trimethylsilyl)buta-1,3-diyne (**3**) was treated with 0.1 equiv of PPh$_3$ in the presence of 16 equiv of ethanol in benzene at 80 °C, compound **3** completely disappeared within 3 h. In the resulting volatile products, ethoxytrimethylsilane and butadiyne were detected by GC–MS and GC–HRMS analyses. When MeOD was used in this reaction, dideuteriobutadiyne was detected by GC–HRMS analysis.[19]

Scheme 9



Similar reaction of methylphenylbis[(trimethylsilyl)-butadiynyl]silane (**9**) under similar conditions for 3 h afforded diethoxymethylphenylsilane in 71% yield as the main product (Scheme 8). However, treatment of **3** with ethanol alone, or triphenylphosphine alone in refluxing benzene gave no products, but the starting compound **3** was recovered quantitatively. In contrast, compounds bearing no diyne unit, such as diethynylmethylphenylsilane (**10**), bis(1-phenyltetramethyldisilanyl)acetylene (**11**), and 2-(triethylsilyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (**4**) did not react with PPh$_3$ in the presence of a large excess of alcohol under similar conditions, but the starting compounds were recovered unchanged (Scheme 9).

Reaction of Disilanylene Polymers. The hydrosilylation of poly[(tetramethyldisilanylene)diethynylene] (**13**) with **6** was also investigated. The starting polymer **13** was synthesized by the reaction of 1,4-dilithio-1,3-butadiyne with 1,2-dichlorotetramethyldisilane in a manner similar to that described above. When the hydrosilylation of **13** (M_w = 4300, M_w/M_n = 4.6) with 0.2 equiv of **6** in the presence of 0.4 mol % of Rh$_6$(CO)$_{16}$ in benzene at 80 °C was carried out and molecular weight changes of the polymer were followed by GPC, the molecular weight of the polymer increased gradually with increasing reaction time, though the rate of hydrosilylation was slower than that of **1a**–**c**. After 21 h of reaction, the IR spectrum of the resulting polymer clearly showed the existence of the enyne and diyne units. The polymer with a molecular weight of M_w = 87 200 was obtained in 55% yield after reprecipitation of the resulting product from ethanol. The strong absorptions due to a diyne group, which can be observed in the IR spectrum of the polymer obtained prior to the reprecipitation from ethanol, become weak after treatment with ethanol. Moreover, this polymer shows broad absorption bands attributed to a siloxy group. When polymer **13** with M_w = 9200 was treated with 5 equiv of triethylsilane in the presence of 0.6 mol % of the

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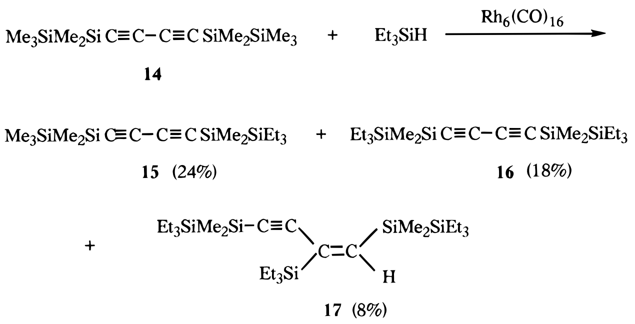
[19] (19) Base-induced decomposition of poly[(diphenylsilylene)diethynylene] using NaOD has been reported.[6]

Scheme 10



catalyst in refluxing benzene for 20 h, the polymer with a molecular weight of M_w = 13 900 was produced, while similar treatment of **13** with 1 equiv of methyldiphenylsilane and dimethylphenylsilane for 24 h afforded the respective polymers with molecular weights of 10 300 and 11 100.

In the hydrosilylation of **13**, the increase of the molecular weight is very small. Presumably, scission of a silicon−silicon or silicon−ethynyl bond occurs, in competition with the hydrosilylation reaction. In fact, scission of the silicon−silicon bond can be observed in the reaction of a model compound, 1,4-bis(pentamethyldisilanyl)butadiyne (**14**), with triethylsilane under the same conditions (see below). The reaction of **13** with bis(dimethylsilyl)benzene under similar conditions led to the formation of insoluble gel.

Treatment of **14** with triethylsilane in the presence of the rhodium(0) catalyst in benzene at 80 °C for 24 h gave 1-(pentamethyldisilanyl)-4-(triethyl-1,1-dimethyldisilanyl)butadiyne (**15**), 1,4-bis(triethyl-1,1-dimethyldisilanyl)butadiyne (**16**), and (*E*)-1,4-bis(triethyl-1,1-dimethyldisilanyl)-2-(triethylsilyl)but-1-en-3-yne (**17**) in 24%, 18%, and 8% yields, in addition to 16% of the unreacted starting compound **14** (Scheme 10).[20] Products **15**−**17** were isolated by preparative GLC and their structures were verified by spectrometric and elemental analysis.

A mechanism for scission of the silicon−silicon bond of compound **14** leading to products **15**−**17** probably involves a metathesis-type reaction between a silicon−silicon bond and a Si−Rh−H group. Although at present, evidence to support this mechanism has not yet been obtained, the metathesis reactions involving a silicon−silicon bond and a silicon−hydrogen bond in the presence of a transition-metal catalyst have been reported to date.[21] The hydrosilylation of polymer **13** probably involves this type of metathesis, in competition with addition of an Si−H bond across the carbon−carbon triple bond, leading to the increase of the molecular weight of the polymer. The metathesis between polymer **13** and triethylsilane obviously decreases the molecular weight of the product. Consequently, the molecular weight of the resulting polymer would be relatively low.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were determined on JEOL Model JNM EX-270 and Bruker AM-X-400 spectrometers. UV spectra were recorded on a Hitachi U-3210 spectrometer. Molecular weights of polymers were determined by gel-permeation chromatography using Shodex 806 and 804 as the column and using THF as the eluent, relative to polystyrene standards. Mass spectra were determined on a Shimadzu Model GCMS-QP 1000 instrument.

Materials. Benzene used as a solvent was dried over lithium aluminum hydride and distilled before use. Tetrahydrofuran (THF) was dried over sodium−benzophenone ketyl and distilled before use. Poly[(silylene)diethynylenes][10] (**1a**−**c**), poly[(tetramethyldisilanylene)diethynylene][9] (**13**), and 1,4-bis(trimethylsilyl)butadiyne[22] (**3**) were prepared as reported previously.

For **1a**: IR 2961, 2072 (C≡CC≡C), 1254 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.45 (s, SiMe); ^{13}C NMR (δ in CDCl$_3$) −0.63 (SiMe), 81.96, 88.91 (C≡C). For **1b**: IR 3071, 2959, 2073 (C≡CC≡C) cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.62 (s, 3H, SiMe), 7.41−7.67 (m, 5H, phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) −1.11 (SiMe), 80.98, 90.19 (C≡C), 128.31, 130.80, 134.09 (phenyl ring carbons); ^{29}Si NMR (δ in CDCl$_3$) −42.12. For **1c**: IR 2961, 2877, 2070 (C≡CC≡C) cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.73 (q, 4H, SiCH$_2$, J = 7.7 Hz), 1.04 (t, 6H, CH$_3$, J = 7.7 Hz); ^{13}C NMR (δ in CDCl$_3$) 5.82, 6.96 (Et), 80.20, 89.60 (C≡C); ^{29}Si NMR (δ in CDCl$_3$) −28.68. For **13**: IR 2960, 2898, 2063 (C≡CC≡C), 1865, 1402, 1250 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.32 (s, 12H, SiMe); ^{13}C NMR (δ in CDCl$_3$) −3.46 (SiMe), 84.14, 90.81 (C≡C); ^{29}Si NMR (δ in CDCl$_3$) −35.49. For **3**: ^{1}H NMR (δ in CDCl$_3$) 0.18 (s, 18H, SiMe); ^{13}C NMR (δ in CDCl$_3$) −0.54 (SiMe), 85.86, 88.02 (C≡C); ^{29}Si NMR (δ in CDCl$_3$) −16.0.

Preparation of 1,4-Bis(methylphenylsilyl)benzene (6). To a mixture of 46.3 g (0.32 mol) of chloromethylphenylsilane and 7.1 g (0.29 mol) of magnesium in 100 mL of THF was added dropwise a solution of 30.7 g (0.13 mol) of 1,4-dibromobenzene in 50 mL of THF at −20 °C over a period of 2 h, and the mixture was stirred overnight at room temperature. The resulting mixture was concentrated, and the magnesium salts were filtered and washed with hexane. The combined filtrate and washings were concentrated, and the residue was distilled under reduced pressure to give 19.0 g (46%) of 1,4-bis(methylphenylsilyl)benzene (**6**): bp 170−188 °C/4 mmHg; IR 3048, 3000, 2960, 2120 cm^{-1} (Si−H); ^{1}H NMR (δ in CDCl$_3$) 0.63 (d, 6H, MeSi, J = 3.7 Hz), 4.95 (q, 2H, SiH, J = 3.7 Hz), 7.28−7.63 (m, 14H, phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) −5.10 (MeSi), 128.0, 129.6, 134.2, 134.8 (phenyl carbons), 135.0, 136.8 (phenyl ipso carbons); ^{29}Si NMR (δ in CDCl$_3$) −17.41; mass m/z 318 (M$^+$), 303 (M$^+$ − CH$_3$). Anal. Calcd for $C_{20}H_{22}Si_2$: C, 75.41; H, 6.96. Found: C, 75.30; H, 6.96.

Preparation of Methylphenylbis[(trimethylsilyl)-butadiynyl]silane (9). A solution of 14.8 mmol of lithium diisopropylamide in 20 mL of ether was added to a solution of 1.91 g (15.6 mmol) of (trimethylsilyl)butadiyne in 50 mL of ether at −80 °C over a period of 10 min. The mixture was stirred at −50 °C for 40 min, and to this was added 1.12 g (5.87 mmol) of dichloromethylphenylsilane. The reaction mixture was stirred at room temperature for 1 h and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed, and the residue was passed through a short silica gel column with hexane as eluent. Recrystallization from ethanol gave 1.09 g (51%) of methylphenylbis[(trimethylsilyl)butadiynyl]silane (**9**) as colorless crystals: mp 55 °C; mass m/z 362 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.25 (s, 18H, Me$_3$Si), 0.49 (s, 3H, Ph*Me*Si), 7.42−7.43 (m, 3H, phenyl ring protons), 7.63−7.67 (m, 2H, phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) −1.33, −0.56 (MeSi), 83.74, 86.45, 88.07,

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[20] Besides these products, four compounds whose molecular weights were determined to be 426, 426, 468, and 468 by GC−mass spectrometric analysis were produced in 8%, 6%, 10%, and 7% yields.

[21] Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22 and references therein.

[22] Ballard, D. H.; Gilman, H. *J. Organomet. Chem.* **1968**, *15*, 321.

89.56 ($C{\equiv}C$), 127.96, 129.70, 133.64, 135.53 (phenyl ring carbons); ^{29}Si NMR (δ in $CDCl_3$) −42.71 (MePhSi<), −15.44 ($SiMe_3$); IR 3071, 2961, 2070 cm^{-1} ($C{\equiv}CC{\equiv}C$). Anal. Calcd for $C_{21}H_{26}Si_3$: C, 69.54; H, 7.23. Found: C, 69.53; H, 7.20.

Preparation of 1,4-Bis(pentamethyldisilanyl)butadiyne (14). A solution of 1.59 g (6.09 mmol) of hexachloro-1,3-butadiyne in 10 mL of THF was added to a solution of 25.0 mmol of *n*-butyllithium (1.6 M hexane solution) in 30 mL of THF at −20 °C over a period of 1 h. The mixture was stirred at −20 °C for 3 h, and to this was added 2.32 g (13.9 mmol) of chloropentamethyldisilane. The reaction mixture was stirred at room temperature for 2 h and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was recrystallized from ethanol to give 1.25 g (79% yield) of **14** as colorless crystals: mp 143 °C; mass m/z 310 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.13 (s, 18H, Me_3Si), 0.21 (s, 12H, Me_2Si); ^{13}C NMR (δ in $CDCl_3$) −3.43 (Me_2Si), 2.59 (Me_3Si), 85.21, 90.30 ($C{\equiv}C$); ^{29}Si NMR (δ in $CDCl_3$) −35.25 ($C{\equiv}CSiMe_2$−), −18.21 ($SiMe_3$); IR 2059 cm^{-1} ($\nu_{C\equiv C}$). Anal. Calcd for $C_{14}H_{30}Si_4$: C, 54.12; H, 9.73. Found: C, 53.92; H, 9.65.

Hydrosilylation of 1a with Triethylsilane in the Presence of a $Rh(CO)_2(acac)$ Catalyst. A solution of 102 mg (0.96 mmol) of **1a** (M_w = 8300, M_w/M_n = 1.7), 500 mg (4.31 mmol) of triethylsilane, and 7 mg (3.0 mol %) of $Rh(CO)_2(acac)$ in 0.3 mL of dry benzene was heated at 50 °C in a sealed tube for 36 h. After evaporation of the solvent, the residue was reprecipitated from methanol−benzene to give 157 mg of the hydrosilylated polymer (M_w = 11 000, M_w/M_n = 3.0): ^{1}H NMR (δ in $CDCl_3$) 0.1−0.9 (m, MeSi and Et_3Si), 0.9−1.3 (m, $-CH_2-$), 6.8−7.1 (m, vinyl protons); ^{13}C NMR (δ in $CDCl_3$) −2−9, 22−24 (MeSi and Et_3Si), 14−16 ($-CH_2-$), 69−71, 74−75 ($\mathit{C}{=}C{=}\mathit{C}$), 100−104, 108−109 ($-\mathit{C}{\equiv}\mathit{C}C{=}C-$), 143−145, 153−158 ($-C{\equiv}C\mathit{C}{=}\mathit{C}-$), 209−210 ($C{=}\mathit{C}{=}C$); IR 2129 ($\nu_{C\equiv CC=C}$), 1875 cm^{-1} ($\nu_{C=C=C}$).

Hydrosilylation of 1a with Triethylsilane in the Presence of a $Rh_6(CO)_{16}$ Catalyst. A solution of 188 mg (1.77 mmol) of **1a** (M_w = 8300, M_w/M_n = 1.7), 806 mg (6.93 mmol) of triethylsilane, and 2 mg (1.9 × 10^{-3} mmol, 0.1 mol %) of $Rh_6(CO)_{16}$ in 5 mL of dry THF was stirred at 40 °C for 24 h. After evaporation of the solvent, the residue was reprecipitated from methanol−benzene to give 191 mg (49% yield) of **2a** (M_w = 7200, M_w/M_n = 2.1): ^{1}H NMR (δ in $CDCl_3$) 0.2−0.4 (m, 6H, MeSi), 0.6−1.0 (m, 15H, Et_3Si), 6.5−6.7 (m, 1H, vinyl proton); ^{13}C NMR (δ in $CDCl_3$) −1.94, −1.05, −1.01, 0.27, 1.02 (MeSi), 2.71, 2.76, 2.78, 2.83, 7.23, 7.27 (EtSi), 99−101, 103−104, 107−108 ($-\mathit{C}{\equiv}\mathit{C}C{=}C-$), 142−144, 153−154, 155−157 ($-C{\equiv}C\mathit{C}{=}\mathit{C}-$); IR 2131 cm^{-1} ($C{\equiv}CC{=}C$).

Hydrosilylation of 1b with Triethylsilane in the Presence of a $Rh_6(CO)_{16}$ Catalyst. A solution of 223 mg (1.33 mmol) of **1b** (M_w = 7400, M_w/M_n = 2.9), 271 mg (2.33 mmol) of triethylsilane, and 7 mg (6.6 × 10^{-3} mmol, 0.5 mol %) of $Rh_6(CO)_{16}$ in 7 mL of dry benzene was stirred at 80 °C for 48 h. After evaporation of the solvent, the residue was reprecipitated from methanol−benzene to give 323 mg (85% yield) of **2b** (M_w = 6000, M_w/M_n = 2.2): ^{1}H NMR (δ in $CDCl_3$) 0.2−0.4 (m, 3H, MeSi), 0.6−1.0 (m, 15H, Et_3Si), 6.5−6.7 (m, 1H, vinyl proton), 7.2−7.9 (m, 5H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.36, −1.57, −0.20 (MeSi), 2.73, 2.76, 2.81, 7.29, 7.42, 7.57 (EtSi), 98−102, 103−104, 108−110 ($-\mathit{C}{\equiv}\mathit{C}C{=}C-$), 143−146, 151−154 ($-C{\equiv}C\mathit{C}{=}\mathit{C}-$); IR 2131 cm^{-1} ($C{\equiv}CC{=}C$).

Hydrosilylation of 3 with Triethylsilane in the Presence of a $Rh_6(CO)_{16}$ Catalyst. A solution of 167 mg (0.86 mmol) of **3**, 500 mg (4.31 mmol) of triethylsilane, and 8 mg (7.5 × 10^{-3} mmol, 0.9 mol %) of $Rh_6(CO)_{16}$ in 8 mL of dry benzene was stirred at 70 °C for 10 min. The resulting mixture was analyzed by GLC and found to contain **4** as the sole volatile product (94% GLC yield). Compound **4** was isolated by silica gel chromatography. All spectral data for **4** were identical with those described in the literature.[13]

Hydrosilylation of 3 with Triethylsilane in the Presence of a $Rh(CO)_2(acac)$ Catalyst. A solution of 300 mg (1.55 mmol) of **3**, 210 mg (1.81 mmol) of triethylsilane, and 3 mg (1.2 × 10^{-2} mmol, 1.0 mol %) of $Rh(CO)_2(acac)$ in 10 mL of dry benzene was stirred at 60 °C for 16 h. GLC analysis of the resulting mixture showed the existence of **4** and **5** in 67% and 6% yields, respectively. Compounds **4** and **5** were isolated in pure form by recycling GPC, and all spectral data for **4** and **5** were identical with those described in the literature.[13]

Hydrosilylation of 3 with Triethylsilane in the Presence of a $RhCl(PPh_3)_3$ Catalyst. A solution of 234 mg (1.21 mmol) of **3**, 450 mg (3.88 mmol) of triethylsilane, and 3 mg (3.6 × 10^{-3} mmol, 0.3 mol %) of $RhCl(PPh_3)_3$ in 2 mL of dry benzene was stirred at 80 °C for 48 h. GLC analysis of the resulting mixture showed the existence of **4** and **5** in 13% and 68% yields, respectively.

Hydrosilylation of 1a with 1,4-Bis(methylphenylsilyl)benzene (6) in the Presence of a $Rh_6(CO)_{16}$ Catalyst. A mixture of 81 mg (0.763 mmol) of **1a** (M_w = 8300, M_w/M_n = 1.7), 55 mg (0.23 mmol) of **6**, and 4 mg (3.8 × 10^{-3} mmol, 0.5 mol %) of $Rh_6(CO)_{16}$ in 4 mL of benzene was heated to 80 °C for 9 h. The solution was filtered to remove traces of insoluble materials and concentrated to one-third of its original volume under reduced pressure at room temperature, and then the resulting residue was poured into ca. 100 mL of ethanol to give 66 mg (49 wt % yield) of polymer **7a**: M_w = 250 000 (M_w/M_n = 28.7); ^{1}H NMR (δ in $CDCl_3$) 0.1−0.7 (m, MeSi), 4.9 (br s, HSi), 6.5−7.8 (m, vinyl and phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −0.57 (MeSi), 82.04, 88.99 ($-C{\equiv}CC{\equiv}C-$), 105−108 ($-\mathit{C}{\equiv}\mathit{C}C{=}C-$), 127.84, 129.57, 134.10, 134.55, 134.83, 135.16 (phenyl ring carbons), 140−144, 152−156 ($-C{\equiv}C\mathit{C}{=}\mathit{C}-$); IR 2132 ($C{\equiv}CC{=}C$ and HSi), 2072 cm^{-1} ($C{\equiv}CC{\equiv}C$).

Hydrosilylation of 1b with 6 in the Presence of a $Rh_6(CO)_{16}$ Catalyst. A solution of 136 mg (0.81 mmol) of **1b** (M_w = 7800, M_w/M_n = 2.5), 131 mg (0.41 mmol) of **6**, and 4 mg (3.8 × 10^{-3} mmol, 0.5 mol %) of $Rh_6(CO)_{16}$ in 4 mL of dry benzene was heated to 80 °C for 8 h. The solution was filtered to remove traces of insoluble materials and concentrated to one-third of its original volume under reduced pressure at room temperature, and then the resulting residue was poured into ca. 200 mL of ethanol to give polymer **7b**. Crude polymer **7b** was reprecipitated twice from ethanol−benzene to give 188 mg (70 wt % yield) of **7b**: M_w = 939 000 (M_w/M_n = 152); ^{1}H NMR (δ in $CDCl_3$) 0.1−1.0 (br m, MeSi), 4.9 (br s, HSi), 6.5−7.9 (m, vinyl and phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −5 to 0 (MeSi), 88−92 ($-C{\equiv}CC{\equiv}C-$), 107−110 ($-\mathit{C}{\equiv}\mathit{C}C{=}C-$), 127.72, 127.95, 129.52, 134.01, 134.54, 134.83, 135.15 (phenyl ring carbons), 140−144, 150−159 ($-C{\equiv}C\mathit{C}{=}\mathit{C}-$); IR 2130 ($C{\equiv}CC{=}C$ and HSi), 2071 cm^{-1} ($C{\equiv}CC{\equiv}C$).

Hydrosilylation of 1c with 6 in the Presence of a $Rh_6(CO)_{16}$ Catalyst. A solution of 197 mg (1.38 mmol) of **1c** (M_w = 6000, M_w/M_n = 2.1), 185 mg (0.581 mmol) of **6**, and 9 mg (8.4 × 10^{-3} mmol, 0.6 mol %) of $Rh_6(CO)_{16}$ in 5 mL of dry benzene was heated to 80 °C for 21 h. The solution was filtered to remove traces of insoluble materials and concentrated to one-third of its original volume under reduced pressure at room temperature, and then the resulting residue was poured into ca. 200 mL of ethanol to give polymer **7c**. Crude polymer **7c** was reprecipitated twice from ethanol−benzene to give 302 mg (79 wt % yield) of **7c**: M_w = 424 000 (M_w/M_n = 58.5); ^{1}H NMR (δ in $CDCl_3$) 0.0−1.5 (br m, MeSi and EtSi), 6.5−6.9 (br s, vinyl proton), 7.0−7.8 (br m, phenyl ring protons) (ratio of alkyl H/vinyl H/phenyl H = 1.0/0.02/0.36); ^{13}C NMR (δ in $CDCl_3$) −4.18 (MeSi), 3.78, 4.12, 4.28, 5.38, 6.47, 7.33, 7.55 (EtSi), 89−90 ($-C{\equiv}CC{\equiv}C-$), 98−104, 108−110 ($-\mathit{C}{\equiv}\mathit{C}C{=}C-$), 127.67, 129.54, 133.93, 134.34, 134.74, 135.09 (phenyl ring carbons), 140−144, 151−160 ($-C{\equiv}C\mathit{C}{=}\mathit{C}-$); IR 2133 ($C{\equiv}CC{=}C$), 2071 cm^{-1} ($C{\equiv}CC{\equiv}C$).

Effects of Reaction Conditions on the Hydrosilylation of 1b with 6. In a typical run, a 0.2 M solution of polymer

1b ($M_w = 7800$, $M_w/M_n = 2.5$) in benzene was treated with 0.3 equiv of **6** in the presence of 0.5 mol % of a $Rh_6(CO)_{16}$ catalyst at 80 °C, and changes in molecular weight of the resulting polymer **7b** were followed by GPC. Some of the results obtained by varying the amounts of the catalyst and **6**, reaction temperature, and concentration of **1b** are summarized in Figures 1 and 2. In the reaction with 0.2 mol % of the catalyst, molecular weights (M_w) of **7b** changed to 13 000 (5 h), 17 500 (10 h), 24 900 (25 h), and 692 000 (50 h). With 0.5 mol % of the catalyst, M_w became 28 100 (3 h), 1 136 000 (5 h), 2 533 000 (6 h), and 4 919 000 (7 h). With 1.0 mol % of the catalyst, M_w became 6700 (1 h), 14 100 (2 h), 1 843 000 (3 h), and 2 793 000 (4 h). At 50 °C, M_w became 1 018 000 (20 h). At 110 °C (in toluene), M_w became 3 694 000 (2.5 h). With 0.05 M of **1b**, M_w became 9600 (36 h). With 0.3 M of **1b**, M_w became 1 778 000 (3 h). With 0.5 equiv of **6**, M_w became 351 000 (6 h).

In all cases, the figure of polydispersity of **7b** went up very high as the value of M_w increased. For example, in the reaction with 0.1 M solution of **1b**, 0.3 equiv of **6**, and 0.5 mol % of $Rh_6(CO)_{16}$ in toluene at 110 °C, M_w (M_w/M_n) became 20 900 (2.8) after 3 h, 919 000 (118) after 4 h, 2 735 000 (211) after 7 h, and 3 917 000 (258) after 9 h.

Hydrosilylation of 3 with 6. A solution of 1.290 g (6.63 mmol) of **3**, 0.85 g (2.67 mmol) of **6**, and 23 mg (2.4×10^{-2} mmol, 0.4 mol %) of $Rh_6(CO)_{16}$ in 23 mL of benzene was stirred at 80 °C for 1 h. After evaporation of the solvent, the residue was passed through a short silica gel column using hexane as the eluent. Recrystallization from ethanol gave 1.73 g (92%) of **8** as colorless crystals: mp 98°C; mass *m/z* 706 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.00 (s, 18H, $Me_3SiC{\equiv}C$), 0.10 (s, 18H, $Me_3SiC{=}C$), 0.61 (s, 6H, MeSi), 6.58 (s, 2H, vinyl protons), 7.27−7.49 (m, 14H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.21 (MeSi), −0.94, −0.24 (Me_3Si), 104.89, 107.42 ($C{\equiv}C$), 127.69, 129.44, 134.34, 135.12, 135.23, 136.49 (phenyl ring carbons), 140.86, 159.97 ($C{=}C$); ^{29}Si NMR (δ in $CDCl_3$) −18.74 ($Me_3SiC{\equiv}C$), −12.30 (MePhSi), −7.97 ($Me_3SiCH{=}C<$); IR 2132 cm^{-1} ($C{\equiv}CC{=}C$). Anal. Calcd for $C_{40}H_{58}Si_6$: C, 67.92; H, 8.26. Found: C, 67.74; H, 8.26.

Degradation of Branched Polymer 7b in the Presence of Triphenylphosphine. A solution of 260 mg (1.55 mmol) of **1b** ($M_w = 9000$, $M_w/M_n = 2.6$), 210 mg (0.66 mmol) of **6**, and 10 mg (1.0×10^{-2} mmol, 0.6 mol %) of $Rh_6(CO)_{16}$ in 6 mL of dry benzene was stirred at 80 °C for 44 h. A small aliquot was taken from the resulting solution and analyzed by GPC. The results indicate that the branched polymer **7b** with a molecular weight of $M_w = 869\,000$ ($M_w/M_n = 142$) was produced. To the solution was added 200 mg (0.76 mmol) of triphenylphosphine, and the solution was stirred overnight at room temperature. After evaporation of the solvent, the residue was reprecipitated from ethanol−benzene to give 339 mg (72 wt % yield) of degradation product: $M_w = 27\,500$, $M_w/M_n = 7.2$; ^{1}H NMR (δ in $CDCl_3$) 0.1−1.0 (br m, MeSi), 1.24, 1.29 (br s, OCH_2CH_3), 1.62 (br s), 3.75 (br m, OCH_2CH_3), 4.85 (br s, HSi), 6.6−7.8 (br m, vinyl proton and phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −5.09, −4.35, −3−2 (MeSi), 14.08, 22.78 (CH_2 and CH_3), 128.01, 128.36, 129.57, 133.46, 134.06, 134.57, 134.86, 135.19 (phenyl ring carbons); IR 3046, 2960, 2131 ($C{\equiv}CC{=}C$), 2072 ($C{\equiv}CC{\equiv}C$), 1428, 1379 cm^{-1}.

A solution of 95 mg of branched polymer **7b** ($M_w = 1\,467\,300$, $M_w/M_n = 170$), 68 mg (0.259 mmol) of triphenylphosphine, and 153 mg (3.32 mmol) of ethanol in 5 mL of dry benzene was stirred at 80 °C for 5 h. Solvent was evaporated, and degradation product ($M_w = 15\,900$, $M_w/M_n = 2.2$) was isolated after reprecipitation from ethanol. IR and NMR spectra of this polymer were identical with those of the product described above.

Degradation of Linear Polymer 1b in the Presence of Triphenylphosphine and Ethanol. A solution of 1.01 g (5.98 mmol) of **1b** ($M_w = 8800$, $M_w/M_n = 3.0$), 165 mg (0.63 mmol) of triphenylphosphine, and 2.7 g (60 mmol) of ethanol in 15 mL of dry benzene was stirred at 80 °C for 22 h. The mixture was concentrated and reprecipitated from ethanol to gave 572 mg (57 wt % yield) of oligomer. Concentration of the mother liquor from reprecipitation, followed by Kugelrohr distillation (60 °C/4 mmHg) gave 0.68 g (54% yield) of diethoxymethylphenylsilane as a colorless liquid.

For the oligomer: $M_w = 1300$, $M_w/M_n = 1.6$; ^{1}H NMR (δ in $CDCl_3$) 0.53, 0.62 (br s, MeSi), 0.90, 1.28, 3.81 (br s, OEt), 7.30−7.65 (m, phenyl ring protons) (ratio of MeSi/EtO/phenyl H = 1.0/0.04/1.33); ^{13}C NMR (δ in $CDCl_3$) −1.09, −0.81, −0.61, −0.54, −0.38, −0.29, 0.29, 0.72, 0.88, 1.01 (MeSi), 13.39, 13.95, 14.05, 14.11, 18.08, 20.74, 22.30, 22.70, 22.77, 27.60, 29.36, 29.71, 31.93 (alkyl carbons), 59.80 (OCH_2), 80.97, 90.23 ($C{\equiv}C$), 127.66, 127.98, 128.01, 128.32, 130.49, 130.78, 133.35, 133.50, 133.85, 134.11 (phenyl ring carbons); ^{29}Si NMR (δ in $CDCl_3$) −33.40 (br), −30.63 (br), −25.31, −25.12, −21.73, −17.66, −15.94; IR 3289 ($C{\equiv}C\text{-}H$), 2958, 2868, 2134, 1068 cm^{-1} (Si−O).

For diethoxymethylphenylsilane: mass *m/z* 210 (M^+), 195 ($M^+ - CH_3$); ^{1}H NMR (δ in $CDCl_3$) 0.37 (s, 3H, MeSi), 1.25 (t, 6H, OCH_2CH_3, J = 7.1 Hz), 3.82 (q, 4H, OCH_2CH_3, J = 7.1 Hz), 7.38−7.40, 7.63−7.67 (m, 5H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.24 (MeSi), 18.28 (OCH_2CH_3), 58.46 (OCH_2CH_3), 127.76, 129.92, 133.96, 134.79 (phenyl ring carbons).

Reaction of 3 with Triphenylphosphine and Ethanol. A solution of 406 mg (2.09 mmol) of **3**, 54 mg (0.21 mmol) of triphenylphosphine, and 1.50 g (32.6 mmol) of ethanol in 5 mL of dry benzene was stirred at 80 °C for 3 h. Starting **3** was consumed completely, and ethoxytrimethylsilane and butadiyne were detected by GC−MS and GC−HRMS analyses, respectively. For butadiyne: HRMS calcd for C_4H_2 50.0157, found 50.0149.

Reaction of 3 with Triphenylphosphine and Methanol-*d*. A mixture of 76 mg (0.39 mmol) of **3**, 104 mg (0.40 mmol) of triphenylphosphine, and 810 mg (25.3 mmol) of methanol-*d* was stirred at 80 °C for 10 min. Starting **3** was consumed completely, and butadiyne-d_2 was detected by GC−HRMS analysis. For butadiyne-d_2: HRMS calcd for C_4D_2 52.0282, found 52.0191.

Reaction of 9 with Triphenylphosphine and Ethanol. A solution of 95 mg (0.26 mmol) of **9**, 71 mg (0.26 mmol) of triphenylphosphine, and 4.10 g (89 mmol) of ethanol in 5 mL of benzene was stirred at 80 °C for 3 h. GC−MS analysis of the resulting mixture showed the formation of diethoxymethylphenylsilane in 71% yield.

Hydrosilylation of 13 with 6. A mixture of 257 mg (1.56 mmol) of **13** ($M_w = 4300$, $M_w/M_n = 4.6$), 112 mg (0.352 mmol) of **6**, and 6 mg (5.6×10^{-3} mmol, 0.4 mol %) of $Rh_6(CO)_{16}$ in 2 mL of benzene was stirred at 80 °C for 21 h. The mixture was concentrated and reprecipitated from ethanol to give 203 mg (55% yield) of the hydrosilylated polymer ($M_w = 87\,200$, $M_w/M_n = 35$): ^{1}H NMR (δ in $CDCl_3$) 0.14 (br s, MeSi), 0.22 (br s, MeSi), 0.65 (br s, MeSi), 4.97 (br s, HSi), 6.1−6.6 (br, vinyl proton), 7.28−7.62 (br m, phenyl ring protons) (ratio of MeSi/SiH/vinyl H/phenyl H = 1.0/0.01/0.02/0.23); ^{13}C NMR (δ in $CDCl_3$) −5.09, −2.53, −0.98, −0.30, 1.03, 1.82 (MeSi), 84.10, 90.82 ($C{\equiv}CC{=}C$), 95−98, 106−109 ($C{\equiv}CC{=}C$), 127.94, 128.32, 129.51, 133.97, 134.33, 134.83, 134.83, 135.16 (phenyl ring carbons), 143−147, 153−160 ($C{\equiv}CC{=}C$); IR 2959, 2899, 2123 ($C{\equiv}CC{=}C$ and HSi), 1876, 1250, 1113 cm^{-1} (Si−O−Si).

Hydrosilylation of 13 with Triethylsilane. A mixture of 192 mg (1.17 mmol) of **13** ($M_w = 9200$, $M_w/M_n = 2.3$), 678 mg (5.83 mmol) of triethylsilane, and 8 mg (7.5×10^{-3} mmol, 0.6 mol %) of $Rh_6(CO)_{16}$ in 2 mL of benzene was stirred at 80 °C for 20 h. The mixture was concentrated and reprecipitated from methanol to gave 103 mg of hydrosilylated polymer ($M_w = 13\,900$, $M_w/M_n = 2.6$): ^{1}H NMR (δ in $CDCl_3$) 0.06, 0.17, 0.21, 0.23, 0.24, 0.26 (6 s, MeSi and CH_2Si), 0.93 (br s, CH_3), 6.66 (br, vinyl proton) (ratio of alkyl H/vinyl H = 1.0/0.02); ^{13}C NMR (δ in $CDCl_3$) −3.45, −3.12, −1.50, −0.89, −0.48, −0.18, 0.65, 1.02, 1.39 (MeSi), 3.16, 3.49, 4.40, 5.35, 5.79, 6.31, 6.59, 7.31, 7.69, 8.35, 29.71 (Et), 84−93, 100−112 ($C{\equiv}C$), 142−144, 154−

158 (C═C); IR 2957, 2901, 2098 (C≡CC═C), 2064 (C≡CC≡C), 1869, 1250, 1019 cm^{-1} (Si—O—Si).

Hydrosilylation of 14 with Triethylsilane. A mixture of 218 mg (0.702 mmol) of **14**, 82 mg (0.705 mmol) of triethylsilane, and 4 mg (3.8×10^{-3} mmol, 0.5 mol %) of $Rh_6(CO)_{16}$ in 7.5 mL of benzene was stirred at 80 °C for 24 h. The mixture was analyzed by GLC as being 1-(pentamethyldisilanyl)-4-(triethyl-1,1-dimethyldisilanyl)butadiyne (**15**; 24% yield), 1,4-bis(triethyl-1,1-dimethyldisilanyl)butadiyne (**16**; 18% yield), (*E*)-1,4-bis(triethyl-1,1-dimethyldisilanyl)-2-(triethylsilyl)but-1-en-3-yne (**17**; 8% yield), and starting **14** (16%). We could also assign other products of *m*/*z* 426 (two compounds) to (*E*)-1-(dimethylsilyl)-4-(pentamethyldisilanyl)-2-(triethylsilyl)-1-(trimethylsilyl)but-1-en-3-yne and its regioisomer (8% and 6%), and those of *m*/*z* 468 (two compounds) to 1-(pentamethyldisilanyl)-4-(triethyl-1,1-dimethyldisilanyl)-2-(triethylsilyl)but-1-en-3-yne and its isomer (10% and 7%), respectively. The products **15**—**17** were isolated by preparative GLC.

For **15**: mp 104 °C; mass *m*/*z* 352 (M^+); ^1H NMR (δ in $CDCl_3$) 0.12 (s, 9H, Me_3Si), 0.19 (s, 6H, Me_3SiMe_2Si), 0.24 (s, 6H, Et_3SiMe_2Si), 0.68 (q, 6H, CH_3CH_2Si, $J = 7.9$ Hz), 0.99 (t, 9H, CH_3CH_2Si, $J = 7.9$ Hz); ^{13}C NMR (δ in $CDCl_3$) −3.45 (Me_3Si), −2.60 (Me_3SiMe_2Si), −1.99 (Et_3SiMe_2Si), 3.02, 8.21 (EtSi), 85.28, 85.81, 90.37, 90.53 (C≡C); ^{29}Si NMR (δ in $CDCl_3$) −36.45, −35.29 ($C≡CSiMe_2$), −18.24 (Me_3Si), −8.09 (Et_3Si); IR 2954, 2875, 2058 cm^{-1} (C≡CC≡C). Anal. Calcd for $C_{17}H_{36}Si_4$: C, 57.87; H, 10.28. Found: C, 57.87; H, 10.22.

For **16**: mp 108 °C; mass *m*/*z* 394 (M^+); ^1H NMR (δ in $CDCl_3$) 0.24 (s, 12H, Me_2Si), 0.70 (t, 18H, CH_3CH_2Si, $J = 7.9$ Hz), 0.97 (q, 12H, CH_3CH_2Si, $J = 7.9$ Hz); ^{13}C NMR (δ in $CDCl_3$) −2.01 (Me_2Si), 3.02, 8.21 (EtSi), 85.86, 90.66 (C≡C); ^{29}Si NMR (δ in $CDCl_3$) −36.46 ($C≡CSiMe_2$), −8.11 (Et_3Si); IR 2954, 2874, 2058 cm^{-1} (C≡CC≡C). Anal. Calcd for $C_{20}H_{42}Si_4$: C, 60.83; H, 10.72. Found: C, 60.58; H, 10.58.

For **17**: mass *m*/*z* 510 (M^+); ^1H NMR (δ in $CDCl_3$) 0.51 (s, 6H, Me_2Si), 0.61 (s, 6H, Me_2Si), 0.82—0.92 (m, 18H, CH_3CH_2Si), 1.14—1.230 (m, 27H, CH_3CH_2Si), 6.87 (s, 1H, olefinic proton); ^{13}C NMR (δ in $CDCl_3$) −0.85, −0.18 (Me_2Si), 4.24, 4.56, 4.92, 8.61, 9.63, 9.69 (EtSi), 104.60, 111.70 (C≡C), 143.43, 157.45 (C═C); IR 2953, 2875, 2120 cm^{-1} (C≡CC═C). HRMS calcd for $C_{24}H_{53}Si_5$ ($M^+ - C_2H_5$) 481.2995, found 481.2986.

NMR Study for the Structures of Branched and Degradated Polymers. Polymers **7b**,**c** with relatively low molecular weights were prepared by the reactions of **1b** and **1c** with 0.3 equiv of **6**, respectively, and their proposed structures were verified by ^1H and ^{29}Si NMR (see Results and Discussion). For **7b**: $M_w = 22\,200$ ($M_w/M_n = 4.0$); ^1H NMR (δ in $CDCl_3$) −0.3—1.2 (br m, 1.0H, Me), 5.0 (s, 0.01H, SiH), 6.5—8.0 (br m, 1.34H, vinyl and phenyl protons); ^{29}Si NMR (δ in $CDCl_3$) −44.4 (br, $-(C≡C)_2MePhSi(C≡C)_2-$ and $-(C≡C)_2MePhSiC≡CC(Si)═CH-$), −21.81 ($-(C≡C)_2PhMeSiCH═C<$), −17.68 (MePhHSi—). Anal. Calcd for $C_{17.3}H_{14.9}Si_{1.6}$: C, 77.35; H, 5.60. Found C, 73.69; H, 6.39. For **7c**: $M_w = 22\,500$ ($M_w/M_n = 2.8$); ^1H NMR (δ in $CDCl_3$) 0.4—1.2 (br m, 1.0H, Me and Et), 5.0 (s, 0.01H, SiH), 6.6—6.9 (br, 0.04H, vinyl proton), and 7.0—7.8 (br m, 0.34H, phenyl protons); ^{29}Si NMR (δ in $CDCl_3$) −28.64 (br, $-(C≡C)_2Et_2Si(C≡C)_2-$ and $-(C≡C)_2Et_2SiC≡CC(Si)═CH-$), −21.86 ($-(C≡C)_2Et_2SiCH═C<$), −17.71 (MePhHSi—), −11.01 (br, —MePhSi—). Anal. Calcd for $C_{14.2}H_{16.8}Si_{1.6}$: C, 73.20; H,7.28. Found: C, 69.62; H, 6.97.

When **7b**,**c** were treated with PPh_3 in the presence of ethanol, the respective ^{29}Si signals at δ −43.4 and −28.6 disappeared, owing to degradation at the bis(diethynyl)silyl moieties, but the other signals remained unchanged. For the polymer obtained from **7b**: $M_w = 5800$ ($M_w/M_n = 2.3$); ^1H NMR (δ in $CDCl_3$) −0.2 to +1.0 (br m, 1.0H, Me), 3.6—3.8 (br, <0.01 H, $SiOCH_2$), 4.9 (s, 0.01H, SiH), 6.5—7.9 (br m, 1.41H, phenyl and vinyl protons); ^{29}Si NMR (δ in $CDCl_3$) −21.86 ($-(C≡C)_2PhMeSiCH═C<$), −17.73 (MePhHSi—). For the polymer obtained from **7c**: $M_w = 6500$ ($M_w/M_n = 2.3$); ^1H NMR (δ in $CDCl_3$) 0.4—1.2 (br m, 1.0H, Me and Et), 3.5—3.9 (br, 0.03H, $SiOCH_2$), 5.0 (s, 0.01H, SiH), 6.5—6.7 (br, 0.03H, vinyl proton), 7.1—7.7 (br m, 0.54H, phenyl protons); ^{29}Si NMR (δ in $CDCl_3$) −21.86 ($-(C≡C)_2Et_2SiCH═C<$), −17.71 (MePhHSi—), −11.01 (br, —MePhSi—).

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