Polymeric Organosilicon Systems. 19. Preparation of Branched Polymers by Selective Hydrosilylation of Poly[(silylene)but-1,3-diynes]

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Summary: The reaction of poly[(dimethylsilylene, methylphenylsilylene, and diethylsilylene)but-1,3-diyne] 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 alternating polymers composed of a silylene or disilanylene unit and π-electron system have been extensively investigated over the past few years because of their potential applications in areas such as 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. In this paper, we report the regiospecific addition of 1,4-bis(methylphenylsilyl)benzene to poly[(silylene)but-1,3-diynes] (**1**),[7,9,10] giving branched polymers composed of a silylene unit and enyne and phenylene π-systems.[11]

We first investigated the reaction of poly[(dimethylsilylene)but-1,3-diyne] (**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 a product with a lower molecular weight than that of the starting polymer **1a**. The $RhCl(PPh_3)_3$ 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, its IR spectrum indicates strong absorptions at 2126 and 1875 cm^{-1}, due to an enyne and allenic bond, respectively.[12] The presence of the allenic bond clearly indicates that the reaction involves 1,4-addition of Et_3SiH into the initially formed enyne structure. We found that a $Rh_6(CO)_{16}$ catalyst[13] gives a 1,2-adduct with high regiospecificity. Thus, the reaction of **1a** with 4 equiv of Et_3SiH in the presence of 0.9 mol % of $Rh_6(CO)_{16}$ at 40 °C for 24 h produced only the monohydrosilylation product, poly[2-(triethylsilyl)(dimethylsilylene)but-1-en-3-yne-1,4-diyl] (**2**)[14] (Scheme 1). No allenic structure was detected in the polymer backbone by IR and ^{13}C NMR spectroscopic analysis. On the basis of the result obtained from hydrosilylation of 1,4-bis(trimethylsilyl)butadiene with triethylsilane, the triethylsilyl group in polymer **2** is presumably located in the C-2 position of an enyne group.[15]

Next, we examined the reaction of poly[(silylene)but-1,3-diynes] with 1,4-bis(methylphenylsilyl)benzene (**3**) using a $Rh_6(CO)_{16}$ 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** (0.76 mmol, $M_w = 8300, M_w/M_n = 1.7$) with 0.3 equiv of **3** in the presence of 0.5 mol % of $Rh_6(CO)_{16}$ in a benzene solution at 80 °C for 9 h gave the soluble polymer **4a**,[16] whose molecular weight is determined to be 250 000 in 49% yield after reprecipitation of the resulting mixture from ethanol–benzene (Scheme 2). Polymer **4a** is soluble in common

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(11) The reaction of poly[(methylphenylsilylene)butadiyne] with 0.05–0.1 equiv of 1,2,4,5-tetrakis(dimethylsilyl)benzene in the presence of a $Pt(CH_2{=}CH_2)(PMe_3)_2$ catalyst leading to the polymer that has a cross-linked structure has been reported by Tanaka et al.; see: Uchimaru, Y.; Brandl, P.; Tanaka, M.; Goto, M. 39th Symposium on Organometallic Chemistry, Yokohama, Japan, Oct 23, 1992; Kinki Chemical Society: Osaka, Japan, 1992; Abstract p 76.

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(14) Polymer **2**: ^1H 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 ($-C{\equiv}\mathrm{CC}{=}\mathrm{C}-$), 142–144, 153–154, 155–157 ($-\mathrm{C}{\equiv}\mathrm{C}C{=}C-$); IR $\nu_{\mathrm{C\equiv CC=C}}$ 2131 cm^{-1}.

(15) Treatment of 1,4-bis(trimethylsilyl)butadiyne with 5 equiv of triethylsilane in the presence of a $Rh_6(CO)_{16}$ catalyst yielded (*E*)-2-(triethylsilyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne[12] with high regiospecificity in 94% yield. No 1,3-bis(triethylsilyl)-1,4-bis(trimethylsilyl)allene was detected in the reaction mixture.

(16) Polymer **4a**: ^1H NMR (δ in $CDCl_3$) 0.1–0.7 (m, MeSi), 4.9 (br s, HSi), 7.1–7.8 (m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −0.57 (MeSi), 82.04, 88.99 ($-\mathrm{C}{\equiv}\mathrm{CC}{\equiv}\mathrm{C}-$), 105–108 ($-C{\equiv}\mathrm{CC}{=}\mathrm{C}-$), 127.84, 129.57, 134.10, 134.55, 134.83, 135.16 (phenyl ring carbons), 140–144, 152–156 ($-\mathrm{C}{\equiv}\mathrm{C}C{=}C-$); IR $\nu_{\mathrm{C\equiv CC\equiv C}}$ 2072, $\nu_{\mathrm{C\equiv CC=C}}$ and ν_{SiH} 2132 cm^{-1}.

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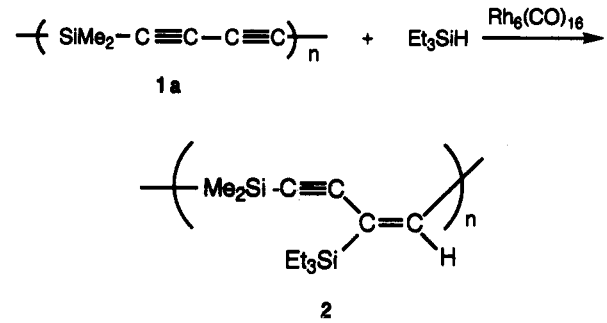
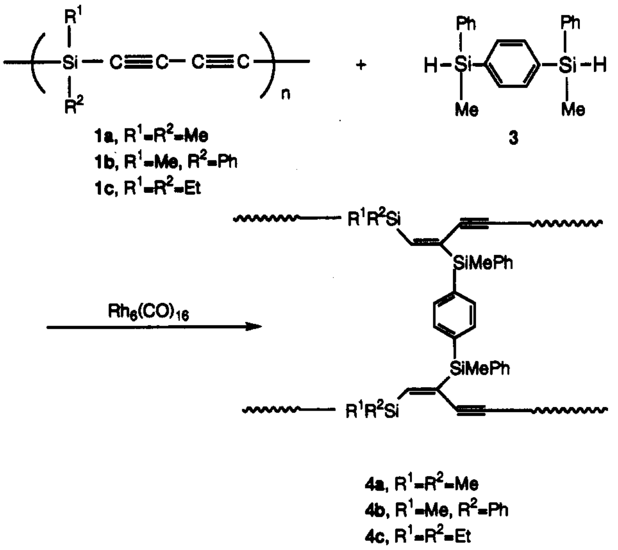
Scheme 1



Scheme 2



organic solvents such as ethers, aromatic solvents, and halocarbons. Its IR and ^{13}C NMR spectra clearly show the presence of an enyne and diyne structure, but not an allenic structure, in the polymer backbone.

Similar reaction of poly[(methylphenylsilylene)but-1,3-diyne] (**1b**) with 0.45 equiv of **3** in the presence of the rhodium(0) catalyst afforded the product **4b** with high molecular weight in 74% yield, after reprecipitation of a crude polymer from ethanol–benzene (see ref 17).

Poly[(diethylsilylene)but-1,3-diyne] (**1c**)[7b] also reacts with **3** in the presence of a catalytic amount of $Rh_6(CO)_{16}$ in a benzene or THF solution, to give branched polymer **4c** in high yield. The molecular weight changes of the hydrosilylation product in the reaction of **1c** ($M_w = 6000$, $M_w/M_n = 2.1$) with 0.42 equiv of **3** in the presence of 0.6 mol % of $Rh_6(CO)_{16}$ in a benzene solution at reflux temperature were followed by GPC. The molecular weight of the hydrosilylation product increased with increasing reaction time. For example, the molecular weight of the product after 1-h reaction was determined to be 70 000. After 4-h reaction, the molecular weight of the product increased to 112 000. Polymer **4c**[18] with a molecular weight of 424 000 was obtained in 79% yield, after 21-h reaction.

Polymers **4a–c** do not melt but are soluble in common organic solvents such as ethers, benzene, and chloroform. Their IR and ^{1}H and ^{13}C NMR spectra clearly indicate the presence of enyne and phenylene groups. The ^{1}H NMR spectra for **4a–b** reveal very weak resonances at 4.9 ppm, due to an Si–H group, while polymer **4c** shows no resonance attributed to the Si–H bond. Polymers **4a–c** reveal very broad molecular weight distribution, and their UV spectra show broad absorptions tailing into 350 nm.[19]

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(17) A solution of 260 mg (1.55 mmol) of **1b** ($M_w = 11\,000$, $M_w/M_n = 3.1$), 227 mg (0.71 mmol) of **3**, and 6 mg (5.6×10^{-3} mmol) of $Rh_6(CO)_{16}$ in 8 mL of dry benzene was heated to 80 °C for 9 h. The solution was 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 **4b**. Crude polymer **4b** was reprecipitated twice from ethanol–benzene to give 359 mg (74 wt % yield) of **4b**: $M_w = 519\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.1–1.0 (br m, MeSi), 4.9 (br s, HSi), 6.8–7.9 (m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) –5 to 0 (MeSi), 88–92 (–C≡CC≡C–), 107–110 (–*C*≡CC=C–), 127.72, 127.95, 129.52, 134.01, 134.54, 134.83, 135.15 (phenyl ring carbons), 140–144, 150–159 (–C≡C*C*=*C*–); IR $\nu_{C\equiv CC\equiv C}$ 2071, $\nu_{C\equiv CC=C}$ and ν_{SiH} 2130 cm^{-1}.

(18) Polymer **4c**: ^{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); ^{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≡CC≡C–), 98–104, 108–110 (–*C*≡CC=C–), 127.67, 129.54, 133 .93, 134.34, 134.74, 135.09 (phenyl ring carbons), 140–144, 151–160, (–C≡C*C*=*C*–); IR $\nu_{C\equiv CC\equiv C}$ 2071, $\nu_{C\equiv CC=C}$ 2133 cm^{-1}.

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