Metal-Free Catalysis

Deutsche Ausgabe: DOI: 10.1002/ange.201507863
Internationale Ausgabe: DOI: 10.1002/anie.201507863

Metal-Free Hydrosilylation Polymerization by Borane Catalyst

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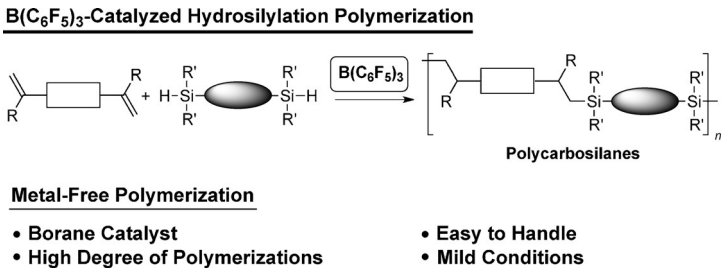
Dedicated to Professor Yoon Sup Lee

Abstract: *The first example of metal-free hydrosilylation polymerization between dienes and disilanes is developed by using a borane catalyst, $B(C_6F_5)_3$ to replace precious transition-metal-based systems. Under the easy-to-handle and mild conditions, a step-growth polymerization of two readily available diene and disilane units was achieved with high degrees of polymerization. Various combinations of dienes and disilanes produced polycarbosilanes with a broad range of structures and properties.*

Hydrosilylation, the insertion of Si–H bond across unsaturated bonds, such as in alkenes, alkynes, carbonyls, and imines, is one of the most versatile reactions in chemical synthesis.[1] The commercial hydrosilylation processes provide various kinds of organosilicon compounds and polymers for the applications of fluids, moldings, paper release coatings, adhesives, paints, and ceramics.[2] The hydrosilylation reactions have also played an important role in the synthesis of complex functional molecules.[3] Since the first hydrosilylation was reported in 1947,[4] various transition-metal-based catalytic systems, mostly platinum complexes such as Karstedt's and Speier's catalysts, have been utilized.[5,6]

However, concerns on low abundance, cost, toxicity, and undesirable side reactions from the precious-metal systems have been driving forces for chemists to search for the next generation catalysts, desirably metal-free reactions.[7,8] This would be particularly beneficial for high molecular weight organosilicon products, because the metallic residue is often hard to remove from the polymeric materials.[9] The residual metals frequently bring complications for the applications in biology, electronics, and optics. In addition, considering that a wide range of polymeric products are being manufactured or fabricated under harsh process conditions, such as extrusion, molding, etching, and curing, the residual metals could be a cause of undesirable polymer degradations or structural alternations.[10] While extensive research efforts resulted promising metal-free methods in controlled radical, ring-opening metathesis, ring-opening polymerizations, and polysiloxane synthesis,[11] no significant studies have been reported so far on the hydrosilylation polymerization. In this context, continuing our efforts on borane-catalyzed hydrosilylative reactions,[12] we have explored transition-metal-free hydrosilylation polymerizations, and present herein our results on a highly efficient $B(C_6F_5)_3$-catalyzed step-growth polymerizations between dienes and disilanes (Scheme 1).



Scheme 1. Metal-free hydrosilylation polymerization.

Extensive efforts to replace precious-metal-based catalysts have resulted in the development of metal-free catalytic hydrosilylations along with earth-abundant metal catalysts.[13] After the initial finding of $B(C_6F_5)_3$-catalyzed hydrosilylative reduction of aldehydes pioneered by Piers and Parks,[14] several Lewis acidic main-group compounds, such as boranes,[13a–d] silanes,[13e] and organophosphonium cations[13f] have been reported to catalyze hydrosilylations.[15] Unlike transition-metal catalysts which trigger the reaction by an oxidative insertion into a Si–H bond (Chalk–Harrold mechanism),[16] the electron-deficient Lewis acids, representatively $B(C_6F_5)_3$, activate a Si–H bond via η^1-coordination to add across unsaturated bonds (Scheme 2). The difference in activation pathways has brought distinctive reactivity and synthetic utility between these two types of activators.[17]

The elegant independent studies of Gevorgyan et al.[13a] and Oestreich et al.[13b] on the Lewis acidic borane-catalyzed hydrosilylation of carbon–carbon multiple bonds and our own investigations on the $B(C_6F_5)_3$-catalyzed silylative reduction of quinolines, nitriles, and other functionalities,[12] presupposed us to envision that this highly reactive catalytic system

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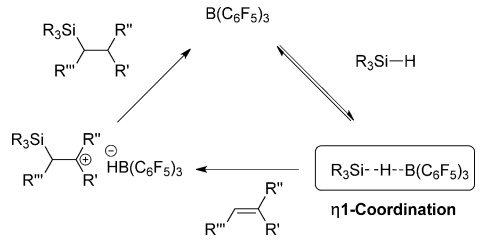
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507863.



Scheme 2. $B(C_6F_5)_3$-catalyzed alkene hydrosilylation.

could bring out a metal-free step-growth hydrosilylation polymerization.[18] After a promising observation of quantitative hydrosilylation of alkene **1a** (1,4-diisopropenylbenzene) with dimethylphenylsilane at room temperature by $B(C_6F_5)_3$ catalyst (Scheme 3a), we started to study the polymerization between **1a** and disilane (**2a**) as a model system (Scheme 3b and Table 1).

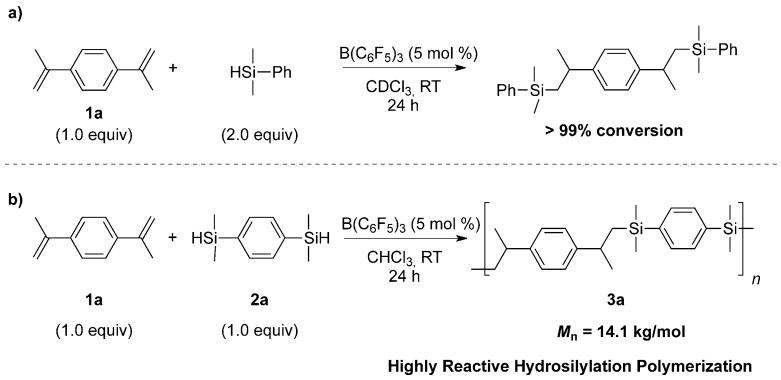
Tris(pentafluorophenyl)borane catalyst (5 mol%) in chloroform successfully produced the desired polycarbosilane (**3a**) with a high degree of polymerization from a stoichiometrically balanced monomer mixture, which is, to our knowledge, the first metal-free hydrosilylation polymerization with a high molecular weight ($M_n = 14.1$ kg mol^{-1}; Table 1, entry 1).[19] The polydispersity index ($M_w/M_n = 1.90$) was close to 2.0, which is expected in a well-controlled step-growth polymerization based on the Carothers equation.[20] The moderate yields were due to the formation of low molecular weight cyclic products (ca. 40%), which were efficiently removed during the precipitation steps.[21]

While polymerization efficiency was proportional to the catalyst loadings, molecular weight stayed in a similar range with more than 5 mol% of $B(C_6F_5)_3$ catalyst (entries 1–4). Effects of altering the monomer ratio on the polymerization were scrutinized (entries 5–8). Tuning of stoichiometry gave a control of molecular weights. In addition, the resulting productions of alkene or silane end telechelic polymers[22] are anticipated to be useful for the construction of functional macrostructures. In terms of reactivity, note that $B(C_6F_5)_3$ is known to promote a cationic polymerization of styrene derivatives.[23] When $B(C_6F_5)_3$ (5 mol%) was mixed with diene **1a** solely, highly cross-linked product was quickly formed within 5 min at room temperature (Figure 1, left). However, when diene was added to the solution of $B(C_6F_5)_3$ and silane, the homopolymerization of diene was fully suppressed (Figure 1, right). It is believed that the unique η^1-coordination of silane to $B(C_6F_5)_3$ completely prevented alkene polymerization, while other Lewis acids, such as $AlCl_3$, furnished hydrosilylation products with a notable amount of alkene polymerization byproducts.[7d,13a]

Upon the preliminary observation that highly reactive hydrosilylation polymerization can be achieved by the action of $B(C_6F_5)_3$ catalyst, a series of dienes and disilanes were subjected to the optimized conditions to furnish polycarbosilanes with controllable structures and properties (Table 2). Structural alternations of dienes were first explored with 1,4-bis(dimethylsilyl)-benzene **2a** (entries 1–4). Changes of the linker shape between double bonds in dienes did not hamper the polymerization efficiency (entries 1–3).

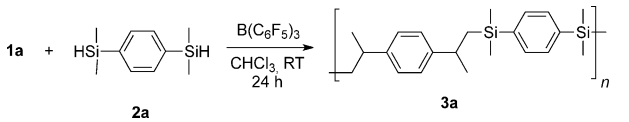
However, the change of double-bond character was found to affect the polymerization efficiency. For instance, whereas 2,2′-dialkyl substituted diene monomers are highly reactive towards polymerizations, a non-substituted terminal diene, 1,8-nonadiene **1d**, furnished only low molecular weight oligomers with disilane **2a** (entry 4). Considering the mechanism of the $B(C_6F_5)_3$-mediated alkene hydrosilylation (Scheme 2), the stabilization of β-silylium cation intermediate is important to attain high reaction efficiency. Tertiary carbocations will be formed in situ more favorably from 2,2′-dialkyl substituted dienes than secondary carbocations from non-substituted terminal dienes, which would be reflected in the difference in the degree of polymerization.

Assorted silanes were subsequently examined under the borane-catalyzed polymerization conditions (entries 1 and 5–8). 1,4-Diisopropenylbenzene (**1a**) was efficiently polymerized with a range of disilanes or dihydrosilanes largely



Scheme 3. a) Highly reactive $B(C_6F_5)_3$-catalyzed hydrosilylation and b) hydrosilylation polymerization.

Table 1: Optimization of the $B(C_6F_5)_3$-catalyzed hydrosilylation polymerization.[a]



Entry	**2a** [equiv]	$B(C_6F_5)_3$ [mol%]	M_n[b] [kg mol^{-1}]	M_w/M_n[b]	Yield[c] [%]
1	1.00	5	14.1	1.90	54
2	1.00	1	11.7	2.00	54
3	1.00	3	13.4	2.01	54
4	1.00	10	14.1	1.88	50
5	0.90	5	5.9	1.99	49
6	0.95	5	7.2	1.83	41
7	1.05	5	8.9	1.77	54
8	1.10	5	6.4	1.61	49

[a] Polymerization conditions: **1a** (1.00 mmol), **2a**, and $B(C_6F_5)_3$ in $CHCl_3$ (1.0 mL). [b] Determined by gel permeation chromatography (GPC) calibrated with polystyrene standards in chloroform at 35 °C. [c] Yield of isolated product.

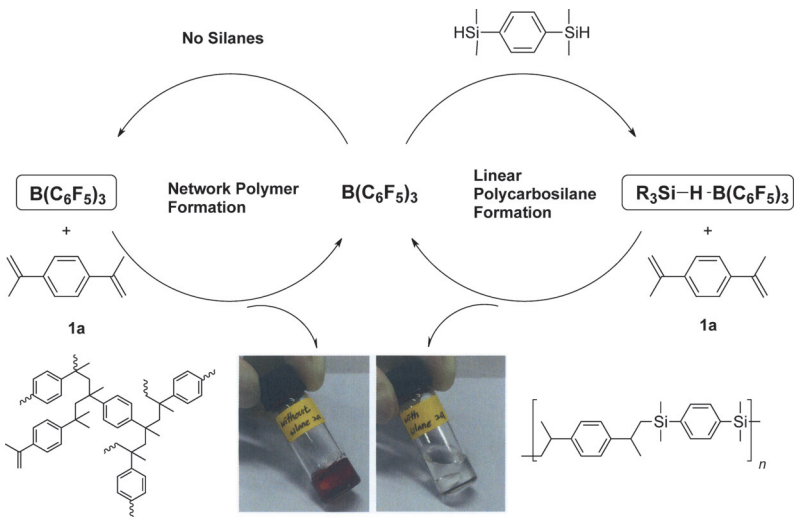
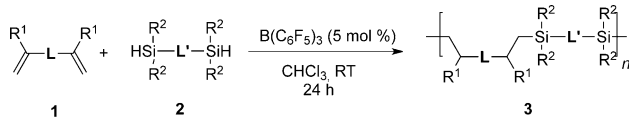
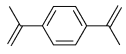
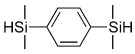
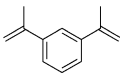
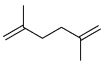
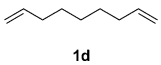
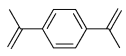
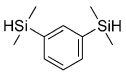


Figure 1. $B(C_6F_5)_3$-catalyzed formation of poly(1,4-diisopropenylbenzene) (left) and $B(C_6F_5)_3$-catalyzed hydrosilylation polymerization (right).

Table 2: Scope of dienes and silanes in the hydrosilylation polymerization.[a]



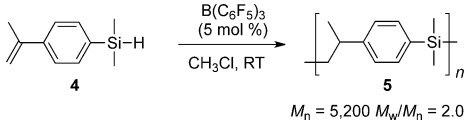
Entry	Diene	Silane	Product	M_n[b] [kg mol^{-1}]	M_w/M_n[b]	T_g[c] [°C]	T_{d5}[d] [°C]
1	 1a	 2a	**3a**	14.1	1.90	14	391
2	 1b	**2a**	**3b**	11.5	1.96	0	361
3	 1c	**2a**	**3c**	6.8	1.78	−36	351
4	 1d	**2a**	**3d**	1.3	1.63	N.D.	N.D.
5	 1a	 2b	**3e**	9.0	1.89	−2	412
6	**1a**	Et_2SiH_2 **2c**	**3f**	6.5	3.39	−22	354
7	**1a**	$MePhSiH_2$ **2d**	**3g**	4.0	1.84	24	375
8	**1a**	Ph_2SiH_2 **2e**	**3h**	4.2	3.53	59	381

[a] Polymerization conditions: **1** (1.0 mmol), **2** (1.0 mmol), and $B(C_6F_5)_3$ (5 mol%) in $CHCl_3$. [b] Determined by GPC calibrated with polystyrene standards in chloroform at 35 °C. [c] T_g was measured using differential scanning calorimeter (DSC). [d] T_d was measured by thermogravimetric analysis (TGA) and indicates the 5% weight-loss temperature.

irrespective of their structural variations. Disilanes, placed either at the *para*- or *meta*-position in the benzene backbone, were almost equally effective for the polymerization (entries 1 and 5). Dihydrosilanes were also successfully applied to the current polymerization conditions, and the expected polycarbosilanes were obtained (entries 6–8). However, the polymerization efficiency was slightly lower in case of phenylsilanes (entries 7 and 8).

As shown in Table 2, a variety of polycarbosilanes were obtained with attractive structural diversity simply by altering the type of dienes and silanes under the convenient-to-perform conditions.[2a] Glass transition temperatures (T_g) of the obtained polymers in this study ranged from −36 to 59 °C, but all products exhibited high decomposition temperatures (T_{d5}) above 350 °C, thereby expecting tunable process windows and high thermal stabilities.

Step-growth polymerization of a single monomer bearing bifunctional groups is also of high interest.[18c] A monomer having both olefinic and silyl groups could eliminate the requirement of stoichiometric balance for a high degree of polymerization. We synthesized (4-isopropenyl phenyl)dimethylsilane (**4**) and subjected it to the $B(C_6F_5)_3$ catalytic system (Scheme 4). We were pleased to observe that the desired hydrosilylation polymerization furnished the



Scheme 4. Hydrosilylation polymerization of a bifunctional monomer (**4**) bearing both olefinic and silyl groups in the same molecule.

corresponding polycarbosilane **5** with high molecular weight. It was noteworthy that even though the $B(C_6F_5)_3$ catalyst was not treated with silane before the polymerization, no trace of poly(α-methyl styrene) was observed. This result implies that the borane, $B(C_6F_5)_3$, has a higher coordination propensity to silanes than to alkenes.

In conclusion, for the first time, the highly reactive hydrosilylation of olefins by a $B(C_6F_5)_3$ catalyst was successfully applied to the polymerization between dienes and disilanes, which was previously carried out only by transition-metal catalysts. Various dialkenes and disilanes underwent the step-growth polymerization to produce polycarbosilanes with high molecular weight, excellent thermal stability, and adjustable thermal properties. In addition to the established merits of metal-free catalysis, such as cost effectiveness and low toxicity, the unique reactivity of the $B(C_6F_5)_3$ catalyst demonstrated expands the realm of hydrosilylation polymerizations. Further studies on the expanding the diene and silane scope as well as applications of polymers obtained are in progress.

Experimental Section

Representative hydrosilylation polymerization between **1a** and **2a** (Table 1, entry 1): In a 5 mL vial equipped with a Teflon coated stir bar, 1,4-bis(dimethylsilyl)benzene (194 mg, 1.00 mmol) was added to a solution of $B(C_6F_5)_3$ (25.6 mg, 0.0500 mmol) in chloroform (1.0 mL) and the resulting solution was stirred briefly. 1,4-Diisopropenylbenzene (158 mg, 1.00 mmol) was then added. The reaction mixture was stirred at room temperature for 24 h. The resulting mixture was diluted with 2.0 mL of chloroform and polymeric product was precipitated upon the addition of methanol. Additional precipitation procedures were performed twice in chloroform and methanol. The final precipitate was isolated and dried in a vacuum oven (60 °C) to give polycarbosilane **3a** (190 mg, 54 %).

Acknowledgements

We thank Prof. Myungeun Seo (KAIST) for valuable comments and sharing gel permeation chromatography analysis equipment. This work was supported financially by the Institute for Basic Science (IBS-R010-D1). Dedicated to Professor Yoon Sup Lee (KAIST) on the occasion of his retirement.

Keywords: borane catalyst · hydrosilylation · metal-free catalysis · polycarbosilanes · polymerization

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 14805–14809
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Received: August 22, 2015
Published online: October 16, 2015

