



Palladium-catalyzed dehydrogenative amination of polyhydrosiloxanes



Zhou Lu^{a, b}, Kazuya Murakami^a, Sayako Koge^a, Tomonobu Mizumo^a, Joji Ohshita^{a, *}

^a Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

^b School of Chemistry, Chemical Engineering and Environment, Qingdao University, Qingdao 266071, China

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ABSTRACT

Palladium-catalyzed dehydrogenative coupling of hydropolysiloxanes with amines was investigated. The reactions of α,ω -dihydropoly(dimethylsiloxane) with pyrrolidine, piperidine, di(isopropyl)amine, and di(*n*-butyl)amine in the presence of a catalytic amount of PdCl₂ or Pd/C at 50–70 °C provided the corresponding aminated polysiloxanes as viscous oils in good to high yields. Poly(dimethylsiloxane-*co*-hydromethylsiloxane) also underwent the Pd-catalyzed dehydrogenation with pyrrolidine to give the amination product. Treatment of glass surface with the resulting α,ω -bis[di(*n*-butyl)amino]-poly(dimethylsiloxane) increased the surface hydrophobicity, indicating the potential applications of the Si–N-containing polysiloxanes as hydrophobic surface modifiers.

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1. Introduction

Aminosilanes containing Si–N bonds are useful compounds as silylating reagents [1]. Moderately high reactivity of the Si–N bonds allows the smooth but not vigorous reactions with hydroxyl groups, allowing the use of aminosilanes as mild silylating reagents for alcohols and inorganic oxide surface. Many methods to provide Si–N bonds have been known, including the reactions of halosilanes with primary and secondary amines in the presence of a base. Dehydrogenative coupling between hydrosilanes and amines has been studied as a convenient and atom-economical route to Si–N containing compounds [2].

A few approaches to Si–N-containing polysiloxanes have been reported, which include (1) ring-opening anionic polymerization of hexamethylcyclotrisiloxane (D3) by using amide anions as initiators, providing an Si–N bond at one chain end [3], and (2) anionic ring-opening polymerization of a mixture of cyclo-oligodimethylsiloxanes catalyzed by ammonium siloxanate in the presence of α,ω -diaminooligosiloxanes as the terminating reagents, introducing Si–N bonds at two ends [4] (Scheme 1). Ring-opening polymerization of cyclosiloxanes leading to the formation of polysiloxanes that are known as precursors of silicon oxynitride ceramics has been also studied (Scheme 1 (3)) [5]. However, no

dehydrogenative amination has been applied for hydropolysiloxanes. Furthermore, none is known for polysiloxane with Si–N bonds in the repeating units.

In the course of our studies concerning the preparation of halo- and alkoxy silanes from hydrosilanes [6], we demonstrated the formation of bromopolysiloxanes from hydropolysiloxanes [7]. In this paper, Pd-catalyzed dehydrogenative amination of hydrosiloxanes is described, which provides Si–N bond-containing polysiloxanes, α,ω -aminopoly(dimethylsiloxane) and poly(aminomethylsiloxane-*co*-dimethylsiloxane), efficiently from the corresponding hydropolysiloxanes. An application of the resulting Si–N-containing polysiloxane as a hydrophobic modifier of glass surface was also examined.

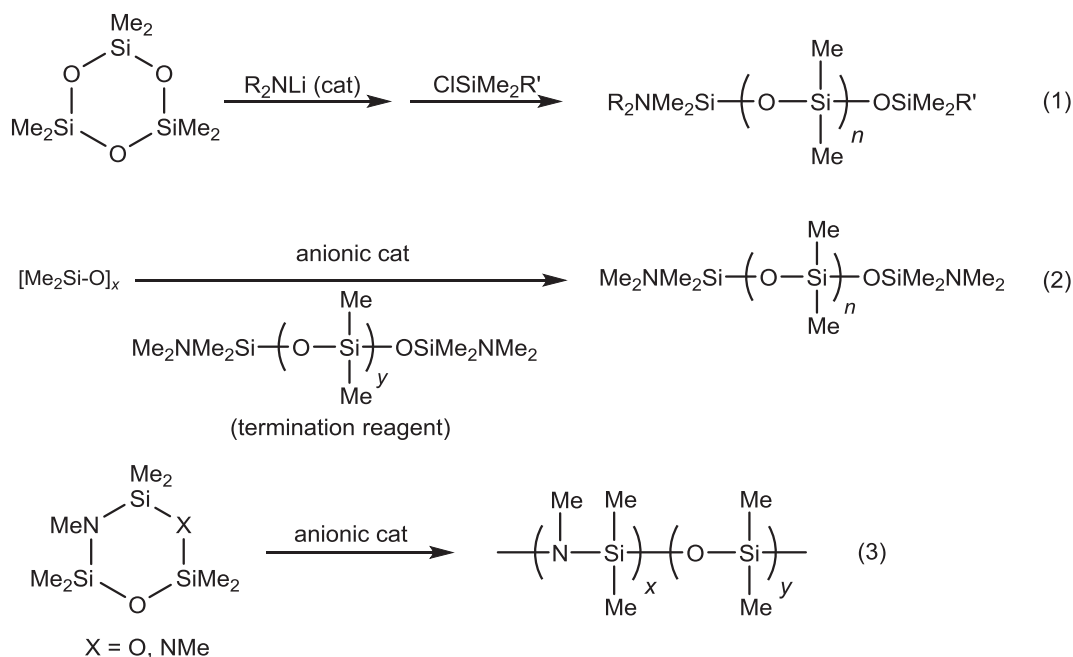
2. Experimental

2.1. General

All reactions were carried out in dry argon. Pyrrolidine, piperidine, di(isopropyl)amine, and di(*n*-butyl)amine were distilled from potassium hydroxide and stored over activated molecular sieves at 4 °C in dark until use. THF used as the reaction solvent was dried over CaH₂ and distilled immediately before use. Polysiloxanes PMS1-4 were purchased from Gelest Inc and were used for the reactions without purification. NMR spectra were recorded on Varian 400 MR and System 500 spectrometers. Water contact angles of glass surface were measured on a Kyowa contact angle

* Corresponding author.

E-mail address: jo@hiroshima-u.ac.jp (J. Ohshita).



Scheme 1. Literature methods for the preparation of aminopolysiloxanes.

meter DM-300.

2.2. PdCl₂-catalyzed amination of hydropolysiloxane

A mixture of **PMS1** (0.10 g, 2.22 mmol), pyrrolidine (0.50 g, 7.03 mmol), and PdCl₂ (12.5 mg) was stirred at 50 °C for 15 h. After filtration of the precipitates including palladium species, the precipitates were extracted with hexane. The solvent and volatile substances were evaporated from the filtrate under reduced pressure (0.1 mmHg) at room temperature to give 0.77 g (59%) of **PMS1a** ($n = 10$) as a colorless viscous oil: ¹H NMR (δ in CDCl₃) 0.05, 0.07, 0.10 (74H, SiMe), 1.71 (br t, 8H, CH₂, $J = 6.0$ Hz), 2.97 (br t, 8H, CH₂, $J = 6.0$ Hz); ¹³C NMR (δ in CDCl₃) -0.99 (terminal SiMe), 1.04 (inner SiMe), 26.74, 46.22 (CH₂).

2.3. Pd/C-catalyzed amination of hydropolysiloxane

A mixture of **PMS1** (0.10 g, 2.22 mmol), piperidine (0.70 g, 8.23 mmol), and Pd/C (5 wt% of Pd) (250 mg, 12.5 mg of Pd), in THF (10 mL) was stirred at 70 °C for 7 h. After filtration of precipitates which included palladium species, the precipitates were extracted with hexane. The solvent and volatile substances were evaporated from the filtrate under reduced pressure (0.1 mmHg) at room temperature to give 1.04 g (76%) of **PMS1b** ($n = 14$) as a colorless viscous oil: ¹H NMR (δ in CDCl₃) 0.05–0.11 (97H, SiMe), 1.39 (t, 8H, CH₂, $J = 5.5$ Hz), 1.56 (quintet, 4H, CH₂, $J = 5.5$ Hz), 2.85 (t, 8H, CH₂, $J = 5.5$ Hz); ¹³C NMR (δ in CDCl₃) -0.96 (terminal SiMe), 1.04, 1.09 (inner SiMe), 25.60, 27.65, 45.82 (CH₂).

Other reactions of amines with hydropolysiloxanes were carried out in a fashion similar to that for **PMS1b**. For the preparation of **PMS1a**, however, a smaller amount of Pd/C (25 mg) must be used to avoid the formation of complex mixtures.

Date for **PMS1c** ($n = 6$): 71% yield; ¹H NMR (δ in CDCl₃) 0.03, 0.14 (46H, SiMe), 1.03 (d, 24H, CMe, $J = 8.0$ Hz), 2.89–2.94 (m, CH, 4H); ¹³C NMR (δ in CDCl₃) 0.67, 0.84, 1.03, 1.13 (SiMe), 19.38, 47.44 (Pr). Data for **PMS1d** ($n = 9$): 70% yield; ¹H NMR (δ in CDCl₃) 0.06–0.12 (66H, SiMe), 0.91 (t, 12H, CH₂, $J = 6.0$ Hz), 1.33 (quintet, 8H, CH₂, $J = 6.0$ Hz), 1.46 (quintet, 8H, CH₂, $J = 6.0$ Hz), 2.58 (t, 8H, CH₂,

$J = 6.0$ Hz); ¹³C NMR (δ in CDCl₃) 0.43, 0.66, 0.82, 1.01 (SiMe), 14.00, 20.51, 32.16, 49.70 (Bu). Data for **PMS2a**: 86% yield; ¹H NMR (δ in CDCl₃) 0.02–0.06 (31H, SiMe), 1.66 (quintet, 4H, CH₂, $J = 3.3$ Hz), 2.82 (quintet, 4H, CH₂, $J = 4.3$ Hz); ¹³C NMR (δ in CDCl₃) 0.46, 0.50, 0.54, 0.58, 0.63, 0.66, 0.69, 0.78, 0.87, 0.96, 1.00, 1.06, 1.70 (SiMe), 25.35, 46.54 (CH₂).

2.4. Modification of glass surface with **PMS1d**

Glass substrates that were used for the modification were sonicated in deionized water and then in acetone for 15 min each. After drying in air at 100 °C, the substrates were subjected to ozone-clearing for 15 min and were immediately used for the surface modification. Some pieces of the pre-treated glass substrates were dipped in a solution of 10 mg of **PMS1d** in THF 10 mL at room temperature in an argon atmosphere. Every after 1 h, one of the pieces was taken out from the solution and washed thoroughly with dry THF. After the substrate was dried under reduced pressure, water contact angle of the substrate surface was measured.

3. Results and discussion

3.1. Amination of hydropolysiloxanes

Treatment of α,ω -dihydropoly(dimethylsiloxane) (**PMS1**, average chain length $n = 8.0$) with an excess of pyrrolidine in the presence of a catalytic amount of PdCl₂ at 50 °C for 15 h, followed by filtration of the palladium species and evaporation of volatile substances under reduced pressure gave a diamination product (**PMS1a**) in 59% yield, as a colorless viscous oil (Scheme 2 and Table 1). No reaction occurred in the absence of PdCl₂ and the starting **PMS1** was recovered unchanged. The polymer structure was verified mainly by the NMR spectra. The ¹H and ¹³C NMR spectra revealed only the signals that were ascribed to a pyrrolidine ring, and terminal and inner dimethylsiloxane units. No other signals including those of SiMe₂H groups were observed in the spectra (see Supplementary materials). The average chain length of **PMS1a** was determined by the ¹H NMR spectrum to be $n = 10$. Presumably, a low

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