Dehydrocoupling Polymerization of Bis-silanes and Disilanols to Poly(silphenylenesiloxane) As Catalyzed by Rhodium Complexes†

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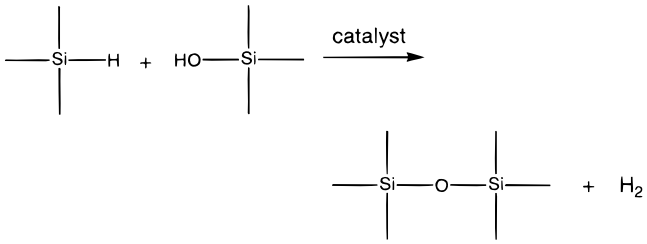
Introduction. The discovery of homogeneously catalyzed silane oligomerization reactions with metallocenes by Harrod's group has promoted considerable interest in the development of dehydrocoupling polymerization.[1] Of particular interest is the polymerization of primary silanes to polysilanes.[2] Although polysiloxanes are the most studied and widely used silicon-containing polymers,[2c,3] little attention has been directed toward development of dehydrocoupling polymerization to prepare polysiloxanes. Very recently, catalytic dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with labile hydrogen-containing compounds was reported by Kawakami et al.[4] They also prepared poly(silyl ether)s through dehydrocoupling polymerization of bis(hydrosilane)s with diols.

During our investigation of the silphenylenesiloxanes,[5] we developed a general method of dehydrocoupling polymerization of bis-silanes and disilanols using organometallic catalysts, based on the dehydrocoupling reaction of SiOH/SiH (Scheme 1).[6] We were especially interested in applying this methodology to prepare high-performance silphenylenesiloxane alternating copolymers, which have very desirable physical and chemical properties for special applications and which are now made through a tedious series of reactions.[7]

A theoretical study using ab initio MO theory has revealed that a dehydrocoupling reaction would be a feasible candidate for the formation of the siloxane bond.[8] Michalska has demonstrated that homogeneous and silica-supported rhodium(I) complexes are very efficient catalysts for the dehydrocoupling reaction of silanols with hydridosilanes to form Si−O−Si bonds.[6b] It has also been reported that Wilkinson's catalyst can be used to prepare alkoxysilanes in approximately quantitative yields.[1d,9] Notably, the reported reaction conditions[9b] are very mild, namely room temperature under an air atmosphere.

Hence, we started our investigation of the dehydrocoupling polymerization to polysiloxanes with Wilkinson's catalyst and applied it to poly(silphenylenesiloxane) systems. Here, we report the first examples of dehydrocoupling polymerization of bis-silanes and disilanols to prepare high-molecular-weight silphenylenesiloxanes homopolymers and copolymers, with control of the microstructures, in high yields under extremely mild conditions.

Scheme 1



Experimental Section. A. Chemicals and Measurements. 1,3-Dibromobenzene, chlorotris(triphenylphosphine)rhodium(I), and 1,2-bis(dimethylsilyl)benzene were purchased from Aldrich and used without further purification. Dimethylchlorosilane was purchased from United Chemical Technologies and also used without purification. Diphenylsilane, diethylsilane, methylphenylsilane, diphenylsilanediol, 1,4-bis(dimethylsilyl)benzene, and 1,4-bis(dimethylhydroxysilyl)benzene were purchased from Gelest and were distilled or recrystallized from a mixture of benzene and petroleum ether before use. 1,3-Bis(dimethylhydroxysilyl)benzene was prepared using methods previously reported.[5a] Tetrahydrofuran (THF) and benzene were distilled from potassium prior to use, and petroleum ether was distilled from molecular sieves. All other chemicals were purchased from Fisher Scientific and used as received.

All mass spectra and GC/MS were obtained on a Hewlett-Packard model 9780 spectrometer using a 0.25 mm × 15 m fused silica capillary SPB-1 column and temperature programming. All infrared spectra were recorded on a Perkin-Elmer model 1600 series FTIR spectrophotometer using KBr cells or pellets. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded on a Bruker 250 MHz spectrometer with ^{1}H NMR spectra referenced to tetramethylsilane at 0.00 ppm and ^{13}C NMR spectra referenced to the center chloroform-*d* peak at 77.0 ppm. Gel permeation chromatography (GPC) was performed on a Waters gel permeation chromatography unit using toluene at 40 °C with a differential refractometer and four in-line columns having pore sizes of 100, 500, 10^3, and 10^4 Å. The eluent flow rate was set at 1 mL/min, and the molecular weights were determined using polystyrene standards. Thermal data were obtained using a STA and a DSC from Rheometric Scientific.

B. Polymerization. The dehydrocoupling polymerization was carried out under the conditions shown in Table 1. A typical procedure is described below, specifically to prepare homopolymer **3a**.

In a 20 mL flask was placed 0.9705 g (5 mmol) of 1,4-bis(dimethylsilyl)benzene, 1.1304 g (5 mmol) of 1,4-bis(dimethylhydroxysilyl)benzene, and 9.3 mg (0.01 mmol) of $(Ph_3P)_3RhCl$ in 5 mL of THF. The mixture was stirred under an argon atmosphere at ambient temperature. Vigorous gas evolution was observed after several minutes, and the reaction was very exothemic. Visible gas evolution stopped in about 25 min, and the solution became cloudy. Then, the contents of the flask were stirred for 5 h. A sample was taken from the system and subjected to GPC analysis. A polymer with a

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† The authors dedicate this paper to Karel Dusek on the occasion of his 70th birthday. This work contains parts of the Ph.D. dissertation of R. Zhang, University of Cincinnati, 1999.

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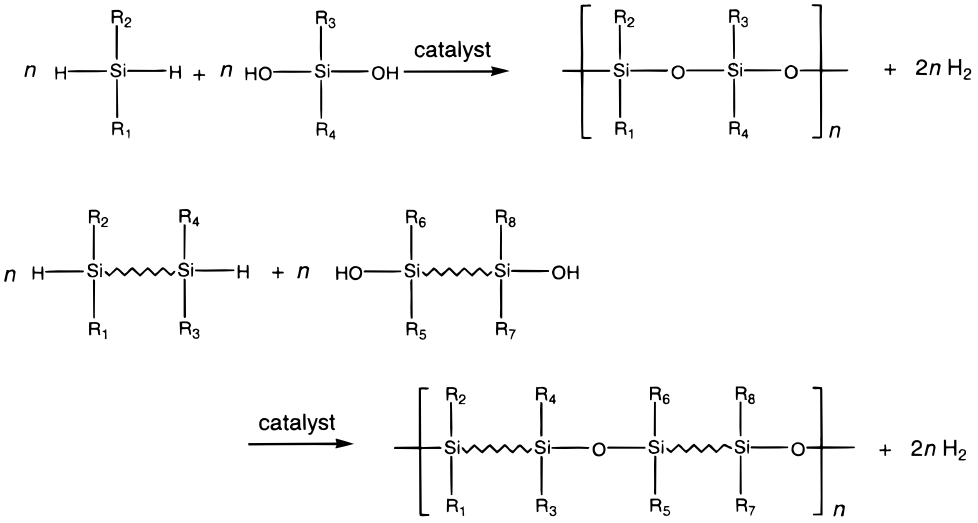
Table 1. Reaction Conditions and Results of the Dehydrocoupling Polymerization of Bis-silanes and Disilanols to Siloxane Polymers[a]

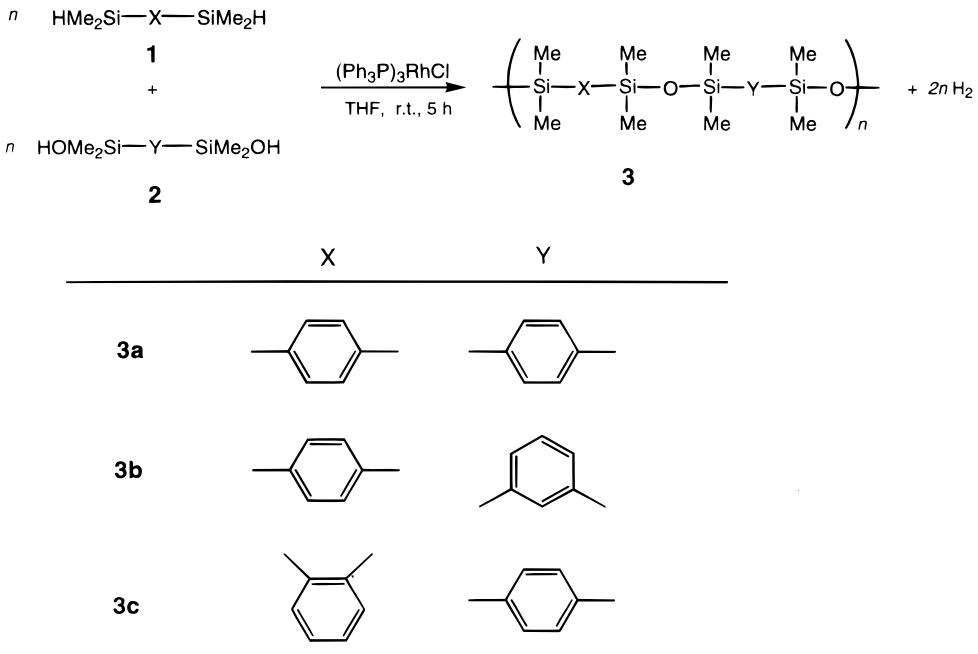
polymer	Wilkinson catalyst (ppm)	temp	solvent	yield (%)[b]	M_n (g mol^{-1})	M_w/M_n
3a	2000	r.t.	THF + benzene	nd[c]	8900	1.02
3a	2000	r.t.	THF	nd	10100	1.73
3a	2000[d]	r.t.	THF	nd	8500	1.52
3a	2000	100 °C (Ar)	THF + toluene	98	17200	1.50
3b	2000	65 °C (Ar)	THF	81	3900	1.42
3b	2000	r.t. (Ar)	THF	nd	3800	1.34
3c	4000	65 °C	THF	72	1000	

[a] The burgundy-red form of Wilkinson's catalyst was used, and the reaction was run at room temperature for 6 h under an air atmosphere unless explicitly stated. [b] Isolated value. [c] nd = not determined; the yield was higher than 85% in most cases according to GPC. [d] The orange polymeric form of Wilkinson's catalyst was used.

Scheme 2



Scheme 3



number-average molecular weight M_n of 10 100 g mol^{-1} and a polydispersity index M_w/M_n of 1.73 was obtained. The polymer sample was purified through fractional precipitation and was dried in a vacuum oven at 60 °C for 24 h. The yield was about 98% based on monomer. Spectroscopic data for PTMPS **3a**: ^{1}H NMR ($CDCl_3$) δ: 7.54 (s, 4H), 0.33 (s, 12H). ^{13}C NMR ($CDCl_3$) δ: 140.8, 132.2, 0.887.

Alternating copolymer **3b**: GPC: M_n = 3862 g mol^{-1} and M_w/M_n = 1.42. Yield: ca. 81%. ^{1}H NMR ($CDCl_3$) δ: 7.76 (s, 1H), 7.55 (distorted doublet, 6H), 7.31 (t, J = 7.24 Hz, 1H), 0.32 and 0.31 (two peaks, 24H). ^{13}C NMR ($CDCl_3$) δ: 140.8, 138.8, 137.5, 134.0, 132.2, 127.0, 0.90.

Results and Discussion. Among the bis-silane compounds that were tested in this research were *p*-bis(dimethylsilyl)benzene, *m*-bis(dimethylsilyl)benzene, *o*-

bis(dimethylsilyl)benzene, diphenylsilane, methylphenylsilane, and diethylsilane. Among the silanol compounds used were *p*-bis(dimethylhydroxysilyl)benzene, *m*-bis(dimethylhydroxysilyl)benzene, and diphenylsilanediol. The generalized reaction is shown in Scheme 2.

Dehydrocoupling polymerization proceeded when both the organosilicon hydride and the organosilanol are bis(silyl)benzene compounds (Scheme 3). Polymerization between *p*-bis(dimethylsilyl)benzene and *p*-bis(dimethylhydroxysilyl)benzene provided the best result (Table 1). No polymer with molecular weight higher than 1000 g mol^{-1} was observed for the trials without bis(silyl)benzene compounds.

The polymerization was found to proceed exothermically at room temperature in an open flask with vigorous gas evolution. Poly(tetramethyl-*p*-silphenylenesiloxane) (PTMPS, **3a**) was obtained as a white crystalline compound with an M_n of 17 200 g mol^{-1} and an M_w/M_n of 1.58. The yield was almost quantitative based on the monomer. An alternating copolymer **3b** of tetramethyl-*m*-silphenylenesiloxane (TMMS) and tetramethyl-*p*-silphenylenesiloxane (TMPS) which was a very viscous and transparent fluid[10] was obtained in a yield of 81%. An alternating copolymer of tetramethyl-*o*-silphenylenesiloxane (TMOS), and TMPS was obtained in about a 70% yield.

These are among the first demonstrations of a coordination polymerization of bis-silanes and disilanols to siloxane polymers through the metal-mediated formation of Si−O−Si bonds. If a step-growth coordination mechanism is considered,[1c] the catalytic efficiency of the rhodium complex is extremely high for the silphenylenesiloxane system. The rhodium complex was extremely robust to the reaction conditions and is specific for the reaction of bis-silanes and disilanols.[6b] Both burgundy-red and orange polymeric forms of Wilkinson's catalyst were tested, and no distinguishable difference in the dehydrocoupling polymerization was observed.[11] The mild reaction conditions and the high yields are ideal for industrial applications, as well as for academic studies. Using this methodology, not only silphenylenesiloxane homopolymers but also siloxane alternating copolymers, which would otherwise be difficult to obtain,[7] can be prepared with ease.

Michalska has reported the reaction of organosilicon hydride with organosilanol catalyzed by rhodium(I) complexes.[6b] However, no polymer formation was reported in that study. It is postulated that the mechanism involves the oxidative addition of the hydridosilane to rhodium as the first step, followed by nucleophilic attack of the silanol oxygen on silicon in the coordinated silyl ligand (rate-determining step), with final elimination of a siloxane molecule and the loss of molecular hydrogen. No polymer was produced in Michalska's study presumably due to the more favorable formation of cyclic siloxane compounds. This can be explained in terms of intramolecular cyclization of the α-hydroxy-ω-hydridosiloxane formed in the first step.[6b] Our results further support the above mechanisms by the observation that intramolecular cyclization may be suppressed by the relatively rigid nature of our intermediate. Because it would be very unfavorable to form the para cyclic dimer, high molecular weight **3a** was formed with ease.

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(10) According to TGA analyses, the temperature of 10% weight loss of **3b** is 426 °C, and that of a random copolymer **4** of TMMS and TMPS (*p*:*m* = 50:50) is 494 °C. The glass transition temperature of copolymer **3b** is −35 °C, and that of **4** is −39 °C.

(11) This work was done independently at almost the same time as Kawakami's study. Their publication inspired us to communicate our research results on dehydrocoupling polymerization. Interestingly, it was reported by Kawakami et al. in ref 4a that rhodium complexes $[RhCl(cod)]_2$ and $RhCl(PPh_3)_3$ are not efficient catalysts for the dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with water.

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