Careful Investigation of the Hydrosilylation of Olefins at Poly(Ethylene Glycol) Chain Ends and Development of a New Silyl Hydride to Avoid Side Reactions

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ABSTRACT: Hydrosilylation of olefin groups at poly(ethylene glycol) chain ends catalyzed by Karstedt catalyst often results in undesired side reactions such as olefin isomerization, hydrogenation, and dehydrosilylation. Since unwanted polymers obtained by side reactions deteriorate the quality of end-functional polymers, maximizing the hydrosilylation efficiency at polymer chain ends becomes crucial. After careful investigation of the factors that govern side reactions under various conditions, it was related that the short lifetime of the unstable Pt catalyst intermediate led to the formation of more side products under the inherently dilute conditions for polymers. Based on these results, two new chelating hydrosilylation reagents, tris(2-methoxyethoxy)silane (5) and 2,10-dimethyl-3,6,9-trioxa-2,10-disilaundecane (6), have been developed. It was demonstrated that the hydrosilylation efficiency at polymer chain ends was significantly increased by employing the internally coordinating hydrosilane 5. In addition, employment of the internally coordinating disilane species 6 in an addition polymerization with 1,5-hexadiene by hydrosilylation reaction yielded a polymer with high molecular weight ($M_n = 9300$ g/mol), which was significantly higher than that ($M_n = 2600$ g/mol) of the corresponding polymer obtained with non-chelating dihydrosilane, 1,1,3,3-tetramethyldisiloxane. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

KEYWORDS: end-functional polymer; hydrosilylation; Karstedt catalyst; poly(ethylene glycol)

INTRODUCTION The hydrosilylation reaction (eq 1) is one of the most powerful and efficient coupling reactions not only in classical small molecule syntheses but also in macromolecular chemistry and surface chemistry.[1]

$$R' \diagup\!\!\!\diagdown \;+\; R_3SiH \longrightarrow R' \diagup\!\!\diagdown\!\!\diagup^{SiR_3} \quad (1)$$

The first hydrosilylation reaction was reported by Sommer and colleagues in 1947, and used free radical chemistry.[2] However, the method was not practical until Speier and coworkers reported the first platinum-catalyzed hydrosilylation reaction under mild conditions with high efficiency in 1957.[3] Since then, a variety of transition metal catalysts for hydrosilylation has been developed. Among them, the Karstedt catalyst (Fig. 1) might be the most popular and has been widely used in industry because of its high catalytic activity and practicality.[4,5]

For example, the Karstedt catalyst-catalyzed hydrosilylation reaction is one of the key reactions to prepare various functional poly(ethylene glycol)s (PEGs). Due to high biocompatibility and low toxicity, PEG-derived functional polymers have been widely employed as core components in many biorelated materials,[6] surface modifications[7,8] microcontact printing,[9] and polymer electrolytes.[10,11]

In general, hydrosilylation reactions catalyzed by platinum species such as Karstedt catalyst are accompanied by undesirable side reactions such as olefin isomerization, hydrogenation, and dehydrosilylation.[12–14] These side reactions are often ignorable in small molecule chemistry because the byproducts can be easily separated by conventional purification methods such as distillation, recrystallization, or chromatography. However, in macromolecular chemistry, undesired side reactions can be a significant problem because the macromolecular side products cannot be separated from the desired macromolecular products by the aforementioned conventional purification methods. Therefore, tuning the applied reactions to high efficiency and selectivity is crucial in polymer modification reactions.

In this work, we carefully investigated the side reactions in the Karstedt catalyst-catalyzed hydrosilylation reaction on PEG chain ends and developed new hydrosilane reagents

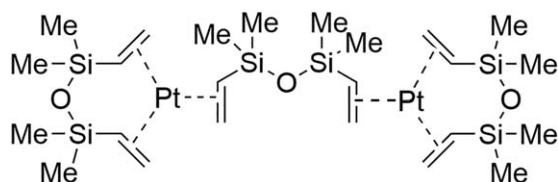Additional Supporting Information may be found in the online version of this article.

FIGURE 1 The chemical structure of Karstedt catalyst.

that yield fewer side products under the same conventional reaction conditions.

EXPERIMENTAL

Materials

All reagents and solvents were obtained from commercial sources and were used without further purification unless otherwise noted. Triethoxysilane, trichlorosilane, chlorodimethylsilane, poly(ethylene glycol) monomethyl ether ($M_n = 750$ g mol^{-1}, 2000 g mol^{-1}, and 5000 g mol^{-1}), and triethylene glycol monomethyl ether were purchased from Sigma-Aldrich. 1,1,3,3-Tetramethyldisiloxane and 1,5-hexadiene were purchased from Alfa Aesar. Karstedt catalyst (2.1–2.4% Pt in xylene) was purchased from Gelest Inc. Dry methylene chloride was obtained by distillation from calcium hydride. Tetrahydrofuran (THF) and diethylene glycol dimethyl ether (diglyme) were distilled from sodium benzophenone ketyl. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F$_{254}$ glass plates, visualized by a dual short wave/long wave UV lamp and staining with an ethanolic solution of potassium permanganate or ceric ammonium molybdate. Column chromatography was performed on Merck silica gel 60 (70–230 mesh).

Instrumentation

^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Varian Inova 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or a Varian Inova 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) NMR spectrometer. Chemical shifts are reported relative to the tetramethylsilane peak (δ0.00) or solvent peak (δ7.26 for CDCl$_3$ in ^{1}H-NMR, δ77.2 for CDCl$_3$ in ^{13}C-NMR). ELEM. ANAL were performed using a Carlo Erba EA 1180 elemental analyzer. These instruments were provided by the Organic Chemistry Research Center (OCRC) at Sogang University. Polymer molecular weights were estimated using a JASCO LC-4000 system equipped with a PU-4285 UHPLC pump, an AS-4050 autosampler, an RI-4030 differential RI detector, and three Shodex KF-800 GPC columns (150, 500, 1500 Å; 300 × 8 mm^2) using chloroform as eluent at a flow rate of 1 mL/min.

General Procedure for the Synthesis of MeO-PEG-OAllyl (1a-1c) (Scheme 1)

Poly(ethylene glycol) (**MeO-PEG45**, $M_n = 2000$ g/mol, 30.0 g, 15 mmol) was dissolved in dry THF (200 mL) in a flame-dried 500 mL round bottom flask, and NaH (60% dispersion in mineral oil; 0.72 g, 18 mmol) was added to the solution under an inert atmosphere. After stirring the yellow suspension for 30 min at room temperature, allyl bromide (1.1 mL, 18 mmol) was added dropwise. The resulting yellow suspension was

stirred at room temperature for 12 h. The solid residue was separated by centrifugation, and the supernatant was decanted into a flask. The decanted solution was dripped into hexanes (1–1.5 L) at 0 °C to precipitate the polymer. The polymer was twice subjected to recrystallization in cold EtOH to provide **1b** as a white solid (22.00 g, 72%): **MeO-PEG$_{45}$-OAllyl (1b)**

^{1}H NMR (400 MHz, CDCl$_3$, δ): 5.96 – 5.86 (m, 1H; C$\underline{H}$ = CH$_2$), 5.29 (dd, J = 1.6, 17.2 Hz, 1H; CH = C$\underline{H}_2$), 5.19 (dd, J = 1.2, 10.4 Hz, 1H; CH = C$\underline{H}_2$), 4.02 (d, J = 5.6 Hz, 2H; OC$\underline{H}_2$CH = CH$_2$), 3.66 (br m; PEG backbone OC$\underline{H}_2$), 3.56 (m, 2 H; OC$\underline{H}_2$), 3.38 (s, 3H; OC$\underline{H}_3$). **MeO-PEG$_{17}$-OAllyl (1a)** MeO-PEG$_{17}$-OH (20.00 g, 27 mmol), NaH (60% dispersion in mineral oil; 2.13 g, 53 mmol), allyl bromide (3.4 mL, 40 mmol); Yield = 10.00 g (47%); ^{1}H NMR (400 MHz, CDCl$_3$, δ): 5.96 – 5.87 (m, 1H; C$\underline{H}$ = CH$_2$), 5.30 (d, J = 17.2 Hz, 1H; CH = C$\underline{H}_a$H$_b$), 5.19 (d, J = 10.0 Hz, 1H; CH$_a$$\underline{H}_b$), 4.03 (d, J = 6.8 Hz, 2H; OC$\underline{H}_2$CH = CH$_2$), 3.66 (br m; PEG backbone OC$\underline{H}_2$), 3.56 (m, 2 H; OC$\underline{H}_2$), 3.38 (s, 3H; OC$\underline{H}_3$). **MeO-PEG$_{113}$-OAllyl (1c)** MeO-PEG$_{113}$-OH (20.00 g, 4 mmol), NaH (60% dispersion in mineral oil; 0.32 g, 8 mmol), allyl bromide (0.5 mL, 6 mmol); Yield = 18.00 g (89%); ^{1}H NMR (400 MHz, CDCl$_3$, δ): 5.95 – 5.88 (m, 1H; C$\underline{H}$ = CH$_2$), 5.30 (dd, J = 1.6, 17.2 Hz, 1H; CH = C$\underline{H}_2$), 5.19 (d, J = 10.4 Hz, 1H; CH = C$\underline{H}_2$), 4.03 (d, J = 5.6 Hz, 2H; OC$\underline{H}_2$CH = CH$_2$), 3.64 (br m; PEG backbone OC$\underline{H}_2$), 3.56 (m, 2 H; OC$\underline{H}_2$), 3.38 (s, 3H; OC$\underline{H}_3$).

Synthesis of 2,5,8,11-Tetraoxatetradec-13-Ene (2)

Triethylene glycol monomethyl ether (**MeO-TEG**, 5.00 g, 30.5 mmol) was slowly added to a vigorously stirred suspension of NaH (60% dispersion in mineral oil; 1.46 g, 36.5 mmol) in dry THF (50 mL) under an inert atmosphere at 0 °C. After stirring for 30 min, the solution was allowed to warm up to room temperature. Allyl bromide (2.26 mL, 36.5 mmol) was dropwise added dropwise, and the resulting yellow suspension was stirred at room temperature for 2 h. The reaction was quenched by adding water (20 mL) and the organics were extracted with CH$_2$Cl$_2$ (3 × 15 mL). The combined organic layers were dried over MgSO$_4$, and then the solvent was removed using a rotary evaporator. The resulting crude product was purified by column chromatography on silica gel using hexanes:EtOAc (10:1) as eluent to give **2** as a colorless oil in 97% yield (6.0 g). R_f = 0.21 (TLC, SiO$_2$, hexanes:EtOAc = 10:1);

^{1}H NMR (400 MHz, CDCl$_3$, δ): 5.95 – 5.86 (m, 1H; C$\underline{H}$ = CH$_2$), 5.30 (dd, J = 1.6 and 17.2 Hz, 1H; CH = C$\underline{H}_2$), 5.19 (d, J = 10.4 Hz, 1H; CH = C$\underline{H}_2$), 4.03 (d, J = 4.4 Hz, 2H; OC$\underline{H}_2$CH = CH$_2$), 3.67 (m, 8H; OC$\underline{H}_2$), 3.56 (dd, J = 5.6, 20.4 Hz, 4H; OC$\underline{H}_2$), 3.38 (s, 3H; OC$\underline{H}_3$). ^{13}C NMR (100 MHz, CDCl$_3$ δ): 134.7, 116.8, 72.0, 71.8, 70.5, 70.4, 69.3.

Synthesis of Tris(2-Methoxyethoxy)Silane (5)

Dichloromethane (100 mL), trichlorosilane (15.00 g, 110 mmol), and a stir bar were placed in a 250 mL three-necked flask equipped with a dropping funnel, condenser, and fritted tube. The flask was then cooled with an ice bath. Nitrogen was introduced through the fritted tube and 2-methoxyethanol (28.70 g, 376 mmol) was then added dropwise from the dropping funnel. After the addition of 2-methoxyethanol, stirring

was continued for 1 h at room temperature, and then the reaction mixture was heated at 50 °C for 3 h. The resulting crude product was purified by vacuum distillation (100 °C, 0.2 mmHg) to give the product **5** as a colorless oil in 39% yield (11.00 g).

^{1}H NMR (400 MHz, C_6D_6, δ): 4.72 (s, 1H; Si-<u>H</u>), 3.93 (t, J = 5.2 Hz, 6H; OC<u>H$_2$</u>), 3.32 (t, J = 5.2 Hz, 6H; OC<u>H$_2$</u>), 3.11 (s, 9H; OC<u>H$_3$</u>); ^{13}C NMR (100 MHz, C_6D_6, δ): 73.3, 61.9, 58.1; Anal. calcd. for $C_9H_{22}O_6Si$: C 42.50, H 8.72, O 37.74, Si 11.04; found: C 42.48, H 8.68.

Synthesis of 2,10-Dimethyl-3,6,9-Trioxa-2,10-Disilaundecane (6)

Dichloromethane (200 mL), diethylene glycol (4.00 g, 37.7 mmol), triethylamine (21 mL, 150.8 mmol), and a stir bar were placed in a 500 mL three-necked flask equipped with a dropping funnel, condenser, and fritted tube. The flask was then cooled with an ice bath. Nitrogen was introduced through the fritted tube, and chlorodimethylsilane (8.20 g, 86.7 mmol) was added dropwise to the reaction mixture from the dropping funnel and stirred for 24 h at room temperature. The resulting crude product was purified by vacuum distillation (80 °C, 0.2 mmHg) to give the product **6** as a colorless oil in 76% yield (6.38 g):

^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.63 (s, 2H; Si-<u>H</u>), 3.78 (m, 4H; OC<u>H$_2$</u>), 3.58 (m, 4H; OC<u>H$_2$</u>), 0.21 (s, 12H; SiC<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 72.5, 63.5, −1.4; Anal. calcd. for $C_8H_{22}O_3Si_2$: C 43.20, H 9.97, O 21.58, Si 25.25; found: C 43.21, H 9.86.

General Procedure A for Hydrosilylation of MeO-PEG-OAllyl Derivatives (1a-c) by Karstedt Catalyst

A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with **1a**, **1b**, or **1c** (0.2–0.5 mmol). The system was vacuum dried at 70 °C and backfilled with nitrogen (3 cycles). Karstedt catalyst (2.1–2.4% Pt in xylene, 20 μL) and trialkoxysilane (1.2–3.0 equiv) were sequentially added to the mixture through the septum with a syringe, and the mixture was stirred at 70 °C for 12 h. The reaction product was filtered, and the filtrate was dripped into diethyl ether (100 mL) at 0 °C to precipitate the polymer.

General Procedure B for Hydrosilylation of 2, 3, and 4 by Karstedt Catalyst

An open screw-capped culture tube was capped with a Teflon-lined septum and charged with **2**, **3**, or **4** (0.2–0.5 mmol). The system was vacuum dried at 70 °C and backfilled with nitrogen (3 cycles). Karstedt catalyst (2.1–2.4% Pt in xylene, 20 μL), trialkoxysilane (1.2–3.0 equiv), and solvent (diglyme) were sequentially added to the mixture through the septum with a syringe, and the mixture was stirred at 70 °C for 12 h. The reaction was monitored by ^{1}H NMR spectroscopy.

Copolymerization of 1,1,3,3-Tetramethyl-Disiloxane with 1,5-Hexadiene by Karstedt Catalyst

A 25 mL Schlenk flask equipped with a magnetic stir bar was flushed with nitrogen. A solution of 1,5-hexadiene (0.61 g, 7.4 mmol) and 1,1,3,3-tetramethyl-disiloxane (1.00 g, 7.4 mmol) was placed in the flask. After adding Karstedt

catalyst (2.1–2.4% Pt in xylene, 5 μL) to the reaction mixture, the reaction was heated at 120 °C for 2 h. After cooling to room temperature, the reaction mixture was diluted with $CHCl_3$ and filtered through activated charcoal/Celite. Volatile substances in the polymer solution were removed using a rotary evaporator. The polymer was obtained as a colorless viscous oil in 94% yield (1.52 g): Poly(2,2,9,9-tetramethyl-2,9-disila-1-oxanona-nylene)[15] (**9**)

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.30 (s, 8H; C<u>H$_2$</u>), 0.51 (br, 4H; SiC<u>H$_2$</u>), 0.04 (s, 12H; SiC<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 33.2, 23.2, 18.5, 0.4; M_w = 3230 gmol^{-1}, M_n = 2560 gmol^{-1}, M_w/M_n = 1.26 by GPC.

Copolymerization of 2,10-Dimethyl-3,6,9-Trioxa-2,10-Disilaundecane (6) with 1,5-Hexadiene by Karstedt Catalyst

A 25 mL Schlenk flask equipped with a magnetic stir bar was flushed with nitrogen. A solution of 1,5-hexadiene (0.61 g, 7.4 mmol) and **6** (1.64 g, 7.4 mmol) was placed in the flask. After adding Karstedt catalyst (2.1–2.4% Pt in xylene, 5 μL) to the flask, the mixture was heated at 120 °C for 2 h. After cooling to room temperature, the reaction mixture was diluted with $CHCl_3$ and filtered through activated charcoal/Celite. Volatile substances in the polymer solution were removed using a rotary evaporator. The polymer was obtained as a colorless viscous oil in 98% yield. (2.23 g): Poly(1,1,9,9-tetramethyl-2,5,8-trioxa-1,9-disilapentadecane) (**10**)

^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.70 (m, 4H; OC<u>H$_2$</u>), 3.53 (m, 4H; OC<u>H$_2$</u>), 1.28 (br, 8H; C<u>H$_2$</u>), 0.57 (br, 4H; SiC<u>H$_2$</u>), 0.07 (s, 12H; SiC<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 72.6, 62.0, 36.2, 33.2, 30.2 23.1, 18.4, 16.3, 15.4, 0.37, −2.1; M_w = 17,700 gmol^{-1}, M_n = 9260 gmol^{-1}, M_w/M_n = 1.91 by GPC.

Calculation of Degree of Conversion

An example of the ^{1}H NMR spectrum of the reaction mixture after hydrosilylation is shown in Supporting Information Figure S1.[16] The degree of conversion (DOC) for the reaction was estimated by ^{1}H NMR spectroscopic analysis according to the following eq 1:

$$\text{DOC} \ (\%) = \frac{I_h/2}{I_{Ei} + I_{Zi} + I_{un} + (I_r/3) + (I_h/2)} \times 100 \qquad (1)$$

where I_h (h = hydrosilylated peak) is the integral peak area of the signals at 0.6 ppm corresponding to —CH_2Si— of the resulting products. Likewise, I_r (r = reduced peak) is the peak area of —CH_3 (0.9 ppm), I_{un} (un = unreacted peak) is the peak area of —CH=CH_2 (5.3 ppm), I_{Ei} (Ei = E-isomer peak) is the peak area of —OCH=CH— (6.2 ppm), and I_{Zi} (Zi = Z-isomer peak) is the peak area of —OCH=CH— (6.0 ppm).

RESULTS AND DISCUSSION

Mechanism of Hydrosilylation

In 1965, Chalk and Harrod suggested a mechanism for the hydrosilylation reaction analogous to the transition metal-catalyzed hydrogenation reaction (Scheme 2).[17] The initial
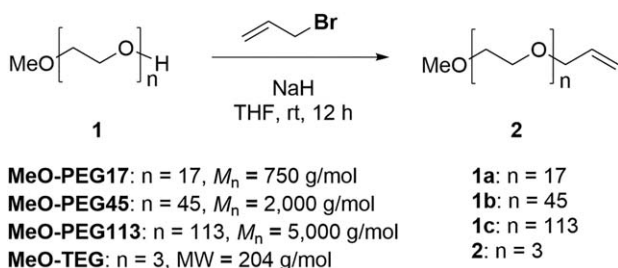
SCHEME 1 Synthesis of allyl functionalized poly(ethylene glycol)s **1a-c** and O-methyltriethylene glycol **2**.

step of the catalytic cycle is oxidative addition of Pt(0) species (**I**) into hydrosilane (R₃SiH). The resulting platinum hydride species (**II**) then coordinates with the olefin to generate intermediate **III**. The complex is then transformed through 1,2-migratory insertion into **IV**. Finally, Pt(0) species (**I**) is regenerated by reductive elimination from intermediate **IV**, expelling the hydrosilylated product **V**.

Since then, many research groups have reported mechanistic studies on Karstedt catalyst, with some experimental evidence.[18–23] Of note among these are Stein and coworkers'experimental results, which provide some hints about the origin of side reactions.[21] They suggested that the main cause of side reactions is the colloidal platinum species formed during the hydrosilylation reaction catalyzed by Karstedt catalyst. Recently, the Kühn group provided further support for this postulation by performing computational calculations and kinetic studies.[24,25]

One of the reasons for the formation of colloidal Pt species is the dissociation of relatively unstable divinyltetramethylsiloxane (dvtms) ligands from the Karstedt catalyst.[26] To avoid this undesirable process, much research effort has been devoted either to developing new Pt catalysts employing stronger ligands such as electron-rich phosphine,[27] quinine,[28] and N-heterocyclic carbene (NHC)[29] or to exploring other transition metals such as Ir, Rh, Co, and Pd or nonmetal catalysts.[14] Nevertheless, Pt-catalyst-based hydrosilylation is still the most popular catalytic technique especially in polysiloxane or silicone-related industries.

Hydrosilylation at PEG Chain Ends

α-O-methyl-ω-O-allyl PEG (**1b**, number average molecular weight $M_n = 2000$ g mol^{-1}) was prepared and subjected to the hydrosilylation reaction under conventional reaction conditions (neat, 70 °C, 12 h) using Karstedt catalyst, and the reaction was monitored by ^{1}H-NMR spectroscopy (Fig. 2). In the ^{1}H-NMR spectrum of the crude reaction mixture, two major undesired products, alkene group-reduced (**RD**) product **1b-RD** and alkene group-isomerized (**IS**) products (**1b-IS**, E and Z isomers), were identified in addition to the expected hydrosilylated (**HS**) product **1b-HS** (See experimental section and Supporting Information). Since no resonance for starting polymer **1b** was observed in the ^{1}H-NMR spectrum of the crude products, the reaction appeared to have been completed in 12 h. A new peak appearing at the most upfield-shifted resonance of 0.62 ppm

was assigned to the characteristic peak of the desired hydrosilylated product **1b-HS** (Si—CH₂). A triplet peak at 0.91 ppm was assigned to the methyl group (CH₂CH₃) of the simple hydrogenation product of the terminal allyl group. Resonances corresponding to the E and Z isomers of **1b-IS** were easily identified [6.26 ppm (d, $J = 12.0$ Hz, OCH = CHCH₃(E)), 5.98 ppm (d, $J = 6.4$ Hz, OCH = CHCH₃ (Z)), 4.81 ppm (dq, $J = 6.8$ and 12.0 Hz, OCH = CHCH₃(E)), 4.42 ppm (dq, $J = 6.8$ and 6.8 Hz, OCH = CHCH₃(Z)), 1.58 ppm (d, $J = 6.8$ Hz, OCH = CHCH₃(Z)), and 1.55 ppm (d, $J = 6.8$, OCH = CHCH₃(E))]. From the integration data of the assigned resonance peaks, the molar ratio of **HS/RD/IS** was determined to be 32/8/60. This result clearly shows that the hydrosilylation reaction on a single alkene group at the PEG terminus was not efficient (only ~32% yield), generating the undesired hydrogenation (~8%) and isomerization (60%) side products in substantial amounts. Conversely, when the same reaction was performed on a small molecule alkene such as allyl ethyl ether [EtOCH₂CH = CH₂ (**3**)], the hydrosilylation was highly selective and efficient (88% yield). It seems that hydrosilylation of a polymer chain end has a molecular weight effect that induces side reactions. In this work, we carefully investigated the hydrosilylation reaction at the PEG chain end to determine the cause of enhanced side reactions and designed a new hydrosilylation reagent that can suppress the side reactions on polymer chain ends.

The aforementioned side reactions in hydrosilylation reactions have also been noted and discussed by several other research groups. Lewis and coworkers suggested that hydrogen gas can be generated either from water or alcohol under conventional hydrosilylation conditions when the Karstedt catalyst is used as the source of the hydrogenated byproduct.[18] According to their subsequent studies, they noticed the formation of colloidal Pt species during the hydrosilylation, which were investigated for their effects on the hydrosilylation reaction.[20,21] In particular, the use of excess hydrosilane and weakly coordinating olefin was claimed to be a major cause of colloidal Pt species formation.
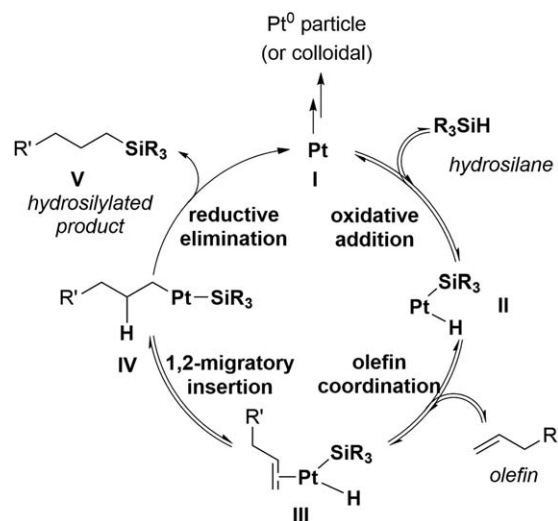
SCHEME 2 Chalk–Harrod mechanism for the platinum catalyzed hydrosilylation of olefins.
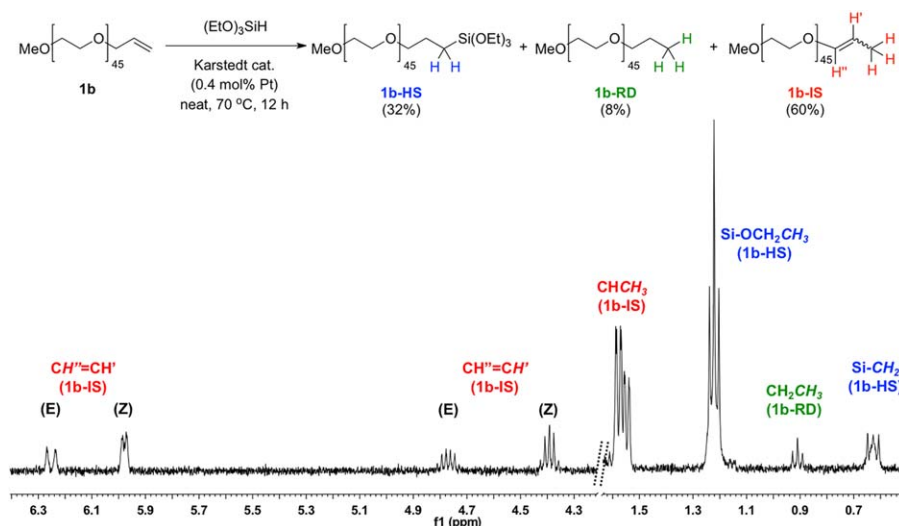
FIGURE 2 A representative ^{1}H-NMR spectrum of the crude hydrosilylation products of allyl group functionalized PEG **1b** ($M_n = 2000$ gmol^{-1}; in CDCl$_3$, 400 MHz). In addition to the set of resonances attributable to the desired hydrosilylation (**HS**) product **1b-HS**, the resonance peaks from the undesired reduction (**RD**) product **1b-RD**, and the isomerization (**IS**) product **1b-IS** can be also identified. [Color figure can be viewed at wileyonlinelibrary.com]

Recently, the Kühn group observed that formation of inactive colloidal Pt species was promoted by increased concentrations of Pt catalyst for hydrosilylation.[25] In the hydrosilylation reaction of 1-octene with HSiCl$_3$, the authors experimentally confirmed that larger amounts of side products were produced as more colloidal Pt particles were formed, while the initial rate of hydrosilylation was decreased.

According to the literature, the main presumed reasons for side reactions in the Karstedt catalyst-catalyzed hydrosilylation are (1) the use of excess hydrosilane,[21] (2) the presence of water or alcohol,[18] and (3) high concentration of Pt catalyst.[21,25] However, since all of these studies were carried out with small alkene molecules, it is uncertain whether these reasons might be sufficient to explain the unusually high yield of the side products in hydrosilylation at polymer chain ends. In general, the concentration of alkene groups at the polymer chain ends is considered to be inherently low due to the high molecular weight of the polymer chains. Therefore, this low concentration effect of the functional group should be taken into account.

Model Study
To examine factors governing aspects of the hydrosilylation reaction, a set of small model compounds (**2**, **3**, **4**) were chosen and subjected to hydrosilylation reactions under various conditions (Table 1).

First, all of the reagents were carefully dried prior to the reactions to prevent side reactions arising from the presence of water. Second, the concentration of Karstedt catalyst was fixed at 0.1 mol % with respect to olefin to rule out a concentration effect of the catalyst. Third, the amount of trialkoxysilane was set to 1.2 equiv. Once these factors were fixed the effect of molar concentration of olefin was investigated by varying its concentration.

In the absence of triethoxysilane [(EtO)$_3$SiH], no reaction occurred (Entry 1). Neither hydrosilylation nor reduction products were observed without triethyoxysilane even if water was added to the reaction mixture (Entry 2). However, when both triethoxysilane and water were present, **2** was completely converted to **2-RD** (Entry 3). From these observations, it is apparent that hydrosilane reacts with water in the presence of Karstedt catalyst to generate hydrogen gas, leading to reduction of the olefin groups (see also Fig. S11 in Supporting Information).

To examine the concentration effect of hydrosilylation, reactions were performed under dilute conditions. Diglyme [CH$_3$(OCH$_2$CH$_2$)$_2$OCH$_3$] was used as the dilution solvent to mimic PEG chains. As olefin **2** was diluted, the production of hydrosilylated compound **2-HS** was significantly diminished, and more byproducts, **2-RD** and **2-IS**, were formed (Entries 4–7, see also Fig. S13 in Supporting Information). Likewise, the hydrosilylation of allyl ethyl ether **3** was similar to that of **2** (Entries 8–10, see also Fig. S14 in Supporting Information). In the case of 1-decene (**4**), which lacks an alkyloxy group at the allylic position, hydrosilylation product **4-HS** was obtained in a comparable yield (80%), but isomerization product **4-IS** was the only side product, formed in 20% yield with no reduction byproduct **4-RD** observed (Entry 11).

Chelation Effect of Hydrosilane
Based on the above results that show a significant olefin concentration effect on the hydrosilylation yield, we propose a new plausible hydrosilylation mechanism, shown in Scheme 3, in which a competitive isomerization catalytic cycle is also considered. Since Pt belongs to group 10 and prefers 16 electron complexes, only 14 or 16 electron species were considered in these catalytic cycles. It should be noted that the Karstedt catalyst is a 16-electron complex.

TABLE 1 Hydrosilylation of Allyl Group-Functionalized Small Molecules **2**, **3**, and **4** using Karstedt Catalyst


Entry	Substrate[a]	$(EtO)_3SiH$ (equiv)	Solvent	Concentration[b] (M)	Additive	Conversion (%)	Product Ratio (%) (HS/RD/IS)
1	**2**	–	neat	5.0	–	0	No rxn
2	**2**	–	neat	5.0	50 μL (H_2O)	0	No rxn
3	**2**	1.2	neat	2.5	50 μL (H_2O)	100	0/100/0
4	**2**	1.2	neat	2.5	–	100	75/24/1
5	**2**	1.2	diglyme	1.0	–	100	75/10/15
6	**2**	1.2	dIglyme	0.1	–	100	59/24/17
7	**2**	1.2	dIglyme	0.05	–	100	54/31/15
8	**3**	1.2	neat	3.3	–	100	88/10/2
9	**3**	1.2	diglyme	1.0	–	100	83/10/7
10	**3**	1.2	dIglyme	0.1	–	100	66/18/16
11	**4**	1.2	neat	2.4		100	80/0/20

[a] 1.0 mmol.

[b] Molar concentration is expressed in moles of the allyl derivatives per total volume of the reaction mixture.
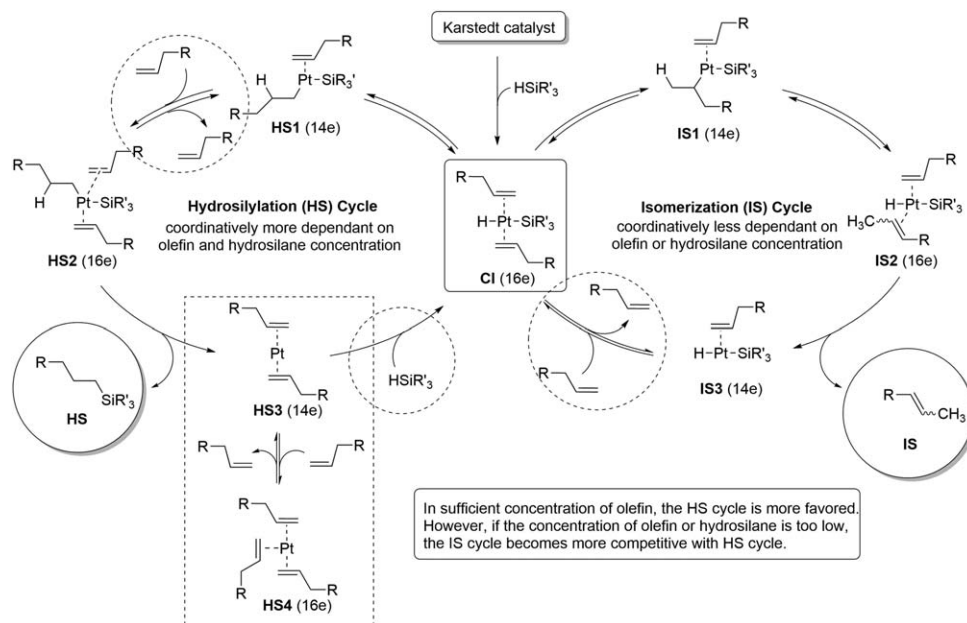
SCHEME 3 Competition of hydrosilylation reaction with isomerization reaction. While the isomerization catalytic cycle requires introduction of alkene only in one step to maintain the cycle with relatively stable 14e or 16e species, the hydrosilylation catalytic cycle requires an additional coordination step with olefin substrate to coordinatively stabilize the 14-electron species **HS3**.
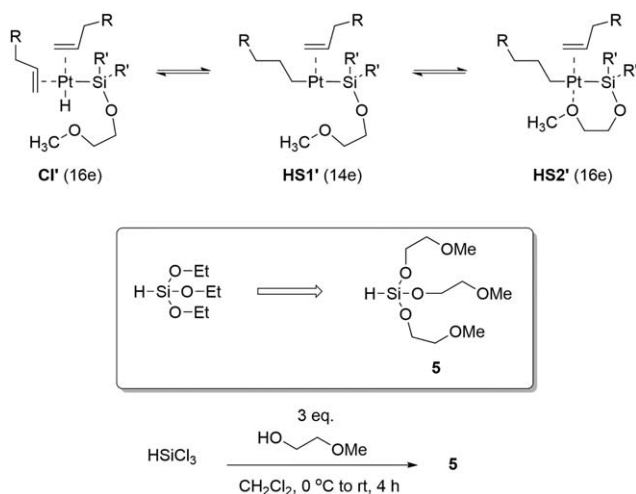
SCHEME 4 Introduction of an internal weakly coordinating group into hydrosilane and synthesis of tris(2-methoxyethoxy)-silane (**5**).

Once the Karstedt catalyst is exposed to both hydrosilane (HSiR$_3$') and olefin substrate, it will be transformed to the platinum hydride common intermediate (**CI**). The common intermediate **CI** can then experience one of two fates, the hydrosilylation catalytic cycle (left-hand side) or the isomerization catalytic cycle (right-hand side). The left-hand-side catalytic cycle in Scheme 3 represents the conventional Chalk–Harrod type hydrosilylation mechanism in which possible ligand association-dissociation steps are described. The cycle is comprised of (1) migratory insertion of the olefin into the platinum hydride bond to form unstable 14-electron complex **HS1**, (2) association with olefin substrate to form more stable 16-electron complex **HS2**, (3) release of the hydrosilylation product **HS** by reductive elimination with concomitant formation of 14- electron complex **HS3**, (4) oxidative addition of hydrosilane (HSiR$_3$') to **HS3** to regenerate **CI**.

Conversely, the isomerization catalytic cycle can be described in four steps starting from the common intermediate **CI**: (1) migratory insertion of olefin into the platinum-hydride bond to form 14e complex **IS1**, which is a regioisomeric complex of **HS1**, (2) reductive elimination to form **IS2**, (3) dissociation of isomerized product **IS** from **IS2** to release the 14-electron species **IS3**, (4) regeneration of **IC** by complexation of an olefin substrate.

On comparing the two catalytic cycles, it is readily apparent that the left-hand side hydrosilylation cycle should be more dependent on the concentration of olefin substrate and hydrosilane because the hydrosilylation cycle includes one olefin association-dissociation step and one hydrosilane addition step while the isomerization cycle includes only one olefin association-dissociation step. In addition, the unstable 14-electron species **HS3** may have a longer lifetime if the concentration of olefin or hydrosilane is high enough to form the more stable 16 electron species **HS4** or **CI**.

From a careful comparative mechanism analysis in which reasonable coordination chemistry is considered, it was envisioned that stabilizing the 14-electron intermediates **HS1** and **HS3** might be crucial to promote the hydrosilylation pathway over the isomerization pathway, especially at a low concentration of olefin substrate. We posited that introduction of an internal weakly coordinating group such as methoxyethyloxy group into the silane might promote the hydrosilylation catalytic cycle even with a low olefin substrate concentration by quickly converting 14-electron species **HS1'** into the more stable 16-electron species **HS2'** by internal coordination (Scheme 4). This process should prolong the lifetime of the reductive elimination pathway bypassing the **HS2** intermediate with the **HS2'** intermediate, which is independent of the concentration of olefin substrate. It is also true that the internally coordinating silane should stabilize **IS1**-like intermediate as it stabilizes **HS1**-like intermediate **HS1'**. However, we thought that the relative stability of **HS1'** compared to the **IS1**-like intermediate would be more enhanced because of the more steric hindrance exerted in **IS1**-like intermediate, thereby promoting hydrosilylation over isomerization. Tris(2-methoxyethoxy)silane **5** was prepared straightforwardly via S$_N$2 reaction of HSiCl$_3$ with 3 equiv of 2-methoxyethanol (Scheme 4).[30]

Hydrosilylation reactions of olefins **3** and **4** with the new tailor-made hydrosilane, tris(2-methoxyethoxy)silane (**5**), are summarized in Table 2. To our surprise, no isomerization byproduct **3-IS** was observed at any concentration of olefin **3** (Entries 1–4, Fig. S15 in Supporting Information), while hydrogenation product **3-RD** was still produced in substantial amounts (12–25%). This result implies that the tighter chelation between the Pt catalyst and the silane significantly diminishes production of isomerization byproduct **3-IS**. Since the reduction product **3-RD** might have been produced through *in situ* generated hydrogen catalyzed by Pt species from moisture (water) in the reaction medium, a reaction was performed in the presence of molecular sieves (4 Å) to remove any residual water in the system (Entry 5). Addition of molecular sieves (4 Å) to the reaction mixture produced the desired hydrosilylated product **3-HS'** in 99% yield (Fig. S16 in Supporting Information). When the solvent was changed from diglyme to THF or toluene, more of the byproducts **3-RD** and **3-IS** were produced (Entries 6–7). Lastly, hydrosilylation of olefin **4** with tris(2-methoxyethoxy)silane **5** also provided the desired product **4-HS'** in higher yield (90%) with less production of isomerized byproduct **4-IS** (10%) compared to the results of Entry 11 in Table 1 (Entry 8).

Hydrosilylation of PEGs with Hydrosilane 5

Subsequently, we investigated whether the same favorable effects would be observed in hydrosilylation with hydrosilane **5** at the polymer chain ends (Table 3). All experiments were conducted under similar conditions as above except for the amounts of Karstedt catalyst loading (0.1–0.4 mol % with respect to olefin). Since the effective concentrations of the olefin in these polymeric systems was too low, more

TABLE 2 Hydrosilylation of Allyl Functionlized Derivatives with Tris(2-methoxyethoxy)silane (**5**)


Entry	Substrate[a]	Solvent	Concentration[b] (M)	Additive	Conversion (%)	Product Ratio (%) (HS'/RD/IS)
1	**3**	neat	2.0	–	100	88/12/0
2	**3**	dIglyme	1.0	–	100	83/17/0
3	**3**	dIglyme	0.1	–	90	75/25/0
4[c]	**3**	dIglyme	0.1	–	100	76/24/0
5	**3**	dIglyme	1.0	4 Å MS	100	99/1/0
6	**3**	THF	0.1	–	100	85/12/3
7	**3**	Toluene	0.1	–	100	86/8/6
8	**4**	neat	1.9		100	90/0/10

[a] 1.0 mmol.
[b] Molar concentration is expressed in moles of allyl derivatives per total volume of reaction mixtures.
[c] Reaction time 24 h.

than 0.1 mol % of catalyst against olefin was required to maintain the reproducibility of the experiments. It was found that the concentration of hydrosilane **5**, reaction time, and olefin molar concentration in the PEG chain end did not affect the reaction. In the ^{1}H-NMR spectra of these reaction mixtures, the molar ratio of **1a,b-HS'/1a,b-RD/1a,b-IS** was determined to be approximately ~88/3/9 (Entries 1–4). In

particular, the molar ratios of isomerized products were significantly lower than that obtained with triethoxysilane under the same conditions (Entries 6–7; Supporting Information Fig. S19). However, the hydrosilylation of the polymer chain ends was not free of olefin isomerization byproducts, unlike reactions with low molecular weight olefins. The molar ratio of isomerized byproduct of olefins tended to

TABLE 3 Hydrosilylation of Allyl Functionlized PEG Derivatives with Tris(2-methoxyethoxy)silane (**5**)
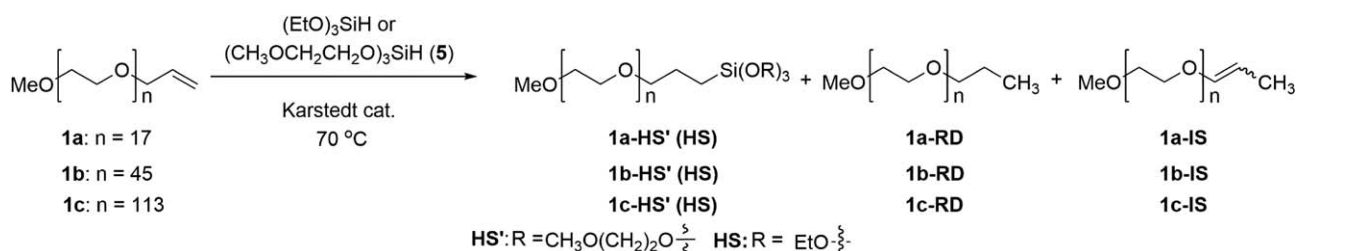
Entry	Substrate	Silane (equiv)	Concentration[a] (M)	Catalyst (mol % Pt)	Time (h)	Conversion (%)	Product Ratio (%) (HS' or HS/RD/IS)
1	**1a**	(CH$_3$OCH$_2$CH$_2$O)$_3$SiH (1.2)	0.96	0.1	12	100	88(**HS'**)/5/7
2	**1b**	(CH$_3$OCH$_2$CH$_2$O)$_3$SiH (3.0)	0.40	0.4	24	100	88(**HS'**)/3/9
3	**1b**	(CH$_3$OCH$_2$CH$_2$O)$_3$SiH (3.0)	0.40	0.4	12	100	87(**HS'**)/3/10
4	**1b**	(CH$_3$OCH$_2$CH$_2$O)$_3$SiH (1.5)	0.48	0.4	12	100	87(**HS'**)/3/10
5	**1c**	(CH$_3$OCH$_2$CH$_2$O)$_3$SiH (1.5)	0.21	0.25	12	100	69(**HS'**)/0/31
6	**1b**	(EtO)$_3$SiH (3.0)	0.45	0.4	12	100	32(**HS**)/8/60
7	**1c**	(EtO)$_3$SiH (3.0)	0.21	0.25	12	100	17(**HS**)/17/66

[a] Molar concentration is expressed in moles of allyl derivatives per total volume of reaction mixtures. Density of PEG (at 20 °C, gmol^{-1}); PEG (200) = 1.12, PEG (400) = 1.13, PEG (1000–10,000) = 1.2.[31]
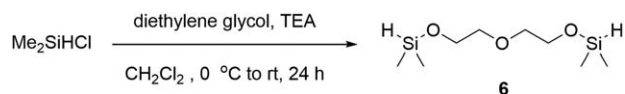
SCHEME 5 Synthesis of 2,10-dimethyl-3,6,9-trioxa-2,10-disilaundecane (**6**).

increase with increasing molecular weight of the polymer (Entry 5). It seems that the degree of inhibition of this side reaction by the chelation effect of the silane group is still influenced to some extent by the molecular weight of the polymer, probably by the inherent dilution effect.
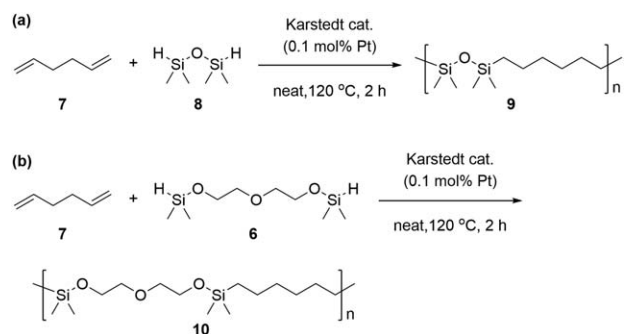
Copolymerization of 1,5-Hexadiene with Disiloxane

In 1999, Weber and coworkers attempted to copolymerize α,ω-diene and 1,3-dihydridotetramethyldisiloxane by hydrosilylation using the Karstedt catalyst.[32] Although hydrosilylation is known to be a high yielding reaction, the maximum molecular weight they could obtain was only 3100 gmol^{-1} (determined by GPC MALLS). The low molecular weight was ascribed to side reactions such as olefin isomerization or reduction at the growing polymer chain ends since these side reactions act to terminate the polymerization.

To demonstrate the importance of a stronger chelating hydrosilane for efficient and selective hydrosilylation, we attempted to synthesize high molecular weight copolymers by hydrosilylation of chelating α,ω-bis(hydrosilane) and α,ω-diene. For this work, a new α,ω-bis(hydrosilane) **6** was synthesized as shown in Scheme 5. A simple substitution reaction between chlorodimethylsilane (Me$_2$SiHCl) and diethylene glycol in the presence of trimethylamine produced α,ω-bis(hydrosilane) **6**. Since α,ω-bis(hydrosilane) **6** bears an ether linkage in the middle of the chain, it might be capable of chelating Pt catalyst intermediates during the catalytic cycle.

For a comparative study of the copolymerization using Karstedt catalyst, a non-chelating dihydroxilane, 1,1,3,3-tetramethyldisiloxane [H(CH$_3$)$_2$SiOSi(CH$_3$)$_2$H] (**8**), was also subjected to the copolymerization with 1,5-hexadiene (**7**) (Scheme 6a).

The copolymerization reaction was carried out at a 1:1 ratio of 1,1,3,3-tetramethyldisiloxane and 1,5-hexadiene in the presence of a catalytic amount of Karstedt catalyst (0.1 mol %) under a nitrogen atmosphere at 120 °C for 2 h. After the reaction, the

TABLE 4 GPC Data of Polymers **9** and **10**

Polymer	DP[a]	M_n[b] (gmol^{-1})	M_w[b] (gmol^{-1})	PDI[b]
9	10.8	2600	3200	1.3
10	29.4	9300	18,000	1.9

[a] Degree of polymerization.
[b] Estimated from the GPC system, eluent:CHCl$_3$ (100) and PS as a standard.

crude copolymer was filtered through activated charcoal to remove the Pt catalyst. The desired copolymer **9** was obtained as a colorless viscous oil in 94% yield and was characterized by GPC and ^{1}H-NMR spectroscopy. According to the GPC profile, the number average molecular weight (M_n) of the resulting poly(2,2,9,9-tetramethyl-2,9-disila-1-oxanona-nylene) (**9**) was only 2600 g mol^{-1} with a degree of polymerization (DP) of 10.8. These results are very similar to the previous results reported by the Webber group (M_n = 3100 gmol^{-1}, DP = 13.3).[32] Subsequently, we performed the hydrosilylation polymerization of 2,10-dimethyl-3,6,9-trioxa-2,10-disilaundecane (**7**) and 1,5-hexadiene (**8**) under the same reaction conditions (Scheme 6b). The desired copolymer, poly(1,1,9,9-tetramethyl-2,5,8-trioxa-1,9-disilapentadecane) (**10**), was obtained as a colorless viscous oil in 98% yield. Characterization of the polymer by GPC and ^{1}H-NMR spectroscopy revealed that the M_n of copolymer **10** was 9300 gmol^{-1} with a DP of 29.4. Small traces of resonance peaks at ~5.4 ppm (C$\underline{H}$=CHCH$_3$) and 1.5–1.7 ppm (CH=CHC$\underline{H}_3$) were identified in both ^{1}H-NMR spectra of Polymers **9** and **10**, which indicates that the polymerization was indeed terminated by the isomerization side reaction (Supporting Information Figs. S20 and S22). The molecular weight and DP of **10** increased about three fold when chelating disilane **6** was used rather than copolymer (**9**) (Table 4 and Fig. 3).

This experiment demonstrated that utilizing the chelating effect of the silane enabled the hydrosilylation polymerization to
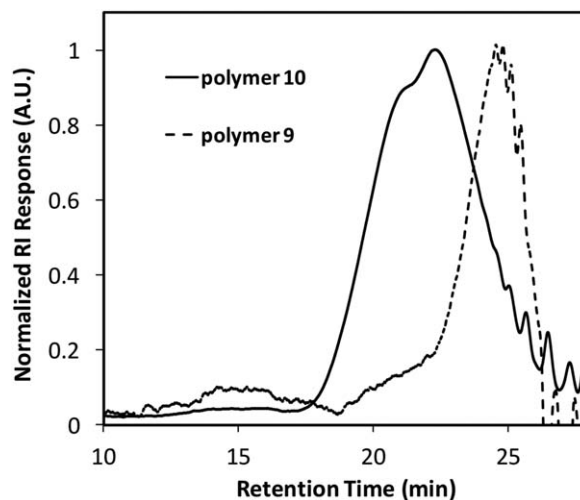

SCHEME 6 Hydrosilylation copolymerization of 1,5-hexadiene (**7**) and disiloxanes (**6** and **8**).

FIGURE 3 GPC curves of Polymer **9** (dashed line) and Polymer **10** (solid line).

efficiently yield a significantly higher molecular weight copolymer through suppression of chain terminating side reactions.

CONCLUSIONS

In this study, the causes of various side reactions occurring in the hydrosilylation of polymers with Karstedt catalyst were investigated, and a new approach to circumvent this problem was developed. The major side reactions that occurred in the hydrosilylation of polymer chain ends were olefin reduction and isomerization. In particular, reduction was mainly caused by hydrogen gas generated from a small amount of water present in the reaction. When the molar concentration of the olefin as reactant was too low, the formation of side products of the isomerization reaction increased. Based on these results and careful analysis of the mechanism, new alkoxysilane **5** capable of forming stronger coordination with the platinum catalyst was designed and synthesized. The use of new silane **5** effectively suppressed isomerization in the hydrosilylation regardless of the concentration of olefin. In addition, it was confirmed that the production of side products by isomerization was significantly decreased by the chelating effect of silane in the hydrosilylation of various allyl- functionalized PEG derivatives at the chain ends. Finally, a relatively high molecular weight copolymer was obtained by copolymerization of 1,5-hexadiene with disilane **6**. This new hydrosilylation method is expected to be widely applicable to the synthesis of various polymeric materials through effective inhibition of side reactions.

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