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Synthesis of organosilicon polymers by using the Lewis-acid-catalyzed *trans*-allylsilylation of alkynes

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Abstract—The HfCl₄ catalyzed polymerization of allyl(4-ethynylphenyl)dimethylsilane (1a) proceeded smoothly to give poly-[dimethyl-(1,4-pentadienyl)phenylsilane] (2a), and the HfCl₄ catalyzed reaction of 1-allyl-2-(4-ethynyphenyl)-1,1,2,2-tetramethyldisilane (1b) afforded poly[1,1,2,2-tetramethyl-1-(1,4-pentadienyl)-2-phenyldisilane] (2b). These polymerization reactions proceeded via the stereoselective *trans*-allylsilylation of the 4-ethynyl group attached to the aromatic ring. © 2004 Elsevier Ltd. All rights reserved.

There has been considerable interest in the chemistry of organosilicon polymers since they are potentially useful as functional materials, such as photoresists, semiconductors, hole-transporting materials, and precursors of silicon carbide.^{1,2} In particular, polymers consisting of oligosilane units and π -electron systems, which are arranged alternately in the main chain, exhibit orbital interactions between the silicon–silicon unit and π -electron system, which is known as σ – π conjugation, leading to extended conjugation along the polymer chain.^{3–5} Although a number of synthetic methods for organosilicon polymers shown in Figure 1 have been reported,⁶ little attention has been paid to the *Z*-selective synthesis of the alkenylsilicon polymers.

For the past few years, we have studied stereoselective carbometallation of alkynes, and the Lewis-acid-catalyzed *trans*-selective carbosilylation of unactivated alkynes using organosilicon reagents, such as allylsilanes, vinylsilanes, propargylsilanes, allenylsilanes, and arylsilanes has been achieved.⁷ It is well known that the carbometallation of alkynes using R–M (M = Cu, Li, Mg, transition metals, etc.) proceeds in the *cis*-fashion to give the corresponding *cis*-alkenyl metals stereoselectively.⁸ However, the Lewis-acid-catalyzed addition of R–Si to alkynes proceeds in a *trans*-manner and the corresponding *trans*-alkenylsilanes are obtained as the sole product as shown in Eq. 1. We have extended this Lewis-acidcatalyzed methodology to the synthesis of organosilicon



Figure 1.

Keywords: Organosilicon polymer; σ–π Conjugation; Allylsilylation; Lewis-acid catalyst; Carbometallation; Hafnium chloride.

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polymers including σ - π conjugated systems; The HfCl₄ catalyzed reaction of allyl(4-ethynylphenyl)-dimethylsilane (**1a**) gave poly[dimethyl(1,4-pentadienyl)-phenylsilane] (**2a**), and the HfCl₄ catalyzed reaction of 1allyl-2-(4-ethynylphenyl)-1,1,2,2-tetramethyldisilane (**1b**) afforded poly[1,1,2,2-tetramethyl-1-(1,4-pentadienyl)-2-phenyldisilane] (**2b**) (Eqs. 2 and 3).

$$\xrightarrow{\quad \text{result}} + R - SiR'_3 \xrightarrow{\quad \text{cat. Lewis acid}} \xrightarrow{\quad \text{R}} \xrightarrow{\quad \text{SiR'}_3} (1)$$



The requisite starting monomers 1a and 1b were prepared as shown in Schemes 1 and 2. Sonogashira coupling of 1-bromo-4-iodobenzene **3** with trimethylsilylacetylene gave (4-bromo-phenylethynyl)trimethylsilane **4** in 98% yield. Treatment of **4** with *n*-BuLi, followed by addition of allylchlorodimethylsilane afforded 1-(allyldimethyl-silanyl)-4-trimethylsilanylethynylbenzene **5** in 93% yield. Desilylation of **5** with aqueous KOH produced **1a** in 90% yield (Scheme 1). On the other hand, treatment of **4** with *n*-BuLi, followed by the addition of 1,2-dichlorotetramethyldisilane and allyl magnesium chloride gave 1-allyl-1,1,2,2-tetramethyl-2-



Scheme 1.

(4-trimethylsilanylethynyl-phenyl)-disilane 6 in 77% yield. Desilylation of 6 produced 1b in 65% yield (Scheme 2).

First, we examined the intermolecular reaction of the allyldisilane 7 with phenylacetylene in order to determine whether the Lewis-acid-catalyzed addition of the allyldisilane proceeds similarly to that of allyltrimethylsilane (Eq. 4). The reaction proceeded smoothly in the *trans*-fashion and the corresponding allylsilylation product **8** was obtained as the sole product in 62% yield.⁹ The stereochemistry of **8** was unambiguously determined by NOE experiments; irradiation of the methyl protons on the dimethylsilyl group enhanced the signal of the *ortho*-protons of the phenyl group (9.5% NOE), whereas no enhancement of any signals of the methylene protons on the allyl group was observed.

$$\overbrace{i}^{i} + Ph = \underbrace{cat. HfCl_4}_{62\%} \xrightarrow{i}_{Ph} \xrightarrow{i}_{Si}^{i}$$

$$(4)$$

Since the model study demonstrated that the allyldisilane, as well as the allylsilane, added to the alkyne regioand stereoselectively, we next examined the polymerization of **1a** and **1b** using $HfCl_4$ as catalyst in CH_2Cl_2 and the results are summarized in Table 1. The reaction of **1a** proceeded smoothly at room temperature to give a crude polymer, which was purified by precipitation into i-PrOH to afford 2a in 57% yield (entry 1). Polymerization of 1b was also performed under the same conditions as above and the corresponding polymer 2b was obtained in 47% yield (entry 2). The structures of 2a and **2b** were determined by ¹H and ¹³C NMR spectroscopy, in which the signal of the olefinic protons neighboring silicon of 2b showed good correspondence with those of (Z)-2-phenyl-1-(trimethylsilyl)-1,4-pentadiene $Z-9^{10}$ and the model compound 8; Z-9, 5.59 ppm; E-9, 5.94 ppm;¹¹ 8, 5.62 ppm; 2a, 5.75 ppm; 2b, 5.53 ppm.¹² The olefinic protons of the Z-derivatives (Z-9, 8, and

Table 1. The HfCl₄-catalyzed polymerization of 1a and 1b^a

Entry	1	2	Yield ^b	$M_{\rm n}^{\ \rm c}$	$M_{ m w}^{ m c}$	$M_{\rm w}/M_{\rm n}$
1 2	1a 1b	2a 2b	57 47	$\begin{array}{c} 1.0\times10^4\\ 1.2\times10^4\end{array}$	$\begin{array}{c} 3.2\times10^4\\ 4.1\times10^4\end{array}$	3.2 3.4

^a The reaction was performed using 1 in the presence of $HfCl_4$ (20mol%) in CH_2Cl_2 at room temperature for 3.5 h.

^b Isolated yield.

^c Determined by GPC using the standard polystyrene calibration curve.



2b) showed similar chemical shifts, but the proton of the *E*-derivative (*E*-9) appeared in lower field than that of the *Z*-derivative; 5.94 versus 5.59 ppm. The stereochemistry of **2a** was not so unambiguous because 5.75 ppm was just in between the model values of 5.59 and 5.94 ppm. However, only a single peak appeared in the olefinic region of ¹H NMR spectra of **2a** and we concluded that **2a** took the *Z*-configuration based on the general rule for the Lewis-acid catalyzed addition (see Eq. 1) and on the analogy of **2b**. Both polymers are soluble in common organic solvents, such as ethers and halocarbons, but are insoluble in methanol.

The molecular weights (M_n) of **2a–b** were found to be 10,000–12,000 and their molecular weight distributions ranged from 3.2 to 3.4 based on GPC analysis using the standard polystyrene calibration curve. Recently, Mori et al. reported that the stereodivergent synthesis of *E*-and *Z*-organosilicon polymers, which was accomplished by Rh-catalyzed hydrosilylation of alkynes.¹³ However, to the best of our knowledge, this is the first example of the stereocontrolled synthesis of σ – π conjugated organosilicon polymers azeromytem organosilicon polymers.

The preparation of **2b** is representative. To a suspension of HfCl₄ (64 mg, 20 mol%) in CH₂Cl₂ (2 mL) was added **1b** (259 mg, 1 mmol) with vigorous stirring at room temperature. The mixture was stirred for 3.5h and then was poured into *i*-PrOH (50 mL). After additional stirring for 20 min, the mixture was filtered through a pad of Celite. A precipitate remained on the Celite, which was washed with *i*-PrOH, and was dissolved in CH₂Cl₂. The solvents were evaporated to give a crude material containing significant amounts of *i*-PrOH. To remove *i*-PrOH completely, the crude product was again dissolved in CH₂Cl₂, the solvents were evaporated, and this procedure was repeated five times. The material was dried in vacuo and **2b** was obtained as a brown gum (122 mg) in 47% yield.

We are now in a position to synthesize organosilicon polymers, bearing (Z)-alkenylsilane moieties, in a regioand stereoselective manner using the Lewis-acid-catalyzed *trans*-allylsilylation of alkynes. While the silicon– silicon bond of disilanes is easily cleaved by a transition metal catalyst,¹⁴ such an undesired reaction does not occur in the present Lewis-acid-catalyzed reaction. Further studies on the properties of these polymers and extension of the present method to the preparation of other functional materials are underway.

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- 9. Compound **8**: ¹H NMR (600 MHz, CDCl₃) δ 7.45–7.25 (m, 5H), 5.85 (ddt, *J* = 6.6, 9.0, 18.0 Hz, 1H), 5.62 (s, 1H), 5.10–5.02 (m, 2H), 3.20 (dd, *J* = 1.2, 6.6 Hz, 2H), 0.02 (s, 9H), -0.15 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 156.7, 143.9, 136.0, 128.0, 127.7, 126.9, 126.5, 116.2, 47.0, -1.9, -2.6.
- 10. See Ref. 7b. (Z)-2-Phenyl-1-(trimethylsilyl)-1,4-pentadiene Z-9: ¹H NMR (CDCl₃, 270 MHz) δ 7.30–7.25 (m, 3H), 7.17–7.13 (m, 2H), 5.83 (ddt, J = 7.0, 9.2, 17.9 Hz, 1H), 5.59 (t, J = 1.5 Hz, 1H), 5.02–4.98 (m, 2H), 3.21 (ddd, J = 1.5, 2.7, 7.0 Hz, 2H), -0.19 (s, 9H); ¹³C NMR (67.9 MHz, CDCl₃) δ 157.3, 143.9, 135.8, 127.88, 127.86, 127.7, 126.9, 116.4, 46.8, 0.1.
- The spectral data of (*E*)-2-phenyl-1-(trimethylsilyl)-1,4-pentadiene *E*-9 was reported, see: Chatani, N.; Amishiro, N.; Murai, S. J. Am. Chem. Soc. 1991, 113, 7778–7780. *E*-9: ¹H NMR (CDCl₃, 270 MHz) δ 7.45–7.42 (m, 2H), 7.33–7.21 (m, 3H), 5.94 (s, 1H), 5.80 (ddt, *J* = 1.7, 10.1, 17.1 Hz, 1H), 5.06 (dt, *J* = 1.7, 17.1 Hz, 1H), 5.00 (dt, *J* = 1.7, 10.1 Hz, 1H), 3.39 (dt, *J* = 1.7, 5.9 Hz, 2H), 0.20 (s, 9H); ¹³C NMR (67.9 MHz, CDCl₃) δ 154.01, 143.36, 136.53, 129.44, 128.08, 127.27, 126.23, 116.06, 38.72, 0.20.
- 12. Compound **2a**: ¹H NMR (300 MHz, CDCl₃) δ 7.70–6.70 (br, 4H), 6.10–5.50 (br, 2H), 5.20–4.90 (br, 2H), 3.35–3.00 (br, 2H), 0.20–0.14 (br, 6H); ¹³C NMR (75.5 MHz, CDCl₃) δ 158.8, 143.8, 139.3, 135.7, 133.0, 127.1, 125.7, 116.5, 46.6, -1.2; IR (KBr) 2955, 1591, 1247, 835 cm⁻¹. Compound **2b**: ¹H NMR (300 MHz, CDCl₃) δ 7.55–7.16 (br, 2H), 7.16–6.78 (br, 2H), 5.93–5.65 (br, 1H), 5.53 (br, 1H), 5.14–4.87 (br, 2H), 3.28–2.99 (br, 2H), 0.25 (br, 6H), -0.23 (br, 6H); ¹³C NMR (75.5 MHz, CDCl₃) δ 157.3, 143.8, 138.2, 136.0, 133.3, 127.3, 125.8, 116.3, 46.7, -2.6, -3.7; IR (KBr) 2951, 1589, 1244, 829 cm⁻¹; UV–vis (CHCl₃) λ_{max}/nm (ε) 252 nm (12,000).
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