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Regio- and Stereocontrolled Hydrosilylation Polyaddition Catalyzed by RhI(PPh$_3$)$_3$. Syntheses of Polymers Containing (*E*)- or (*Z*)-Alkenylsilane Moieties

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There has recently been increasing interest in polymers with π-conjugation bearing poly(arylene−vinylene) moieties in the main chain in connection with properties such as conductivity[1] and electroluminescence.[2] Incorporation of organosilicon moieties into the polymer has also attracted attention and a wide variety of such silicon-containing polymers have been designed and synthesized.[3] Despite much effort on the polymers few studies have been devoted to providing the stereochemical control that would form the *E*- and *Z*-vinylenes highly selectively.

On the other hand, we reported that stereodivergent hydrosilylation of 1-alkynes, as shown in Scheme 1, by the catalysis of RhCl(PPh$_3$)$_3$/NaI or RhI(PPh$_3$)$_3$ enabled the syntheses of *E*- and *Z*-alkenylsilanes, respectively, in a highly regio- and stereocontrolled manner.[4] The findings, if applicable to the syntheses of such polymers, would lead to a solution of the issue of stereochemical control.

Accordingly, we envisaged the use of hydrosilylation polyaddition,[5] whose protocol would afford a polymer bearing alkenylsilane moieties in the main chain with a stereochemically controlled manner. In particular, a polymer containing *Z*-alkenylsilane moieties would be our major concern in connection with a characteristic behavior as materials since there have been few practical synthetic methodologies leading to such *Z*-polymers.[6,7] Studies of spectroscopic change based on the stereochemistries of polymers would also be a part of our interest.

The polymerization was carried out using 1,*m*-diethynylbenzene (**1**) and 1,*n*-bis(dimethylsilyl)benzene (**2**) as monomers (*m* and *n*: 3 or 4) via polyaddition catalyzed by RhI(PPh$_3$)$_3$ (**3**).[4] In our previous studies based on the synthetic utilization of the obtained organosilicon compounds, however, selective hydrosilylation has been focused on the use of hydrosilanes with heteroatom substituent(s)[8] and the use of aryldialkylsilane as a substrate has not been examined. Therefore, a model study was initially carried out.

The reaction of ethynylbenzene (**1c**) with 1,4-bis(dimethylsilyl)benzene (**2a**) was performed under the conditions to form *E*-silanes; the reaction of **1c** (2.0 mmol) and **2a** (1.1 mmol) in the presence of 0.1 mol % of **3** at 80 °C for 2 h, afforded the (*E*)-silane **4** with high selectivity (>95%) in >99% yield. Characteristic signals of the ^{1}H NMR spectrum at 6.60 and 6.98 (doublet, J = 19.2 Hz, respectively) of **4** clearly shows the formation of *E*-alkenylsilane. On the other hand, under the conditions to form (*Z*)-alkenylsilane—pretreatment of 0.1 mol % of **3** and **2a** (1.0 mmol) at 0 °C for 1 h followed by the addition of **1c** (2.0 mmol)—the bis[(*Z*)-alkenylsilane] **5** was obtained in quantitative yield after stirring at room temperature for 4 h (^{1}H NMR: δ 6.00 and 7.50 ppm, d, J = 15.0 Hz).[9]

Scheme 1

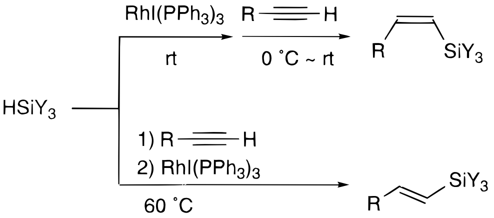
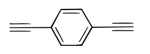


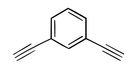
Table 1. Syntheses of 4-13 by RhI(PPh$_3$)$_3$-Catalyzed Hydrosilylation Polyaddition

	monomers					
product	alkyne	silane	yield, %[a]	*E*/*Z*[b]	M_n[c]	M_w/M_n[c]
6	**1a**	**2a**	88	96:4	20 000	5.5
7	**1a**	**2b**	74	93:7	10 000	5.2
8	**1b**	**2a**	98	96:4	12 000	3.5
9	**1b**	**2b**	74	96:4	12 000	3.9
10	**1a**	**2a**	70	4:96	9400	2.4
11	**1a**	**2b**	73	9:91	8400	2.7
12	**1b**	**2a**	93	3:97	8500	3.8
13	**1b**	**2b**	91	3:97	5900	2.6
4	**1c**	**2a**	77	98:2	399[d]	
5	**1c**	**2a**	54	4:96	399[d]	

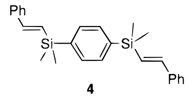
[a] Isolated yield. [b] The ratio was determined by ^{1}H NMR. [c] Measured by SEC using THF as an eluent (polystyrene standards), unless noted. [d] The molecular weight calculated.



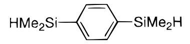
1a



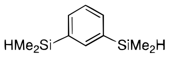
1b



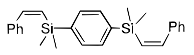
4



2a



2b



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With the successful regio- and stereocontrolled hydrosilylations as model studies in hand, the bifunctional dialkynes (**1a** and **1b**) and hydrosilanes (**2a** and **2b**) were subjected to the polymerization reaction. As shown in Table 1, the stereochemistries of polymers **6**−**13** were highly controlled to give the corresponding *E*- and *Z*-polymers. The polymers with *E*-configurations **6**−**9** can be generally purified by simple reprecipitation−filtration procedures suggesting relatively good crystallinity. In addition, the polymers derived from para-substituted diyne **1a** and/or disilane **2a** afforded powders by reprecipitation. By contrast, the polymer from **1b** and **2b** (both meta-substituted monomers) was a gummy paste. On the other hand, all *Z*-polymers **10**−**13** appeared to be glassy at ambient temperature.

The ratios of regio- and stereoselectivities were estimated by ^{1}H NMR analyses, in which the signals of the olefinic protons showed good correspondence with those

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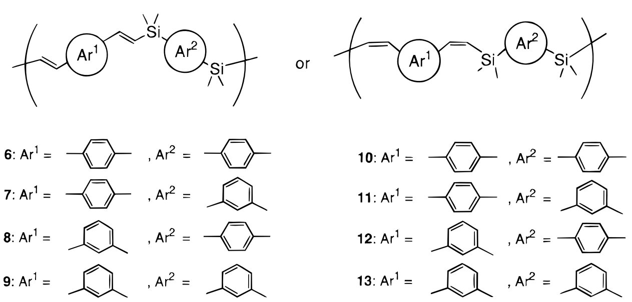
of the model compounds **4** and **5**. As a result, the ratios of stereochemistry (*E*/*Z*) were as high as 90% while no α-adducts, the regioisomers, were observed. In addition, neither isomerization of the stereochemistry nor decomposition of the polymer was observed during the isolation and purification procedures.

The molecular weights (M_n) of **6**−**13** obtained were found to be 6000−20000 and their molecular weight distributions ranged from 2.4 to 5.5 based on SEC analyses. The molecular weights of the polymers of *E*-configuration appear to be generally higher than those of the *Z*-polymers.



The syntheses and characterizations of polymers which bear (*E*)-alkenylsilane moieties in their main-chain were recently reported by Luh,[5a] in which the polymers were synthesized by nickel-catalyzed cross-coupling and $RhCl(PPh_3)_3$-catalyzed hydrosilylation−polyaddition sequence, showing remarkable absorption and emission spectroscopic character. By contrast, our approach represents a more straightforward synthetic pathway. Moreover, the polymers containing (*Z*)-alkenylsilane moieties have not been synthesized yet in a highly selective manner.

In conclusion, we have stereodivergent syntheses of *E*- and *Z*-polymers of the alkenylsilane moiety in hand by hydrosilylation polyaddition using diethynylbenzene and bis(dimethylsilyl)benzene. The method would be a strong tool to study the relationship of polymer properties with the stereochemistry of vinylene moieties. Further studies on the UV absorption and emission spectroscopic characters of these polymers in connection with stereochemistry of the alkenylsilane moiety are underway.

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Supporting Information Available: Text giving experimental procedures for the synthesis of polymers **4**−**13** and figures showing their ^{13}C and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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