# Catalytic Cross-Dehydrocoupling Polymerization of 1,4-Bis(dimethylsilyl)benzene with Water. A New Approach to Poly[(oxydimethylsilylene)-(1,4-phenylene)(dimethylsilylene)]

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**Introduction.** The combination of the flexible and thermally stable siloxane linkages and the rigid aromatic groups in the main chain should provide polymers with both long-term thermal stability to $\geq 300-350$ °C and excellent flexibility to very low temperatures, which have potential applications in some advanced technology areas.[1,2c] However, progress of the development of these materials has been impeded by a lack of efficient synthetic methods and readily available starting materials. For instance, poly[(oxydimethylsilylene)(1,4-phenylene)(dimethylsilylene)] (**3**) and poly[(oxydimethylsilylene)(1,3-phenylene)(dimethylsilylene)] (**3′**), which show good thermal stability (the temperature for 10% weight loss is 445 °C (**3**)[2b] and the onset temperature is 415 °C under $N_2$ and 495 °C in air (**3′**)[2c] and low glass transition temperatures ($T_g = -18$ °C (**3**)[2b] and $-52$ °C (**3′**)[2c] and are expected to be high-temperature elastomer materials,[2] have been prepared by Merker's route, the condensation of 1,4- (or 1,3-) bis(dimethylhydroxysilyl)benzene (**2**) (Scheme 2). The conversion of 1,4-bis(dimethylsilyl)benzene (**1**) to disilanol **2** by this route requires a number of steps, and the product requires tedious recrystallization, resulting in low yields of the pure compound **2**.[2c,d]

Although the transition-metal-catalyzed dehydrocoupling of hydrosilanes to afford poly(silane)s has been extensively studied over the past decade[3] for a number of reasons,[4] little attention has been paid to the application of the cross-dehydrocoupling reaction of organosilanes with functionalized reagents, e.g., SiH/OH,[5-7] SiH/SH,[8a,9b] SiH/NH,[9] SiH/CH,[10] etc (Scheme 1), for polymer syntheses.[8] Here we report the first example of cross-dehydrocoupling reaction of SiH/OH to produce high molecular weight poly(carbosiloxane)s under mild reaction conditions. Thus, high molecular weight **3** was prepared conveniently by treatment of **1** with water in the presence of various transition metal catalysts; a catalytic cross-dehydrocoupling polymerization (Scheme 2). The readily available monomers (**1** and water), the high yield of polymer (about 90%), a single reaction step, producing only $H_2$ as a byproduct, and the mild reaction conditions (room temperature) make this method not only attractive in the laboratory but also promising for industrial applications.

**Experimental Section. General Data.** The 500 MHz $^1$H, 75.3 MHz $^{13}$C, and 79.6 MHz $^{29}$Si NMR spectra were obtained in CDCl$_3$; the chemical shifts are reported in ppm, referenced to internal CHCl$_3$ ($\delta$ 7.26), CDCl$_3$ ($\delta$ 77.00), and external tetramethylsilane ($\delta$ 0.00), respectively. IR spectra were obtained on a JASCO VALOR-III spectrophotometer. Size exclusion chromatography

## Scheme 1

$$R_3SiH + HX \xrightarrow{\text{catalyst}} R_3SiX + H_2$$
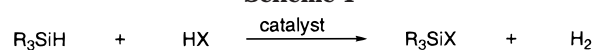
X = OH, SH, RO, ArO, RNH$_2$, R, etc.

(SEC) analysis was performed on a JASCO HPLC on the combination of Shodex KF-803L (exclusion limit: $M_n = 7 \times 10^4$, polystyrene) and KF-804 (exclusion limit: $M_n = 4 \times 10^5$, polystyrene) columns using tetrahydrofuran (THF) as an eluent.
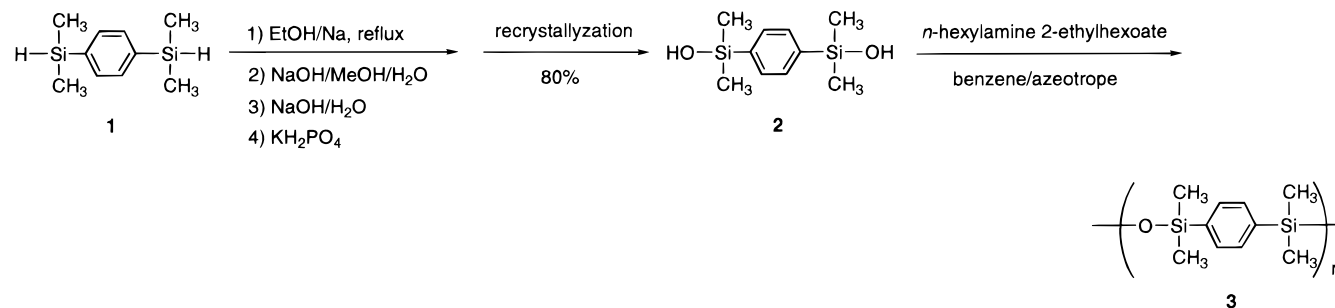
**Polymerization.** The polymerization was conducted under the conditions shown in Table 1. A typical polymerization procedure is shown below (run 1 in Table 1).

To a 30 mL Schlenk flask were added tris(dibenzylideneacetone)dipalladium(0)−chloroform (Pd$_2$(dba)$_3$)[11] (25.9 mg, 2.5 × 10$^{-5}$ mol), 1,4-bis(dimethylsilyl)benzene (**1**) (1.94 g, 0.01 mol), and H$_2$O (0.18 g, 0.01 mol). As THF (4 mL) was added, a violent evolution of hydrogen occurred and the flask was cooled in an ice−water bath to remove the heat generated (the hydrogen generated was released to a balloon). After 2 h, the reaction was stopped and the catalyst was removed by filtration through a short Florisil column (CHCl$_3$ eluent). Reprecipitation of the concentrated polymer solution into methanol gave a white solid **3** (1.86 g, yield 89%). SEC: $M_w/M_n$ = 35800/16300. $^1$H NMR: $\delta$ 0.33 (s, 12 H, C$H_3$) and 7.54 (s, 4 H, C$_6H_4$). $^{13}$C NMR: $\delta$ 0.78 (s, 4 C, $C$H$_3$), 132.35 (s, 4 C), 140.97 (s, 2 C). $^{29}$Si NMR: $\delta$ −1.2 (s). IR (neat) $\nu$ 3046−2900, 1251, 1073 ($\nu_{SiOSi}$), 826, 781 cm$^{-1}$.

**Results and Discussion.** It has been reported that many compounds readily catalyze (i) the hydrolysis of SiH to produce silanols (SiOH)[5] or (ii) the dehydrocoupling of SiH/SiOH to form the siloxane (SiOSi) linkage.[6] We considered that if a dihydrosilane (or a bis(hydro)silane) reacts with water in the presence of a catalyst that can catalyze both the hydrolysis of SiH and the dehydrocoupling of the resulting SiOH with unreacted SiH, then a polymer with the main chain linked by SiOSi bonds could be produced. Although the hydrolysis of SiH and the dehydrocoupling of SiH/SiOH have been extensively studied respectively, efficient catalysts for both reactions have not been documented.

In this study, a number of transition metal derivatives were investigated and some of them were found efficient catalysts for the cross-dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene (**1**) with water (Table 1). Among them, Pd$_2$(dba)$_3$ afforded a high molecular weight polymer **3** ($M_n$ = 16 300) in 2 h, showing very high catalytic activities for both the hydrolysis and the subsequent SiOSi bond formation. The structure of polymer **3** was easily verified by NMR spectra. Palladium chloride (PdCl$_2$) catalyzed polymerization also yielded a high molecular weight **3** with $M_n$ = 23 000 in 2 h. Another good catalyst in this dehydrocoupling polymerization is H$_2$PtCl$_6$·6H$_2$O, which afforded a high molecular weight polymer ($M_n$ = 15 700) within 2 h. Palladium on charcoal (10% Pd/C), which has been widely used as a catalyst for hydrolysis of organosilanes, caused a rapid evolution of hydrogen, indicating that hydrolysis of SiH occurred smoothly; however, only oligomers ($M_n$ = 2400) were obtained after 42 h, indicating the dehydrocoupling of SiH/SiOH is slow.

**Scheme 2**

**1) Merker's route.[2a]**

1) EtOH/Na, reflux
2) NaOH/MeOH/$H_2O$
3) NaOH/$H_2O$
4) $KH_2PO_4$

recrystallyzation 80%

**1** → **2**

*n*-hexylamine 2-ethylhexoate

benzene/azeotrope

**3**

**2) Cross-dehydrocoupling polymerization (this work).**

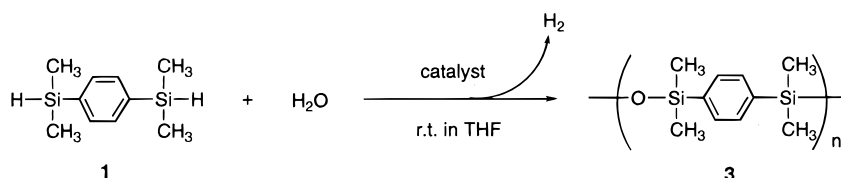**1** + $H_2O$ $\xrightarrow[\text{r.t. in THF}]{\text{catalyst} \quad H_2}$ **3**

**Table 1. Cross-Dehydrocoupling Polymerization of 1 with Water at Room Temperature in THF[a]**

| run | catalyst | time, h | polymer **3**, %[b] | $M_n{}^b$ | $M_w/M_n{}^b$ |
|---|---|---|---|---|---|
| 1 | $Pd_2(dba)_3$ | 2 | 92 (89[c]) | 16300 | 2.19 |
| 2[d] | | 42 | 87 (90[c]) | 29600 | 2.06 |
| 3 | $PdCl_2$ | 2 | 94 (88[c]) | 23000 | 1.92 |
| 4[d] | | 42 | ~100 | 1900 | 1.81 |
| 5 | 10% Pd/C | 42 | ~100 | 2400 | 1.96 |
| 6[e] | $H_2PtCl_6·6H_2O$ | 2 | 95 | 15700 | 2.19 |
| 7[d] | | 24 | ~100 | 1540 | 1.31 |
| 8 | $Pt(PPh_3)_4$ | 42 | 24 | 780 | 1.12 |
| 9 | $[RhCl(cod)]_2$ | 42 | ~100 | 4600 | 12.6 |
| 10 | $RhCl(PPh_3)_3$ | 42 | 58 | 1230 | 1.20 |
| 11[f] | | 42 | 93 | 4370 | 2.12 |

[a] Reaction conditions: 0.01 mol of 1,4-bis(dimethylsilyl)benzene (**1**) and 0.01 mol of water in 4 mL THF; $5 \times 10^{-3}$ mol of metal/mol of silane. [b] Estimated by SEC with polystyrene standards. [c] Isolated. [d] $1 \times 10^{-4}$ mol of metal/mol of silane. [e] Water comprised in $H_2PtCl_6·6H_2O$ was considered as a part of the reactant. [f] In benzene.

Tetrakis(triphenylphosphine)platinum(0) ($Pt(PPh_3)_4$) is also an efficient catalyst for the hydrolysis step (confirmed by the evolution of hydrogen at the early stage), but SiOSi formation is slow, and therefore only low molecular weight oligomers ($M_n = 780$ after 42 h) are produced. Rhodium complexes $[RhCl(cod)]_2$ and $RhCl(PPh_3)_3$ are not suitable catalysts for polymerization, although they have been reported to be good catalysts for the dehydrocoupling reaction of SiH/ROH and SiH/SiOH.[5i,6f] Both of them gave only low molecular weight products after 42 h ($M_n = 4600$ (run 9), 1230 (run 10), and 4370 (run 11)). Interestingly, the polymer obtained using $[RhCl(cod)]_2$ (run 9) had a very broad molecular weight distribution ($M_w/M_n = 12.6$) and its SEC curve showed a multimodal pattern. The reason for this is still unclear. Other transition metal derivatives, such as, $NiCl_2$, [1,3-bis(diphenylphosphine)propane]nickel(II) chloride ($NiCl_2$(dppp)), dicyclopentadienyltitanium dichloride ($Cp_2TiCl_2$), $ZrCl_4$, and dicyclopentadienylzirconium dichloride ($Cp_2ZrCl_2$) were also investigated but showed no catalytic activity in this polymerization. Thus, among the transition metal derivatives investigated, $Pd_2(dba)_3$, $PdCl_2$, and $H_2PtCl_6·6H_2O$ are the best catalysts for the dehydrocoupling

polymerization of **1** with water. To investigate the catalytic activities of these three catalysts in more detail, the catalyst concentrations were further reduced ($10^{-4}$ mol of metal/mol of silane). Obviously, $Pd_2(dba)_3$ (run 2), which gave a high molecular weight polymer ($M_n = 29\,600$) in 42 h, is a more active catalyst than $PdCl_2$ (run 4) and $H_2PtCl_6·6H_2O$ (run 7).

We are now extending the cross-dehydrocoupling reaction of organosilanes to the syntheses of poly(silyl ether)s, poly(ester)s, etc., to prove that this is a promising and useful approach to various silicon-containing polymers.

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