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A Catalytic Route to Grafted Silicones

Bhanu P. S. Chauhan,[†] Thomas E. Ready, Zoha AL-Badri, and Philip Boudjouk*

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

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Twelve new linear polysiloxanes were prepared in high yields by catalytic ($RhCl(PPh_3)_3$) alcoholysis of poly(methylhydrosiloxane). The reaction conditions preserve the backbone and are tolerant of a variety of functional groups.

Introduction

Considerable effort is currently focused on the development of new synthetic routes to functional silicones.[1,2] Appropriate substitution on the polysiloxane backbone can lead to diverse materials: liquid crystals,[3] cross-linking agents,[4] conductive[5] and electroluminescent[6] polymers, nonlinear optical materials,[7] and bactericides.[8] In this context, hydrosilylation of olefins has been the methodology of choice to attach organic groups onto the polymer backbone.[3−9] However, formation of mixtures of α- and β-isomers, insoluble materials, and rearrangement products are common drawbacks.[10]

Metal-catalyzed oxidation reactions of monomeric hydrosilanes are well-documented and have been successfully applied to the synthesis of alkoxysilanes under mild and neutral reaction conditions.[11] On the other hand, selective modification of Si−H bonds in a polymeric system has been a challenging problem because of the susceptibility of these bonds toward dehydrocoupling, rearrangement, and backbone degradation reactions.[12,13] However, recently we have shown that metal-catalyzed oxidation reactions can be successfully applied to linear and cyclic polyhydrosiloxanes to generate well-defined polyfunctional silicones.[14] In this paper, we detail our studies of Rh-catalyzed selective alcoholysis of a linear poly(hydrosiloxane).

Results and Discussion

Rh-catalyzed alcoholysis reactions of poly(methylhydrosiloxane) (PMHS; **1**) were optimized with benzyl alcohol and were monitored by multinuclear NMR. In a typical experiment, $RhCl(PPh_3)_3$ (0.04 mmol) was dissolved in benzene-d_6 (0.5 mL) in an NMR tube, followed by the addition of benzyl alcohol (0.216 mL, 2 mmol) and **1** (0.120 mL, 2 mmol). This mixture was degassed by three to four freeze−pump−thaw cycles and heated in an oil bath at 78 °C, just below the refluxing temperature, under a constant flow of argon. During the course of the reaction, evolution of a gas, presumably H_2, was observed.

After 5 h, ^{29}Si and ^{1}H NMR indicated ~50% consumption of the Si−H bonds in **1** and the appearance of new silicon signals at δ −57.26, −57.34, −57.41 ($-SiMeOCH_2Ph-$), and +9.51 (terminal $OSiMe_3$), reflecting the change in the electronic environment of the central $-(MeSiHO_2)-$ units to $-(MeSiO_3)-$ units (Figure 1a).

[†] Department of Chemistry, The Catholic University of America, Washington, DC 20064. Email: Chauhan@cua.edu.

(1) (a) Wisian-Neilson, P., Allcock, H. R., Wayne, K. J., Eds. *Inorganic and Organometallic Polymers II*; American Chemical Society: Washington, DC, 1994. (b) Hench, L. L.; West, J. K. *Chemical Processing of Advanced Materials*; Wiley: New York, 1992. (c) Clarson, S. J., Semlyen, J. A., Eds. *Silicon Based Polymer Science. A Comprehensive Resource;* American Chemical Society: Washington, DC, 1990.

(2) (a) Rochow, E. G. *Silicon and Silicones*; Springer-Verlag: Berlin, Heidelberg, 1987. (b) Kendrick, T. C.; Parbhoo, B.; White, J. W. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 21, 1289. (c) Yilgör, I.; McGrath, J. E. *Advances in Polymer Science*; Springer-Verlag: Berlin, Heidelberg, 1986. (d) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236. (e) Yilgör, I.; Riffle, J. S.; McGrath, J. E. *ACS Symp. Ser.* **1983**, *No. 282*, 161. (f) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

(3) (a) Gray, G. W.; Hawthorne, W. D.; Lacey, D.; White, M. S.; Semlyen, J. A. *Liq. Cryst.* **1989**, *6*, 503. (b) Richard, H.; Mauzac, M.; Sigaud, G.; Achard, M.-F.; Hardouin, F. *Liq. Cryst.* **1991**, *9*, 679.

(4) Coqueret, X.; El Achari, A.; Hajaiej, A.; Lablache-Combier, A.; Loucheux, C.; Randrianarisoa, L. *Makromol. Chem.* **1991**, *192*, 1517.

(5) Zhu, Z.; Einset, A. G.; Yang, C.-Y.; Chen, W.-X.; Wnek, G. E. *Macromolecules* **1994**, *27*, 4076.

(6) Bisberg, J.; Cumming, W. J.; Gaudiana, R. A.; Hutchinson, K. D.; Ingwall, R. T.; Kolb, E. S.; Mehta, P. G.; Minns, R. A.; Petersen, C. P. *Macromolecules* **1995**, *28*, 386.

(7) Belfield, K. D.; Chinna, C.; Najjar, O. *Macromolecules* **1998**, *31*, 2918.

(8) (a) Nohr, R. S.; McDonald, J. G. *J. Biomater. Sci. Polym. Ed.* **1994**, *5*, 607. (b) Hazziza-Laskar, J.; Helarry, G.; Sauvet, G. *J. Appl. Polym. Sci.* **1995**, *58*, 77.

(9) (a) Bratcher, M. S.; DeClue, M. S.; Grunnet-Jepsen; A.; Wright, D.; Smith, B. R.; Moerner, W. E.; Siegel, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 9680. (b) Chang-Chien, G.-P.; Kuo, J.-F. *Appl. Polym. Sci.* **1995**, *57*, 1183. (c) Mauzac, M.; Hardouin, F.; Richard, H.; Achard, M. F.; Sigaud, G.; Gasparoux, H. *Eur. Polym. J.* **1986**, *22*, 137.

(10) (a) Torres, G.; Madec, P.-J.; Marechal, E. *Makromol. Chem.* **1989**, *190*, 203.

(11) For rhodium-catalyzed alcoholysis of monomeric organosilanes see: (a) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* **1973**, 38. (b) Corriu, R. J. P.; Moreau, J. J. E. *Tetrahedron Lett.* **1973**, 4469. (c) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *114*, 135. (d) Ogima, I.; Nihonyanagi, M. Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 938.

(12) (a) Bedard, T. C.; Corey, J. Y. *J. Organomet. Chem.* **1992**, *428*, 315. (b) Corey, J. Y. *Adv. Silicon Chem.* **1991**, *1*, 327. (c) Matarasso-Tchiroukhine, E. *J. Chem. Soc., Chem. Commun.* **1990**, 681. (d) Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265.

(13) (a) For a recent review see: Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363 and references therein. (c) Lestel, L.; Cheradame, H.; Boileau, S. *Polymer* **1990**, *31*, 1154.

(14) (a) Chauhan, B. P. S.; Boudjouk, P. Presented at the 2nd Fargo Conference on Main Group Chemistry, Fargo, ND, June 4−6, 1998; Abstract No. O-32. (b) Chauhan, B. P. S.; Boudjouk, P. *Tetrahedron Lett.* **1999**, *40 (22)*, 4123. (c) Arruda, A.; Campiglia, A.; Chauhan, B. P. S.; Boudjouk, P. *Anal. Chim. Acta* **1999**, *396*, 263. (d) Chauhan, B. P. S.; Boudjouk, P. *Tetrahedron Lett.* **2000**, *41(8)*, 1127. (e) Chauhan, M.; Chauhan, B. P. S.; Boudjouk, P. *Org. Lett.* **2000**, *2*, 1027.

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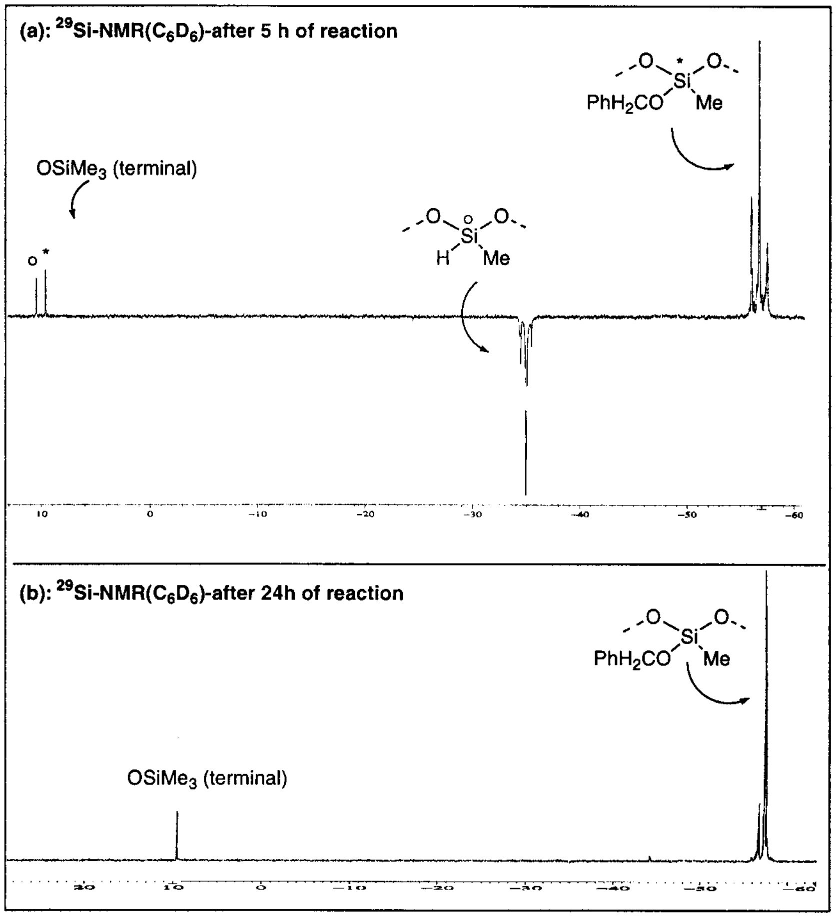
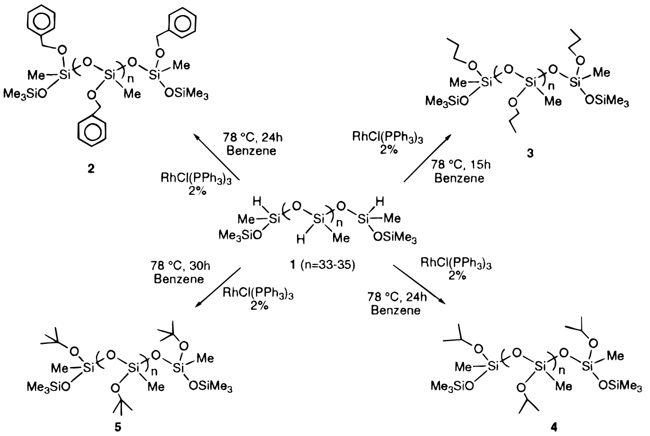


Figure 1. ^{29}Si NMR of the reaction mixture of Rh-catalyzed oxidation of PMHS in the presence of benzyl alcohol.

Scheme 1



After 24 h, the ^{29}Si spectrum displayed complete consumption of **1** (δ −34.16, −34.20, −34.26, +10.58 (terminal OSiMe$_3$)) and formation of polymer **2** in essentially quantitative yield (Figure 1b). Color changes during the course of the reaction are also noteworthy and provide an indication of the reaction progress. As the reaction proceeded, the yellow color turned orange and returned to light red after 24 h when the reaction was completed. Polymer **2** (Scheme 1) was characterized by a combination of ^{29}Si, ^{13}C, and ^{1}H NMR and IR spectroscopy. The ^{1}H NMR of **2** showed the absence of Si−H signals and Si−CH$_3$/O−CH$_2$Ph resonances in a ratio consistent with the proposed structure. The molecular weight (M_w) determined by gel permeation chromatography (GPC) was 5600 ($M_w/M_n = 1.19$) relative to polystyrene standard. This is in good agreement with calculated values ($M_w \approx 5445-5775$).

This methodology provides access to a variety of functionalized polysiloxanes. Primary, secondary, and tertiary alcohols were treated with PMHS under convenient reaction conditions. We observed that primary alcohols were the most reactive (Scheme 1) and that even the hindered *tert*-butoxy group could be fully substituted on the backbone. The advantages of this methodology are (i) mild reaction conditions, (ii) high yields, (iii) high selectivity, (iv) soluble products, (v) simple purification, and (vi) easy monitoring of the reaction progress by NMR. The results are summarized in Table 1.

Alcohols with functionalities also fared well, leading to fully substituted polysiloxanes. Under our conditions, alcoholysis of PMHS was achieved with 2,5-dimethoxybenzyl alcohol, 2-pyridylpropanol, 4-pyridylpropanol, 4-hydroxy-1-methylpiperidine, and 9-phenanthrolinemethanol in good yields (entries 1−5). Pendant functional groups (entries 3 and 4) lead to polymers potentially useful as catalyst supports.

The activity of an epoxy alcohol was also examined. Reaction of glycidol with PMHS led to the formation of polymer **11** without side reactions (entry 6).[15] The successful couplings of **1** with 4-(phenylazo)phenol (entry 7) and 4-(dimethylamino)phenol (entry 8) il-

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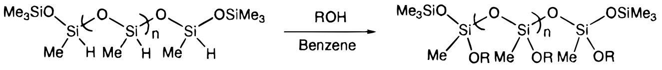
(15) (a) Buekers, J.; Bier, P.; Schlitte, S.; Eversheim, E.; Helmut-Martin, M. U.S. Patent 5623026, 1997. (b) Ghoshal, R.; Mukerji, P. U.S. Patent 5863970, 1997. (c) Zhang, C.; Laine, R. *J. Organomet. Chem.* **1996**, *521*, 199.

Table 1. Rh-Catalyzed Dehydrogenative Oxidation of Poly(methylhydrosiloxane) to Poly(methylalkoxysiloxanes)



n=33-35

1

2-13

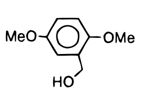
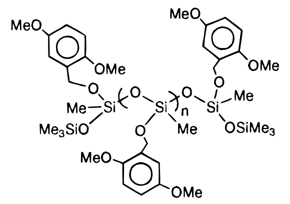
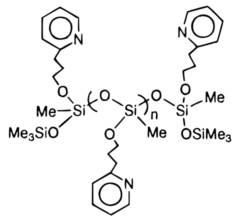
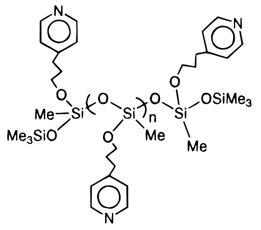
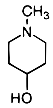
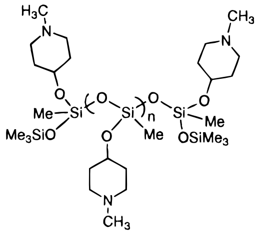
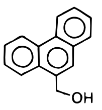
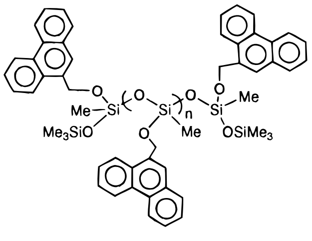
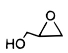
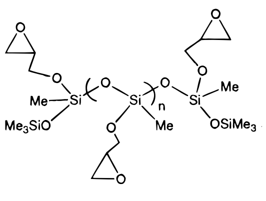
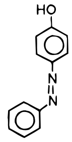
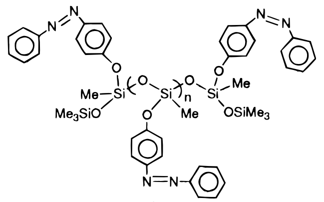
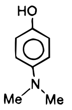
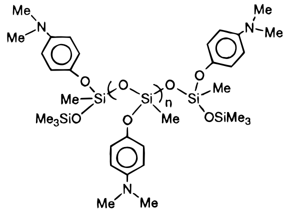
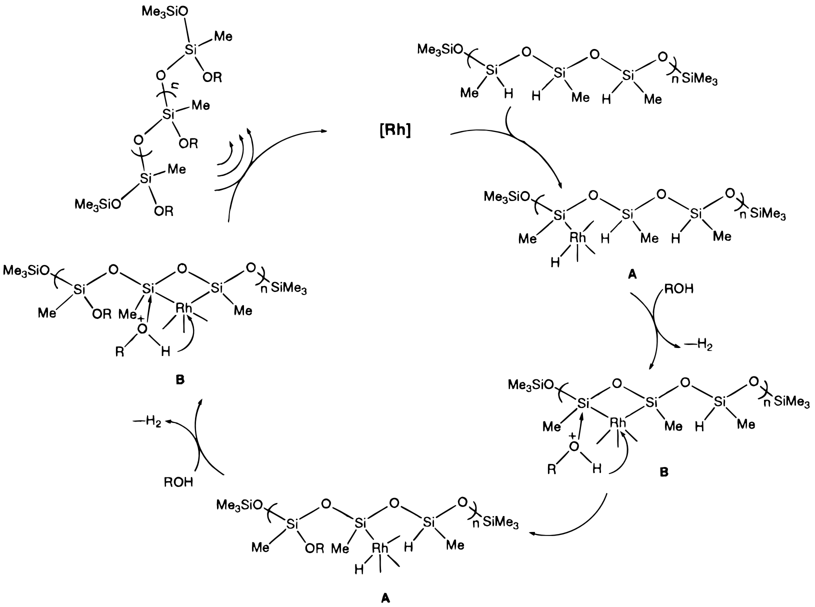
Entry	Alcohol (ROH)	Reaction Conditions	Product	Yield %	^{29}Si NMR (C_6D_6)
1		$RhCl(PPh_3)_3$, 2% 78 °C, 24h Benzene	 6	93	-56.87; -56.93 -56.97 +9.57 (Terminal $OSiMe_3$)
2		$RhCl(PPh_3)_3$, 2% 78 °C, 24h Benzene	 7	94	-57.10 (broad); -57.83 -57.92; -58.02 +9.59 (Terminal $OSiMe_3$)
3		$RhCl(PPh_3)_3$, 2% 78 °C, 24h Benzene	 8	91	-57.20; -57.95 -58.06; -58.16 +9.08 (Terminal $OSiMe_3$)
4		$RhCl(PPh_3)_3$, 2% 78 °C, 48h Benzene	 9	89	-58.10; -58.78 -59.78; -59.85 -59.95, -60.04 +9.59 (Terminal $OSiMe_3$)
5		$RhCl(PPh_3)_3$, 2% 78 °C, 36h Benzene	 10	94	-57.10 (broad); -57.83 -57.92; -58.02 +9.59 (Terminal $OSiMe_3$)
6		$RhCl(PPh_3)_3$, 2% 78 °C, 24h Benzene	 11	93	-57.10; -57.83 -57.92; -58.02 +9.59 (Terminal $OSiMe_3$)

Table 1 (Continued)

Entry	Alcohol (ROH)	Reaction Conditions	Product	Yield %	^{29}Si NMR (C_6D_6)
7		$RhCl(PPh_3)_3$, 2% 78 °C, 24h Benzene	 12	97	-59.75; -60.35 +10.67 (Terminal $OSiMe_3$)
8		$RhCl(PPh_3)_3$, 2% 78 °C, 24h Benzene	 13	93	-56.46; -56.67; -56.97 +9.46 (Terminal $OSiMe_3$)

Scheme 2



lustrate the utility of PMHS as a potential support for NLO chromophores.[16]

All the polymers are stable as solids or in hydrocarbon solutions for more than 3 months. To assess hydrolytic stability, polymer **2** was dissolved in benzene-d_6 and treated with a 3-fold excess of D_2O. Polymer degradation was monitored by NMR. After 3 h at room temperature <10% conversion of $SiOCH_2Ph$ bonds to SiOH/SiOSi bonds was observed. After 2.5 h of heating at 78 °C only 25% of the $SiOCH_2Ph$ bonds were cleaved. The hydrolysis products were not identified. Similar results were obtained for polymers **6**, **7**, **9**, and **13**.

Proposed Mechanism. A reasonable mechanism is given in Scheme 2. The first step involves insertion of rhodium into the Si−H bond to form the silyl−rhodium complex, A. On the basis of previous reactivity studies[17] of disiloxanes with metal complexes, it is reasonable to assume the generation of the rhodacycle B. Nucleophilic attack[11] of the alcohol at one of the silicon atoms of B leads to the corresponding silyl ether and A, which can then insert into an adjacent Si−H bond.

Conclusions

The methodology allows for complete replacement of the silane hydrogens in poly(methylhydrosiloxane) with a wide variety of alkoxy groups under mild conditions. These polymers represent some of the first examples of selectively modified linear polysiloxanes.

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[16] (a) For reviews of NLO chromophores attached to silicon-containing polymers see: Samyn, C.; Verbiest, T.; Persons, A. *Macromol. Rapid Commun.* **2000**, *21*, 1. (b) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.

[17] (a) Bell, L. G.; Gustavson, W. A.; Thanedar, S.; Curtis, M. D. *Organometallics* **1983**, *2*, 740. (b) Curtis, M. D.; Epstien, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213. (c) Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362. (d) Eaborn, C. *J. Organomet. Chem.* **1973**, *C3*, 54. (e) Sakada, K.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 2063. (f) Osakada, K.; Hataya, K.; Nakamura, Y.; Tanaka, M.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1993**, 576. (g) Nagashima, H.; Ueda, T.; Nishiyama, H.; Itoh, K. *Chem. Lett.* **1993**, 347. (h) Nagashima, H.; Tatebe, K.; Ishibashi, T.; Sakakibara, J.; Itoh, K. *Organometallics* **1989**, *8*, 2495.

Experimental Section

All reactions were carried out under an atmosphere of argon. Air-sensitive products and reagents were handled by standard Schlenk techniques. All solvents were dried and distilled from purple solutions of sodium/benzophenone or P_2O_5. Glassware was dried in an oven at 110−120 °C prior to use. Poly(methylhydrosiloxane), $Me_3Si-(O-SiMeH-)_n-O-SiMe_3$ ($M_w \approx 2000$; $n = 33-35$), and $RhCl(PPh_3)_3$ (99.99%) were obtained from Aldrich and used as received. Commercially available alcohols were used as such without any further purification, except for benzyl alcohol and 2,5-dimethoxybenzyl alcohol, which were distilled prior to use.

^{29}Si, ^{13}C, and ^{1}H NMR spectra were recorded on JEOL GSX270 and GSX400 spectrometers. ^{1}H and ^{13}C chemical shifts were measured against Me_4Si using solvent resonances as standard locks. ^{29}Si chemical shifts were referenced to external Me_4Si in the same solvent. The molecular weight of the polymers was determined by Waters GPC with polystyrene as standard and THF as solvent. IR spectra were recorded on a Matheson Instruments 2020 Galaxy Series spectrometer as KBr pellets or solutions in CaF_2 cells. Elemental analyses were carried out by Galbraith Laboratories Inc.

Synthesis of Polymers 2−13. In a Schlenk tube, $RhCl(PPh_3)_3$ (∼36 mg, 0.04 mmol) was suspended in dry benzene (0.8 mL), followed by the addition of benzyl alcohol (0.22 mL, 2 mmol) and PMHS (0.12 mL, 2 mmol). This mixture was degassed by three to four freeze−pump−thaw cycles and heated in an oil bath at 78 °C, under a constant flow of argon. The red color of the catalyst disappeared within 15 min of heating, and the reaction mixture turned yellow and homogeneous. During the entire course of the reaction, evolution of H_2 was observed. After 24 h, the mixture was cooled to room temperature and passed through a dry silica gel pad and eluted with pentane/benzene (20/80). Solvent evaporation under reduced pressure provided polymer **2** in 97% yield. Polymers **3**−**12** were obtained using the same reaction conditions and molar ratios. For gram-scale preparations (4−7 g) of these polymers longer reaction times (48−72 h) were employed.

Poly[methyl(benzyloxy)siloxane] (2). Yield: 97%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.13 (s, $OSiMe_3$); 0.30 (s, broad, SiMe); 4.84−4.90 (s, broad, OCH_2); 7.14, 7.32 (broad, aromatics). ^{13}C NMR (C_6D_6, 25 °C): δ 1.55 ($OSiMe_3$); −4.12 (broad, SiMe); 64.35 (broad, OCH_2); 126.53, 127.14, 128.30, 140.44 (broad, aromatics). ^{29}Si NMR (C_6D_6, 25 °C): −56.63, −56.7 (very small); −57.26; −57.34; −57.41 (SiMe); +9.62 (terminal $OSiMe_3$). Anal. Calcd for $C_8H_{10}O_2Si$: C, 57.83; H, 6.02; Si, 16.86. Found: C, 57.85; H, 6.00; Si, 16.88. GPC (THF/polystyrene): M_w = 5600 (M_w/M_n = 1.19).

Poly(methyl-*n*-propoxysiloxane) (3). Yield: 93%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.14 (s, $OSiMe_3$); 0.34 (s, broad, SiMe); 1.22 (t, broad, CH_3); 1.88 (m, broad, CH_2); 4.01 (t, broad, OCH_2). ^{13}C NMR (C_6D_6, 25 °C): δ 1.42 ($OSiMe_3$); −0.5 (SiMe); 10.60 (CH_3); 24.70 (CH_2); 62.91 (OCH_2). ^{29}Si NMR (C_6D_6, 25 °C): −57.94 (SiMe); +8.51 (terminal $OSiMe_3$).

Poly(methylisopropoxysiloxane) (4). Yield: 95%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.15 (s, $OSiMe_3$); −0.014 (s, broad, SiMe); 1.11 (d, CH_3); 4.12 (q, broad, OCH). ^{13}C NMR (C_6D_6, 25 °C): δ 1.72 ($OSiMe_3$); −3.02 (SiMe); 15.69 (CH_3); 64.60 (OCH). ^{29}Si NMR (C_6D_6, 25 °C): −60.01 (broad, SiMe); +7.95 (terminal $OSiMe_3$).

Poly(methyl-*tert*-butoxysiloxane) (5). Yield: 93%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.026 (s, $OSiMe_3$); −0.001 (s, broad, SiMe); 1.26 (CH_3). ^{13}C NMR (C_6D_6, 25 °C): δ 1.82 ($OSiMe_3$); −0.91 (SiMe); 15.69 (CH_3); 69.01 (OC). ^{29}Si NMR (C_6D_6, 25 °C): −63.50 (broad, SiMe); +7.35 (terminal $OSiMe_3$).

Poly{methyl[(2,5-dimethoxybenzyl)oxy]siloxane} (6). Yield: 93%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.12 (s, $OSiMe_3$); 0.35 (s, broad, SiMe); 3.35 (s, broad, OCH_3); 3.46 (s, broad, OCH_3); 5.10 (s, broad, OCH_2); 6.43, 6.62, 7.31 (broad, aromatics). ^{13}C NMR (C_6D_6, 25 °C): δ 1.41 ($OSiMe_3$); −4.47 (SiMe); 54.88, 54.93 (broad, OCH_3); 59.66 (OCH_2); 110.36, 112.20, 113.83, 130.10, 150.38, 153.98 (broad, aromatics). ^{29}Si NMR (C_6D_6, 25 °C): −56.87, −56.93, −56.99 (SiMe); +9.57 (terminal $OSiMe_3$). Anal. Calcd for $C_{10}H_{14}O_4Si$: C, 53.09; H, 6.19; Si, 12.38. Found: C, 53.07; H, 6.16; Si, 12.40. GPC (THF/polystyrene): M_w = 7463 (M_w/M_n = 1.16).

Poly{methyl[3-(2-pyridyl)-1-propoxy]siloxane} (7). Yield: 94%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.17 (s, $OSiMe_3$); 0.36 (s, broad, SiMe); 1.74 (s, broad, CH_2); 2.49 (s, broad, CH_2); 3.76 (s, broad, OCH_2); 6.83, 7.01, 8.52 (broad, aromatics). ^{13}C NMR (C_6D_6, 25 °C): δ 1.59 ($OSiMe_3$); −4.18 (broad, SiMe); 31.28 (broad, CH_2); 32.98 (broad, CH_2); 61.55 (broad, OCH_2); 123.70, 127.19, 128.41, 150.14 (broad, aromatics). ^{29}Si NMR (C_6D_6, 25 °C): −57.10 (broad), −57.83, −57.92, −58.02 (SiMe); +9.59 (terminal $OSiMe_3$). Anal. Calcd for $C_9H_{13}O_2NSi$: C, 55.38; H, 6.66; N, 7.17. Found: C, 55.36; H, 6.68; N, 7.18.

Poly{methyl[3-(4-pyridyl)-1-propoxy]siloxane} (8). Yield: 91%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.13 (s, $OSiMe_3$); 0.32 (s, broad, SiMe); 2.12 (m, broad, CH_2); 2.91 (t, broad, CH_2); 3.92 (t, broad, OCH_2); 6.69 (t, broad), 6.94 (d, broad), 7.18 (m, broad), 8.43 (broad) (aromatics). ^{29}Si NMR (C_6D_6, 25 °C): δ −57.20, −57.95, −58.06, −58.16 (SiMe); +9.08 (terminal $OSiMe_3$). Anal. Calcd for $C_9H_{13}O_2NSi$: C, 55.38; H, 6.66; N, 7.17. Found: C, 55.39; H, 6.67; N, 7.19. GPC (THF/polystyrene): M_w = 6538 (M_w/M_n = 1.12).

Poly{methyl-[4-(1-methylpiperidyl)oxy]siloxane} (9). Yield: 89%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.18 (s, $OSiMe_3$); 0.38 (s, broad, SiMe); 1.84, 1.87, 195, 198 (broad, CH_2 and NCH_2); 2.10 (s, broad, NCH_3); 4.08 (s, broad, OCH). ^{29}Si NMR (C_6D_6, 25 °C): δ −57.10 (broad), −58.78 (broad), −59.78, −59.85 to −59.95, −60.04 (SiMe); +9.59 (terminal $OSiMe_3$); an unknown but very small sharp peak at −52.81 was also observed. Anal. Calcd for $C_7H_{15}O_2NSi$: C, 48.55; H, 8.67; N, 8.09. Found: C, 48.54; H, 8.65; N, 8.11. GPC (THF/polystyrene): M_w = 5782 (M_w/M_n = 1.17).

Poly[methyl(9-phenanthrylmethoxy)siloxane] (10). Yield: 95%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.19 (s, $OSiMe_3$); 0.30 (s, broad, SiMe); 5.13, 5.37 (s, broad, OCH_2); 6.99, 7.17, 7.34, 7.67, 7.91, 8.00, 8.36 (broad, aromatics). ^{13}C NMR (C_6D_6, 25 °C): δ 1.20 ($OSiMe_3$); −3.78 (broad, SiMe); 63.51 (broad, OCH_2); 122.81, 123.35, 124.56, 125.68, 126.76, 128.61, 128.72, 128.91, 130.65, 130.93, 131.97, 134.24, 135.18 (broad, aromatics). ^{29}Si NMR (C_6D_6, 25 °C): δ −56.10, −56.76 (SiMe); +10.14 (terminal $OSiMe_3$).

Poly{methyl[(±)-oxirane-2-methoxy]siloxane} (11). Yield: 93%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.17 (s, $OSiMe_3$); 0.36 (s, broad, SiMe); 1.74 (s, broad, CH_2); 2.49 (s, broad, CH_2); 3.76 (s, broad, OCH_2); 6.83, 7.01, 8.52 (broad, aromatics). ^{13}C NMR (C_6D_6, 25 °C): δ 1.42 ($OSiMe_3$); −4.50, −4.98, −6.00 (broad, SiMe); 43.61 (broad, CH_2); 51.65 (broad, CH); 63.54 (broad, OCH_2). ^{29}Si NMR (C_6D_6, 25 °C): −57.10 (broad), −57.83, −57.92, −58.02 (SiMe); +9.59 (terminal $OSiMe_3$). Anal. Calcd for $C_4H_8O_3Si$: C, 36.36; H, 6.06. Found: C, 36.37; H, 6.05.

Poly{methyl[4-(phenylazo)phenoxy]siloxane} (12). ^{1}H NMR (C_6D_6, 25 °C): δ 0.11 (s, $OSiMe_3$); 0.32 (s, broad, SiMe); 7.10, 7.15, 7.99 (broad, aromatics). ^{29}Si NMR (C_6D_6, 25 °C): −59.75, −60.35 (SiMe); +10.67 (broad, terminal $OSiMe_3$).

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