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Rhodium-Catalyzed Modification of Poly(methylhydrosiloxane) into a Highly Cross-Linked Polysiloxane

Nistala Satyanarayana and Howard Alper*

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, Canada K1N 6N5

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ABSTRACT: Rhodium-catalyzed modification of poly(methylhydrosiloxane) (PMHS) via a dehydrogenative coupling reaction followed by in-situ oxidation under mild conditions gives a thermally stable and cross-linked polysiloxane. The polysiloxane was characterized by solid state ^{29}Si NMR spectroscopy.

Introduction

The Wurtz-type coupling of halosilanes in the presence of alkali metals is a general method for the formation of Si–Si bonds.[1] Transition-metal-catalyzed dehydrogenative coupling of silanes is an alternative method for Si–Si bond formation.[2] Reactions using titanium,[3] zirconium,[4] and rhodium[5] catalysts with various silanes have been reported in the literature. A mixture of several products such as disilanes, trisilanes, and disiloxanes was isolated together with disproportionation products in all cases. Disiloxanes are formed by the oxidation of an Si–Si bond.[5d,6] In some cases disiloxanes are isolated as major products when the reaction was carried out in the presence of oxygen.[5d,7] Even though the dehydrogenative coupling reaction has been known for some time, the application of this reaction to polymeric systems has not been investigated. The titanium-catalyzed dehydrogenative coupling reaction of primary and secondary silanes to oligomers of linear polysilanes was described in 1985.[2] We now report a novel rhodium-catalyzed modification (via dehydrogenative coupling and subsequent in situ oxidation of the Si–Si bond) of poly(methylhydrosiloxanes) {-$(CH_3)_3SiO[(CH_3)(H)SiO]_nSi(CH_3)_3$, n = ~35} to give thermally stable and cross-linked polysiloxane under mild conditions (Scheme 1).

Experimental Section

Instruments. TGA and DSC experiments were performed with a STA 1500H thermoanalysis dual system (version V5.32,

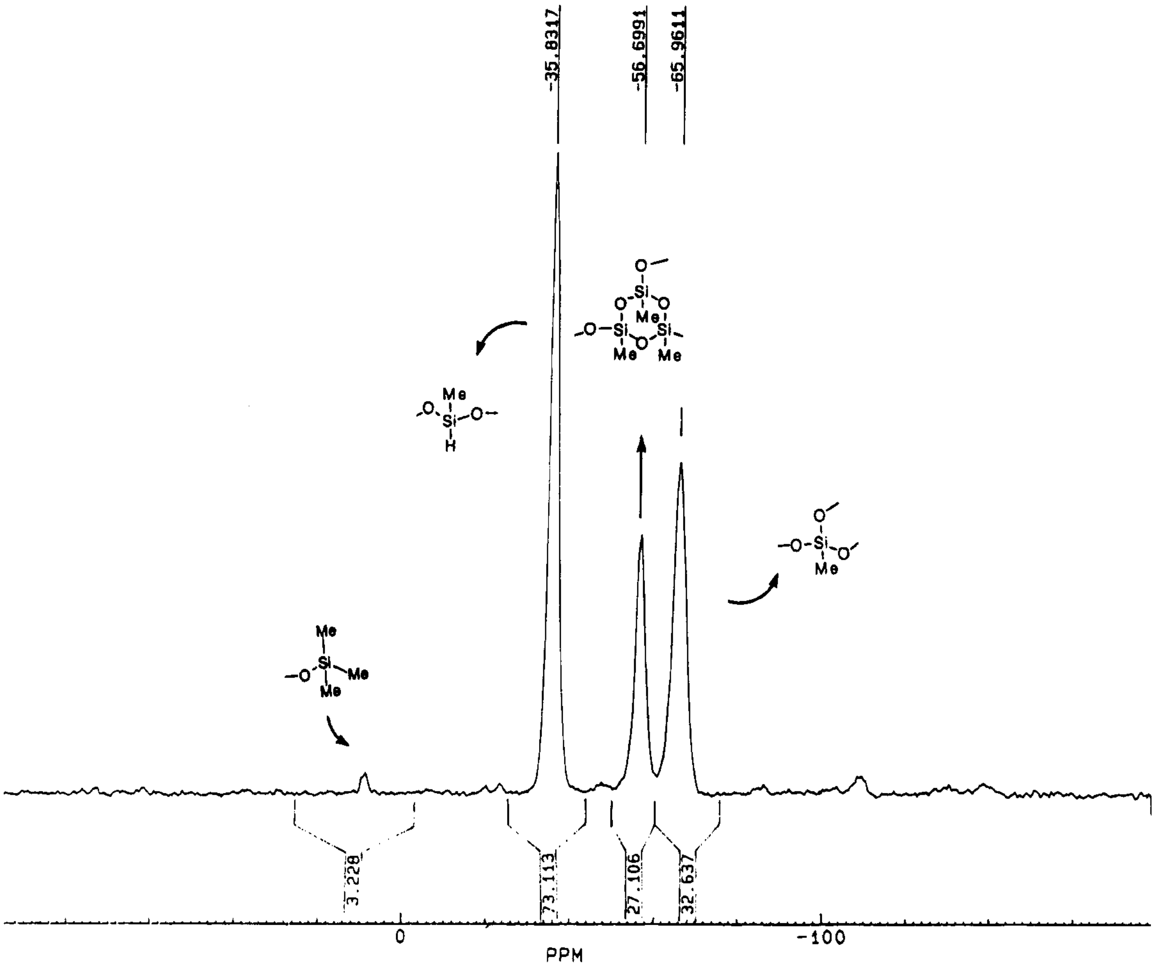

Figure 1. Solid-state ^{29}Si NMR spectrum of polysiloxane.

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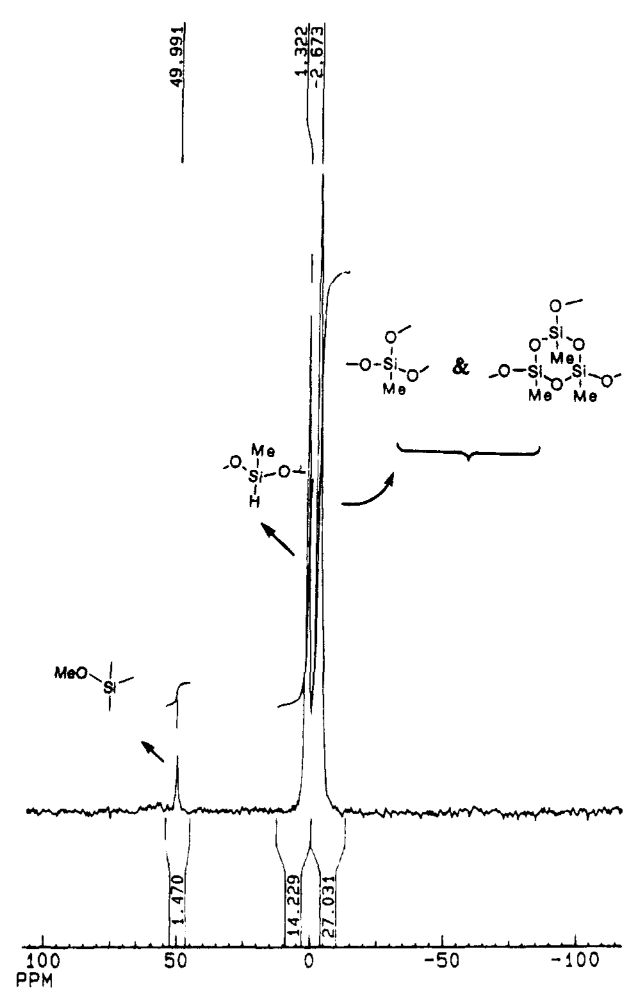
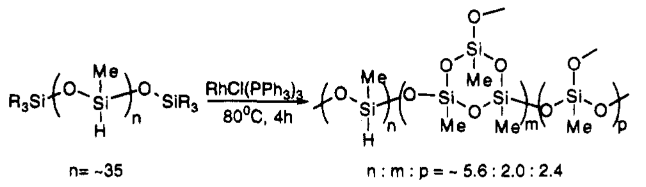
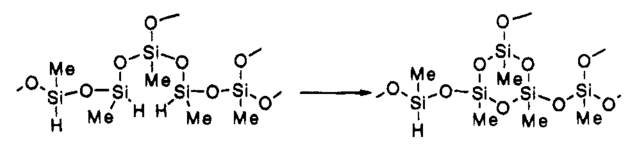


Figure 2. Solid-State ^{13}C NMR spectrum of polysiloxane.

Scheme 1



Scheme 2



Polymer Lab Instrumentation) at a heating rate of 10 °C/min under nitrogen. IR spectra were recorded using a Bomem MB100-C15 (FT-IR) instrument. Solution (^1H, ^{13}C) NMR spectra were recorded on either a Varian Gemini 200 or a Bruker 500 spectrometer, and solid-state (^{13}C, ^{29}Si) NMR spectra measurements were made on a Brucker 200 spectrometer. An X-ray powder spectrum was recorded with a Philips PW 3710 based analytical diffractometer using Ni-filtered Cu Kα radiation. Polymerization reactions were carried out in a 45-mL stainless steel autoclave.

Procedure. In a typical reaction, degassed toluene (3 mL) containing poly(methylhydrosiloxane) (3.0 g, ~1.8 mmol, calculated by taking $n = 35$) was transferred by a cannula into a 45-mL stainless steel autoclave reactor containing catalytic amounts (20 mg, 0.02 mmol) of $RhCl(PPh_3)_3$. The autoclave was flushed several times with nitrogen and pressurized, initially with oxygen (20 psi) followed by nitrogen (80 psi). The reaction mixture was stirred for 4–12 h at 80 °C, cooled to room temperature, and quenched with methanol (0.25 mL). The resulting white solid was filtered, washed several times[8] with toluene and pentane, and then vacuum dried for 10 h (3.9 g). The isolated polymer was insoluble in common organic solvents.

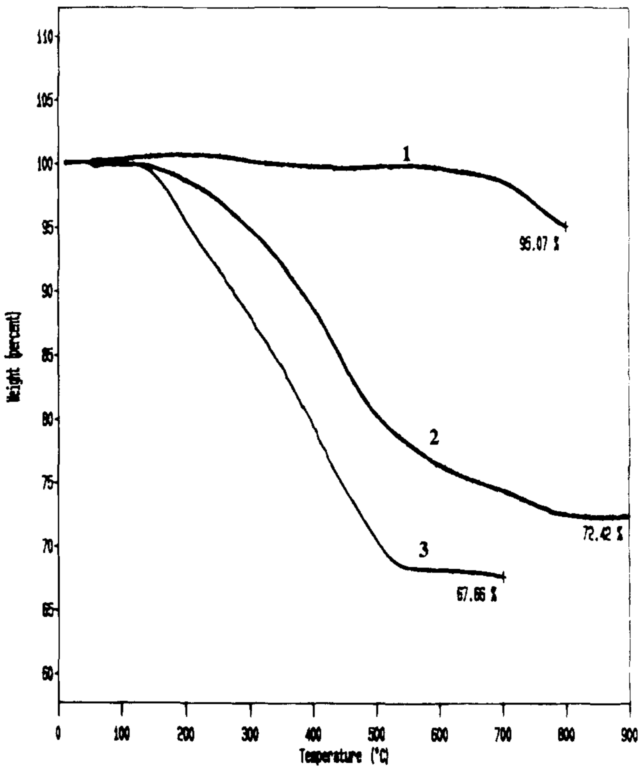


Figure 3. Comparison of the thermal analysis of polysiloxanes obtained by the catalytic systems: (1) $RhCl(PPh_3)_3$; (2) $Co_2(CO)_8$; (3) $[Rh(CO)_2Cl]_2$.

Results and Discussion

The FT-IR (KBr) spectrum of the cross-linked polysiloxane showed absorbances at 2092, 1266, and 1071 cm^{-1} characteristic of Si–H, $Si-CH_3$, and Si–O bonds, respectively. The solid-state ^{29}Si NMR spectrum (Figure 1) revealed detailed information about the types of Si units present in the polymer chain.

The ^{29}Si NMR spectrum exhibited three types of resonances in the ratio of 5.6:2.0:2.4. The signal at −35.8 ppm with a relatively high intensity was assigned to the silicon in the $-O[(CH_3)(H)SiO]-$ units,[9,10] and the remaining two signals are due to the cross-linking present in the polysiloxane. The combined integral ratio of these two signals suggested that up to 44% cross-linking is present in the polymer. The peak at −66.0 ppm was assigned to the silicon atom in the $-O[(CH_3)(O-)SiO]-$ units, whereas the resonance at −56.7 ppm may be due to the formation of trisiloxane rings along the backbone of the polymer.[9,11] The formation of cyclotrisiloxanes can be explained via intramolecular dehydrogenative coupling followed by oxidation of the Si–Si bond (Scheme 2).

It should be pointed out that the solid-state ^{29}Si NMR spectrum of the methylsilicone polymer $[(CH_3)(O-)SiO]_n$ exhibited similar resonances at −65.9 and −55.8 ppm which were assigned to the silicon in $-O[(CH_3)(O-)SiO]-$ and silicon in trisiloxane rings, respectively.[11] These assignments are in accord with the solid-state ^{13}C-NMR shown in Figure 2.

The solid-state ^{13}C NMR spectrum contains two principal signals at +1.32 and −2.67 ppm which cor-

Table 1. Influence of Various Parameters on the Modification of Poly(methylhydrosiloxane)[a]

catalyst	temp (°C)	time (h)	atm (gas)	yield (g)	productivity $P \times 10^3$ = g/[M]·h
$RhCl(PPh_3)_3$	80	4	N_2/O_2	3.9	44.3
$RhCl(PPh_3)_3$	RT	72	N_2/O_2		
$RhCl(PPh_3)_3$	80	36	N_2/O_2[b]	1.8	2.27
$RhCl(PPh_3)_3$	80	24	N_2	0.7	1.32
$[RhCl(CO)_2]_2$	80	4	N_2/O_2	*c*	
$[RhCl(CO)_2]_2$	80	12	CO[d]	2.7	3.75
$Co_2(CO)_8$	80	4	N_2/O_2	*c*	
$Co_2(CO)_8$	80	12	CO[d]	3.1	4.44

[a] Conditions: catalyst **1** (20 mg, 0.02 mmol), PMHS (3 mL), toluene (10 mL), N_2/O_2 = 80/20 psi. [b] Under 1 atm pressure of N_2/O_2 (4:1). [c] Dark polymeric materials were isolated. [d] 100 psi of CO was used.

respond to the $-O[(CH_3)(H)SiO]-$ and $-O[(CH_3)(O-)SiO]-$ carbon, respectively. The intensity of the peak at −2.67 ppm with respect to that at −1.32 ppm indicates that the $Si-CH_3$ carbon of trisilicon rings and $Si-CH_3$ carbon in $-O[(CH_3)(O-)Si(O)]-$ occurred together at −2.67 ppm. The small resonance at −49.9 ppm was assigned to $Si-OCH_3$, formed when the reaction was terminated by methanol. However, possible alcoholysis of several other Si−H groups in the polymer chain to the $Si-OCH_3$ functionality cannot be ruled out. The rhodium-catalyzed alcoholysis of various silanes has been documented in the literature.[12] An X-ray powder diffractogram of the cross-linked polysiloxane showed a broad signal indicating that the polymer is not highly crystalline.

The reactivity of poly(methylhydrosiloxane) was examined under different conditions using catalytic amounts of $RhCl(PPh_3)_3$ (Table 1). Low reactivity was observed when the reaction was effected in the presence of nitrogen under similar conditions. This suggests that the presence of oxygen in the reaction medium facilitates reaction[7,14] and serves as an oxygen source for the disiloxane oxygen. Also, it is interesting to note that the reaction did not proceed at room temperature using longer reaction times (3 days). Lower reactivity was observed when the reaction was carried out in a 4:1 gaseous mixture of N_2/O_2 under similar conditions.

Two other catalysts were tested for reactivity toward poly(methylhydrosiloxane) under similar conditions. Dark and gummy polymeric materials were obtained when the reaction was carried out in the presence of $Co_2(CO)_8$ or $[Rh(CO)_2Cl]_2$. Light brown polymers were formed by replacing oxygen with carbon monoxide using a longer reaction time (12 h). This may be due the stability of the catalyst in the presence of carbon monoxide. FT-IR spectra recorded for these polymers were identical to the spectra obtained from the $RhCl(PPh_3)_3$ catalytic system, indicating the formation of similar polysiloxanes. Thermogravimetric analysis (TGA) experiments were conducted on the polymers obtained from reactions carried out in the presence of different catalytic systems (Figure 3). The polysiloxanes obtained from the reaction with the $RhCl(PPh_3)_3$ catalytic system showed higher thermal stability due to the higher cross-linking (residue of 95.1% by weight remained at 800 °C) when compared with the polymers obtained using $Co_2(CO)_8$ and $[Rh(CO)_2Cl]_2$ as catalysts (residues of 72.4% and 67.7% remained at 800 °C, respectively). The glass transition temperatures were not recorded as the differential scanning calorimetry traces obtained were quite featureless.

In conclusion, transition-metal-catalyzed modification of poly(methylhydrosiloxane) into a highly cross-linked polysiloxane has been developed and application of this methodology to several other low molecular weight polysilanes is in progress.

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References and Notes

(1) West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U. K., 1982; Vol. 2, Chapter 9.4, p 365.

(2) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11. Here the formation of Si−Si bonds from Si−H bonds is referred to as the dehydrogenative coupling of organosilanes.

(3) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

(4) Aitken, C. T.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986**, *64*, 1677.

(5) (a) Ojima, I.; Inaba, S. I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7. (b) Haszeldine, R. N.; Parish, R. V.; Parry, D. J. *J. Chem. Soc. London, A* **1969**, 683. (c) Wesley, K. A. B. *Organometallics* **1987**, *6*, 1590. (d) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595.

(6) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217.

(7) For a discussion of the effect of molecular oxygen on hydrosilation reaction, see: Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308.

(8) At this stage, any traces of the catalyst and PPh_3O formed during reaction were removed.

(9) Coleman, B. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 7, p 197.

(10) Harris, R. K.; Kimber, B. J.; Wood, M. D. *J. Organomet. Chem.* **1976**, *116*, 291.

(11) Engelhardt, G.; Jancke, H.; Lippmaa, E.; Samoson, A. *J. Organomet. Chem.* **1981**, *210*, 295.

(12) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *114*, 135.

(13) At present we do not have any evidence about the active catalytic species; however, it should be noted that the $[RhCl(C_8H_{14})_2]_2$ complex has been shown to give a dioxygen complex in the presence of molecular oxygen. See: James, B. R.; Ng, F. T. T.; Ochai, E. *Can. J. Chem.* **1972**, *50*, 590.

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