Palladium-Catalyzed Dehydrogenative Polymerization between Hydrosilanes and Quinones or Hydroquinone

Poreddy Narsi Reddy,† Bhanu Pratap Singh Chauhan, Teruyuki Hayashi, and Masato Tanaka*
National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565
†Advanced Materials Laboratory, Japan Chemical Innovation Institute, Tsukuba, Ibaraki 305-8565

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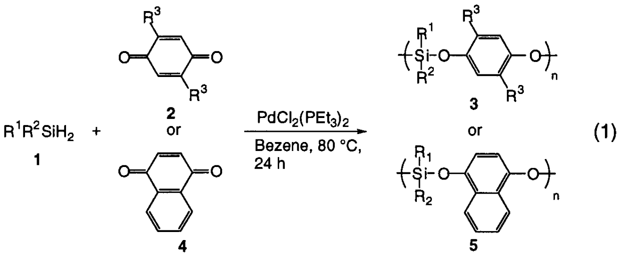
Dehydrogenative copolymerization between dihydrosilanes or a trihydrosilane and quinones proceeded in the presence of $PdCl_2(PEt_3)_2$ as catalyst to give poly[(arylenedioxy)(silylene)]s.

Silicon containing polymers are an interesting class of polymers of great practical potential because of their intriguing physicochemical properties.[1] Incorporation of silylene, arylene, and oxygen units to the backbone has been a strategy to achieve high thermal stability.[2] Poly[(arylenedioxy)(silylene)]s in particular have attracted much attention in view of thermal stability, flame retardation, and stability to ultraviolet irradiation.[3] These polymers are synthesized via 1) ring opening polymerization of oligo[(arylenedioxy)(silylene)] cycles[4] or 2) condensation of aromatic diols with dichloro-, diethoxy-, or diaminosilanes.[3] We also have reported transition metal-catalyzed insertion of quinones into silicon-silicon bonds of silicon-containing polymers[5] and ring opening copolymerization of cyclopolysilanes or disilanes with quinones to afford regular poly[(*p*-arylenedioxy)(silylene)]s.[6] As a third method we have found a new and general route based on palladium-catalyzed copolymerization reaction of hydrosilanes with *p*-benzoquinone derivatives (eq. 1).[7] A recent presentation[8] on a similar methodology prompted us to disclose our preliminary results of the copolymerization between di- or trihydrosilanes with *p*-quinones.



	R^1	R^2
1a	Me	Ph
1b	Ph	Ph
1c	n-Bu	n-Bu
1d	Me	n-Hex
1e	Me	n-Dodec

	R^3
2a	H
2b	Me

	R^1	R^2	R^3
3a, 5a	Me	Ph	H
3a'	Me	Ph	Me
3b, 5b	Ph	Ph	H
3c, 5c	n-Bu	n-Bu	H
3d, 5d	Me	n-Hex	H
3e, 5e	Me	n-Dodec	H

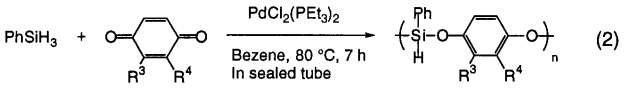
In a typical experimental procedure, phenylmethylsilane (**1a**) (0.5 mmol) was added to a benzene (0.5 ml) solution of *p*-benzoquinone (**2a**, 0.6 mmol[9]) and $PdCl_2(PEt_3)_2$ (0.020 mmol) in a glass tube under nitrogen. The tube was degassed by three freeze-thaw cycles and was sealed under vacuum. Initial dark green color of the reaction mixture changed to light yellow upon heating the reaction mixture at 80 °C and evolution of hydrogen gas started.[10] After 20 min, the gas evolution was no longer evident but heating was continued for 24 h. The tube was opened and the resulting mixture was poured into 2 ml of toluene and filtered. The filtrate was purified by preparative GPC to give a polymer as pale yellow oil (62%). Spectroscopic analyses (^1H, ^{29}Si and ^{13}C NMR, and IR) and elemental analysis [found: C 68.00, H 5.51% (calcd for $C_{13}H_{12}O_2Si$: C 68.38, H 5.29%)] support to the structure of regular poly[(1,4-benzenedioxy)(phenylmethylsilylene)] (**3a**). The molecular weight (M_w) determined by GPC was 7500 (M_w/Mn = 2.42) relative to polystyrene standards. Polymer **3a** is soluble in benzene, toluene, and tetrahydrofurane and insoluble in hexane and methanol.

Table 1. Synthesis by dehydrogenative copolymerization between secondary silanes and quinones and properties of poly[(1,4-arylenedioxy)(silylene)]s

Polymer	Yield/%	Appearance	M_w (M_w/M_n)
3a	62	Pale yellow oil	7500 (2.42)
3a'	73	Pale yellow oil	8100 (2.24)
3b	68	White solid	4200 (2.04)
3c	69	Pale yellow oil	2500 (1.74)
3d	73	Pale yellow oil	5800 (1.78)
3e	83	Colorless oil	9000 (1.50)
5a	54	Brown solid	9500 (1.86)
5b	65	White solid	2600 (1.86)
5c	76	Colorless oil	2800 (1.69)
5d	64	Pale brown oil	6100 (2.08)
5e	79	Pale brown oil	8200 (1.59)

As shown in Table 1, the dehydrogenative copolymerization reaction starting with other silanes (**1a**-**1e**) and quinones (**2a**, **2b**, **4**) proceeds smoothly irrespective of the substituents to result in high yields of **3** or **5**. The M_w values of the copolymers were less than 5000 when both substituents on the silicon atom were bulky like in diphenyl- or dibutylsilane (**3b**, **3c**, **5b**, and **5c**). The copolymers were stable toward moist air; for example, no significant change in the IR spectrum was observed when **3a** was exposed to moist air for 10 h at room temperature.

Recently, the chemistry of polymers containing reactive functional groups such as Si-H is an active area of research, because the functional groups provide an access to a subsequent modification of the polymers. With this in mind, we applied the same recipe to the reaction of phenylsilane with quinones. This reaction also proceeded in the presence of $PdCl_2(PEt_3)_2$ to afford poly[(1,4-arylenedioxy)(phenylsilylene)]s (eq. 2). The

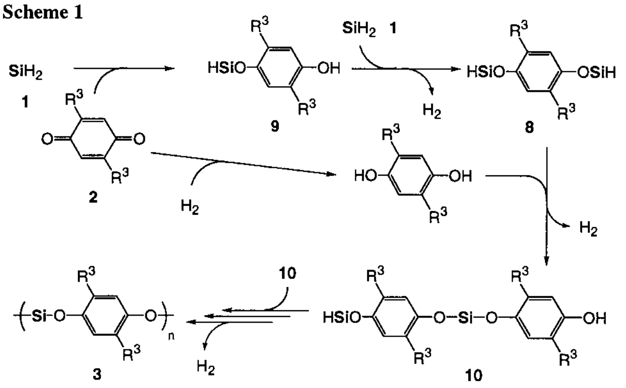


2a : $R^3 = R^4 = H$; **4** : $R^3,R^4 = (CH)_4$ **6** : $R^3 = R^4 = H$; **7** : $R^3,R^4 = (CH)_4$

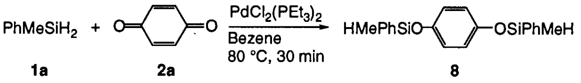
structures of the products were confirmed by spectroscopic and elemental analyses.[11]

The new polymerization is envisioned to take place via three major events, 1,6-hydrosilylation of quinone giving siloxyphenols,[12] hydrogenation of benzoquinone,[13] and dehydrogenative silylation of OH groups with hydrosilanes,[12,14] as depicted in Scheme 1.

Scheme 1



In an experiment to clarify the possible route, we found 1,4-bis(phenylmethylsiloxy)benzene (**8**) being formed as a transient intermediate leading to the polymerization. Thus, the mixture of **1a** (0.5 mmol) and **2a** (0.6 mmol) in C_6D_6 (0.5 ml) was heated with $PdCl_2(PEt_3)_2$ (0.02 mmol) as catalyst at 80 °C for 30 min, while dark green color of the starting solution changed to light yellow and white powder precipitated. At this stage, the ^{29}Si NMR spectrum of the reaction mixture showed the total consumption of **1a** and formation of 1,4-bis(phenylmethylsiloxy)benzene (**8**, 0.15 mmol, 60% yield based on **1a**) as confirmed by the disappearance of a signal due to **1a** (-35.56 ppm) and the appearance of a new signal assignable to **8** (-3.81 ppm) (eq. 3).[15] Polymer **3a** was also found to be formed in 34% yield based on the intensity of a new signal at –20.66 ppm.

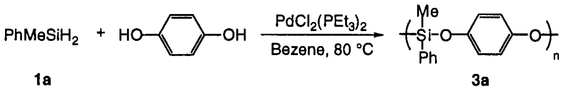


(3)

p-(Phenylmethylsiloxy)phenol (**9**), a possible intermediate leading to **8** was not found in this mixture by ^{29}Si NMR spectroscopy. However, ^{1}H NMR spectroscopy indicated that the solution contained 0.11 mmol of hydroquinone and the powder that precipitated (*vide supra*) was also hydroquinone (0.17 mmol), suggesting that hydrogen generated in the formation of **8** and **3a** was consumed to hydrogenate **2a** to hydroquinone. Continued heating of the reaction mixture for 24 h further transformed intermediate **8** (and hydroquinone) into copolymer **3a**, as confirmed by the disappearance of the signal due to **8** (-3.81 ppm) and the growth of the signal at –20.66 ppm. The hydrosilylation of **2** with **1** generating **9** and dehydrogenative silylation of **9** with **1** appear to proceed faster than dehydrogenative silylation of hydroquinone with **8**, which presumably is associated with the reactivity difference between secondary and tertiary silanes, i.e., **1** vs. **8**.

One can envision an alternative sequence of events that involve dehydrogenative coupling of **1** forming 1,2-dimethyl-1,2-diphenyldisilane and double silylation of **2** with its Si-Si bond. However, ^{29}Si and ^{1}H NMR spectra of reaction mixtures during the progress of the reaction showed the lack of formation of 1,2-dimethyl-1,2-diphenyldisilane. In addition, the double silylation requires somewhat severer conditions.[5b] Accordingly this possibility can be safely ruled out.

In line with Scheme 1, the polymerization starting with **1a** and *p*-hydroquinone used in place of **2a** similarly proceeded to



(4)

give **3a** (M_w/M_n = 7000/2900) in 74% yield.

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References and Notes

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

2 a) R. Corriu, D. Leclercq, P. H. Mutin, H. Samson, and A. Vioux, *J. Polym. Sci., A, Polym. Chem.*, **32**, 187 (1994). b) R. E. Burks, Jr., E. R. Covington, M. V. Jackson, and J. E. Curry, *J. Polym. Sci., Polym. Chem.*, **11**, 319 (1973). c) P. R. Dvornic and R. W. Lenz, *J. Polym. Sci., Polym. Chem.*, **20**, 951 (1982). d) E. A. Williams, J. H. Wengrovius, V. M. Van Valkenburgh, and J. F. Smith, *Macromolecules*, **24**, 1445 (1991).

3 a) S. A. Nye and S. A. Swint, *J. Polym. Sci., A, Polym. Chem.*, **32**, 131 (1994). b) J. E. Curry and J. D. Byrd, *J. Appl. Polym. Sci.*, **9**, 295 (1965).

4 H. Krimm and H. Schnell, Ger. 1136114 (to Farben-fabriken Bayer A.–G.); *Chem. Abstr.*, **59**, 11732g (1963).

5 a) H. Yamashita, N. P. Reddy, and M. Tanaka, *Macromolecules*, **26**, 2143 (1993). b). H. Yamashita, N. P. Reddy, and M. Tanaka, *Organometallics*, **16**, 5223 (1997).

6 N. P. Reddy, H. Yamashita, and M. Tanaka, *J. Am. Chem. Soc.*, **114**, 6596 (1992).

7 B. P. S. Chauhan, P. N. Reddy, T. Hayashi, and M. Tanaka, the 76th Annual Meeting of the Chemical Society of Japan, Yokohama, March 31, 1999, Abstr., No. 4B501. Very recently, an Indian group has presented the similar copolymerization between diphenylsilane and *p*-benzoquinone.[8]

8 A. Purkayashtha and J. B. Baruah, the 12th International Symposium on Organosilicon Chemistry, Sendai, May 24, 1999, Abstr., No. P171.

9 Almost the same result was obtained when **1a** and **2a** were used in a 1 : 1 ratio.

10 The quantity of hydrogen generated in the reaction of **1a** with **2a** was finally 0.51 mmol.

11 **6**: M_w/M_n = 11800/5200. δ ^{29}Si = -35.41 and δ ^{1}H-Si = 5.49 ppm (C_6D_6). Found: C 66.32; H 4.83%. Calcd for $C_{12}H_{10}O_2Si$: C 67.04; H 4.70%. When the reaction with **2a** was continued for 24 h, partial gelation took place. **7**: M_w/M_n = 5400/1800. δ ^{29}Si = -33.98 and δ ^{1}H-Si = 5.76 ppm (C_6D_6). Found: C 72.52; H 4.57%. Calcd for $C_{16}H_{12}O_2Si$: C 72.70; H 4.57%.

12 Bakola-Christianopoulou, *J. Mol. Catal.*, **65**, 307 (1991).

13 a) Y. Tamai and K. Itoi, Japan. Kokai 73-91024 (to Kuraray Co., Ltd.); *Chem. Abstr.*, **80**, 145798c (1974). b) A. S. Berenblyum, A. G. Knizhnik, S. L. Mund, and I. I. Moiseev, *J. Organomet. Chem.*, **234**, 219 (1982).

14 a) L. H. Sommer and J. E. Lyons, *J. Am. Chem. Soc.*, **91**, 7061 (1969). b) Y. Li and Y. Kawakami, *Macromolecules*, **32**, 3540 (1999).

15 The structure of **8** was confirmed by comparing the spectral data with those of an authentic sample [δ ^{29}Si = -3.81 and δ ^{1}H-Si = 5.40 ppm (C_6D_6)] synthesized according to a literature. See B. Rezzonico and M. Grignon-Dubois, *Organometallics*, **17**, 2656 (1998).