Reconstruction of Backbones of Silicon Polymers by Palladium-Catalyzed Insertion of Quinones into Silicon-Silicon Bonds

Hiroshi Yamashita, N. Prabhakar Reddy, and Masato Tanaka*

National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

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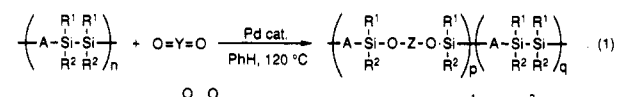
Recently increasing attention has been directed toward silicon polymers due to their intriguing physicochemical properties and possible applications to various functional materials.[1] However, the methods to modify the chemical structure of preformed polymers, aimed at the control of the properties, are limited to some transformation reactions at the side chains. We report herein an entirely new process that involves direct conversion of the backbones via palladium-catalyzed insertion of quinones into Si–Si bonds.[2-4]

Preliminary model experiments using hexamethyldisilane revealed that Pd–$P(OCH_2)_3CEt$ (catalyst A) and Pd–PEt_3 (catalyst B) complexes were the catalysts of choice for the insertion of 9,10-phenanthraquinone (**1a**) and *p*-benzoquinone (**1b**), respectively.[5] These catalyst systems could be successfully applied to the backbone reconstruction. Thus, a mixture of poly[(1,2-dimethyl-1,2-diphenyldisilanylene)(*p*-phenylene)][6] (**2a**; M_w = 4.6 × 10^4, M_w/M_n = 2.6, 0.20 mmol of monomer unit), 9,10-phenanthraquinone (**1a**; 0.21 mmol), $Pd(dba)_2$ (dba = dibenzylideneacetone; 0.004 mmol), $P(OCH_2)_3CEt$ (0.008 mmol), and benzene (0.10 mL) was heated under nitrogen in a sealed tube at 120 °C for 3 h. The brown reaction mixture was dissolved in benzene (4 mL), and the solution was filtered. The filtrate was concentrated (~1 mL) and was added dropwise to 2-propanol (~4 mL). The precipitated off-white solid was separated and dried in vacuo to give an exhaustively modified polymer **3a**[7a] (M_w = 5.8 × 10^4, M_w/M_n = 3.0) with 9,10-phenanthrylenedioxy units incorporated in the backbone in 90% isolated yield (eq 1 and Table I). Since the insertion proceeds nearly quantitatively, the extent of the modification can be easily controlled by the charged amount of **1a**; e.g., the use of 0.3 equiv of **1a** resulted in a partially (29%) modified polymer **3b**.[7b,8]



(1)

2a: A = *p*-C_6H_4, R^1 = Ph, R^2 = Me
2b: A = $(CH_2)_2$, R^1 = R^2 = Me
2c: A = O, R^1 = R^2 = Me

1a: 
1b:

3a, b: A = *p*-C_6H_4, R^1 = Ph, R^2 = Me, Z = 9,10-phenanthrylene
3c: A = $(CH_2)_2$, R^1 = R^2 = Me, Z = 9,10-phenanthrylene
3d: A = O, R^1 = R^2 = Me, Z = 9,10-phenanthrylene
3e: A = $(CH_2)_2$, R^1 = R^2 = Me, Z = *p*-C_6H_4

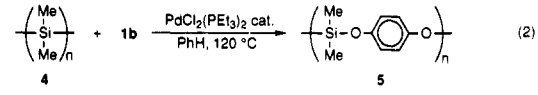
Similarly, catalyst A promoted the reconstruction with **1a** of poly[(tetramethyldisilanylene)(ethylene)] (**2b**)[9] and poly(tetramethyldisiloxane) (**2c**)[10] to give new polymers **3c**[7c] and **3d**,[7d,8] although degradation of the polymer seemed to have concomitantly taken place, as judged from the resulting molecular weight. When catalyst B was used, the backbone of **2b** was reconstructed with **1b** as well to afford a *p*-phenylenedioxy unit-containing polymer **3e**[7e] in a high yield.

Table I
Reactions of Si–Si Bond-Containing Polymers (2) with Quinones (1)[a]

2[b]	1 (equiv)	Pd cat.[c]	time (min)	3 (% yield[d])	p:q	M_w (M_w/M_n)[e]
a	**a** (1.05)	A	180	**a** (90)	~100:~0	5.8 × 10^4 (3.0)
a	**a** (0.30)	A[f]	180	**b** (86)	29:71	5.2 × 10^4 (2.9)
b	**a** (1.05)	A	60	**c** (84)	~100:~0	5.0 × 10^4 (2.5)
c[g]	**a** (0.30)	A	40	**d** (~100)[h]	22:78	1.8 × 10^5 (2.4)
b	**b** (1.05)	B	180	**e** (83)	~100:~0	1.9 × 10^4 (2.4)

[a] Reaction conditions: **2** (0.20 mmol of monomer unit), **1** (1.05 or 0.30 equiv/monomer unit of **2**), Pd cat. (ca. 2 mol %/1), benzene (0.10 mL), 120 °C, 40–180 min. [b] **2a**: M_w = 4.6 × 10^4, M_w/M_n = 2.6. **2b**: M_w = 2.5 × 10^5, M_w/M_n = 2.3. **2c**: M_w = 1.9 × 10^5, M_w/M_n = 2.3. [c] A: $Pd(dba)_2$-$2P(OCH_2)_3CEt$. B: $PdCl_2(PEt_3)_2$. [d] Yield after purification by precipitation from benzene–2-propanol. [e] Determined by GPC with polystyrene standards. [f] 4 mol %/**1a**. [g] 0.50 mmol. [h] Purified by short-path Florisil column chromatography.

Very interestingly, catalyst B proved to be capable of insertion of **1b** into the Si–Si bonds of poly(dimethylsilylene) (**4**).[11] Thus, heating a mixture of **4** (1.0 mmol monomer unit), **1b** (1.1 mmol), catalyst B (0.01 mmol), and benzene (0.5 mL) at 120 °C for 18 h gave an exhaustively modified soluble polymer, poly[(*p*-phenylenedioxy)dimethylsilylene] (**5**; M_w = 1.5 × 10^4) in 85% yield[12] (eq 2).



4 5 (2)

In the present reaction, thermally stable aromatic rings and Si–O bonds can be introduced into polymer backbones. Indeed, thermogravimetric analyses revealed that the modified polymers **3a** and **3b** possessed improved thermal stability as compared with the parent **2a**. The temperatures at 5 and 10% weight loss upon heating (under He, 10 °C/min heating rate) were respectively 480 and 513 °C for **3a** and 470 and 485 °C for **3b**, while they were 455 and 466 °C for **2a**. Accordingly, the present procedure for the backbone reconstruction provides a versatile tool to design thermally stable silicon-containing polymers.

Further investigations on the detailed properties of the modified polymers and the extension to other polymers are under way.

Supplementary Material Available: Physical, spectral (^1H and/or ^{13}C NMR, IR, and/or UV), and analytical data of the product polymers **3a–e** and **5** as well as the UV spectral data of the starting polymers **2a** and **2c** (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; Americal Chemical Society: Washington, DC, 1988. (b) *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988. (c) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990.

(2) For our recent papers on insertion of acetylenes into silicon polymers, see: (a) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. (b) Yamashita, H.; Tanaka, M. *Chem. Lett.* **1992**, 1547.

(3) For previous studies on insertion of unsaturated compounds into activated Si–Si bonds, see: Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989; p 1463.

(4) Recently insertion of isocyanides or an acetylene into oligosilanes was reported. See: (a) Ito, Y.; Suginome, M.; Matsuura,

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T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899. (b) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948.

(5) Although insertion of *p*-benzoquinone into an *activated* disilane ($FMe_2SiSiMe_2F$) using Pd–PPh_3 catalysts was reported, we found that $PdCl_2(PEt_3)_2$ was much more active for a nonactivated disilane ($Me_3SiSiMe_3$); in the reaction of *p*-benzoquinone (0.40 mmol) with $Me_3SiSiMe_3$ (0.44 mmol) in benzene (0.05 mL) at 120 °C for 5 min (Pd catalyst, 1 mol %), the yields of 1,4-$(Me_3SiO)_2C_6H_4$ were ~100% ($PdCl_2(PEt_3)_2$) and 10% ($PdCl_2(PPh_3)_2$). For the reaction of $FMe_2SiSiMe_2F$, see: Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87.

(6) Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673.

(7) All reconstructed polymers gave satisfactory analytical data. Selected physical and spectral data are as follows. (a) **3a**: off-white solid; softening temperature 177–195 °C; ^1H NMR ($CDCl_3$) δ 0.47 (br s, 6 H, H_3CSi), 7.03–7.63 (m, 18 H, benzene and phenanthrene rings' H), 7.73–7.95 and 8.37–8.60 (each m, 4 H, phenanthrene ring's H); UV (THF) λ_{max} ($\epsilon_{monomer\ unit}$) 259 (5.4×10^4), 273 (2.3×10^4), 299 (1.4×10^4), 312 (1.4×10^4), 348 (1.5×10^3), 365 (1.6×10^3) nm. (b) **3b**: off-white solid; softening temperature 145–155 °C; ^1H NMR ($CDCl_3$) δ 0.40–0.88 (m, H_3CSi), 7.03–7.76 (m, benzene and phenanthrene rings' H), 7.76–7.91 and 8.35–8.58 (each m, phenanthrene ring's H); UV (THF) λ_{max} ($\epsilon_{monomer\ unit}$) 258 (2.8×10^4), 299 (3.9×10^3), 312 (4.0×10^3), 348 (3.1×10^2), 366 (3.3×10^2) nm. (c) **3c**: pale gray solid; softening temperature 82–90 °C; ^1H NMR ($CDCl_3$) δ 0.08 (s, 12 H, H_3CSi), 0.61 (s, 4 H, CH_2CH_2Si), 7.37–7.52, 7.92–8.04, and 8.44–8.59 (each m, 8 H, ring's H); UV (THF) λ_{max} ($\epsilon_{monomer\ unit}$) 258 (4.1×10^4), 273 (1.5×10^4), 299 (8.8×10^3), 311 (9.4×10^3), 350 (9.6×10^2), 367 (9.8×10^2) nm. (d) **3d**: off-white gummy solid; softening temperature 50–59 °C; ^1H NMR ($CDCl_3$) δ –0.10 to 0.36 (m, H_3CSi), 7.10–7.67, 8.01–8.30, and 8.44–8.71 (each m, ring's H); UV (THF) λ_{max} ($\epsilon_{monomer\ unit}$) 257 (1.2×10^4), 273 (4.0×10^3), 297 (2.6×10^3), 309 (2.9×10^3), 348 (2.3×10^2), 365 (2.2×10^2) nm. (e) **3e**: pale gray solid; softening temperature 76–79 °C; ^1H NMR ($CDCl_3$) δ 0.20 (s, 12 H, H_3CSi), 0.67 (s, 4 H, CH_2CH_2Si), 6.67 (s, 4 H, ring's H); UV (THF) λ_{max} ($\epsilon_{monomer\ unit}$) 287 (2.4×10^3) nm.

(8) At the moment, it is not clear whether the partially modified polymers have random- or block-type structures.

(9) Hayashi, T.; Kobayashi, T.-a.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.

(10) Chojnowski, J.; Kurjata, J.; Rubinsztajn, S. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 469.

(11) Poly(dimethylsilylene) is commercially available from Nippon Soda Co., Ltd. The molecular weight was estimated at about 4.7×10^3 for M_w (M_w/M_n = 1.8).

(12) The reaction mixture was filtered and concentrated. The residual sticky solid was washed with hexane and dried to give **5** in 85% yield. Reprecipitation from benzene–2-propanol and slight evaporation of the solvent gave a higher molecular weight fraction in 46% yield: $M_w = 2.3 \times 10^4$; $M_w/M_n = 3.8$; ^1H NMR (C_6D_6) δ 0.22 (br s, 6 H, H_3CSi), 6.91 (br s, 4 H, ring's H); ^{13}C NMR (C_6D_6) δ –2.5 (2 C, CSi), 120.9 (4 C), 149.5 (2 C); ^{29}Si NMR (C_6D_6) δ –5.2.