Palladium-Catalyzed Insertion of 1,2- and 1,4-Quinones into Si−Si Bonds and Its Application to the Modification of Si−Si-Bond-Containing Polymers

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$Me_3SiSiMe_3$ reacted with 1,2- and 1,4-quinones (*p*-benzoquinone (**2a**), its derivatives, 1,2- and 1,4-naphthoquinone, 9,10-phenanthraquinone (**2f**), 9,10-anthraquinone) in the presence of palladium catalysts to give the corresponding bis(trimethylsiloxy) aromatics in excellent to moderate yields. Active palladium catalysts were $PdCl_2L_2$ (L = tertiary phosphine) and Pd(dibenzylideneacetone)$_2$−2P(OCH$_2$)$_3$CEt, among which $PdCl_2(PEt_3)_2$ was in general the most efficient. A 1,2-disilacyclohexane cleanly underwent the reaction with **2f** to form a 10-membered cyclic adduct. The reaction of $Me_3SiSiMe_2SiMe_3$ with **2a** also afforded *p*-$(Me_3SiO)_2C_6H_4$, via formal extrusion of a silylene unit. Treatment of *cis*-$(PhMe_2Si)_2Pt(PMe_2Ph)_2$ with **2a** gave *p*-$(PhMe_2SiO)_2C_6H_4$, indicative of the involvement of bis(silyl)palladium species in the catalysis. Quinones **2a**,**f** smoothly underwent the palladium-catalyzed insertion into the Si−Si bonds of (SiMePhSiMePh-*p*-$C_6H_4)_n$ (**9a**), $(SiMe_2SiMe_2CH_2CH_2)_n$, and $(SiMe_2SiMe_2O)_n$ to give partially or exhaustively modified polymers with arylenedioxy units incorporated in the backbones. A polysilane, $(SiMe_2)_n$, also reacted with **2a** to provide a polymer with −SiMe$_2$−O−*p*-C$_6$H$_4$−O− linkages. Upon UV irradiation, a partially modified polymer obtained from **9a** and **2f** showed a smaller extent of decrease in molecular weight than did the original polymer. Modification with **2f** improved the thermal stability of **9a** in thermogravimetric analysis.

Introduction

Increasing attention has been directed toward organosilicon compounds owing to their versatile synthetic utility and unique physicochemical properties.[1] One of the most promising methods for their preparation is transition-metal-catalyzed addition of Si−Si bonds[2] to unsaturated compounds such as acetylenes,[3] olefins,[3r,u,v,4] dienes,[3g,h,m,n,5] allenes,[3q,6] a diyne,[7] α,*β*-unsaturated ketones,[5c,8] quinones,[5c,9a,b] α-diketones,[9c] an α-keto ester,[9c] aldehydes,[3p−r,v,10] a ketone,[10] isocyanides,[3w,11] and imines.[12] However, when conventional Pd−PPh$_3$ catalysts are used, disilane linkages that are not activated by electron-withdrawing substituents or ring strain are in general reluctant to undergo the reaction.[3a,c,d,f,5b,7] In order to overcome this drawback, we have surveyed effective catalysts for nonactivated Si−Si bonds. As a result, we have found that the Pd−P(OCH$_2$)$_3$CEt system is highly efficient in the insertion of acetylenes into the Si−Si bonds of hexamethyldisilane, octamethyltrisilane, and Si−Si-bond-containing polymers.[3j,l,13,14] In addition, we have discovered that α-diketones and an α-keto ester respectively undergo double silylation or double silylative reductive coupling with hexamethyldisilane in the presence of palladium or platinum catalysts.[9c] Further studies along this line have revealed that 1,2- and 1,4-quinones also smoothly react with nonactivated disi-

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Table 1. Reactions of Hexamethyldisilane (1a) with 1,2- and 1,4-Quinones (2)[a]

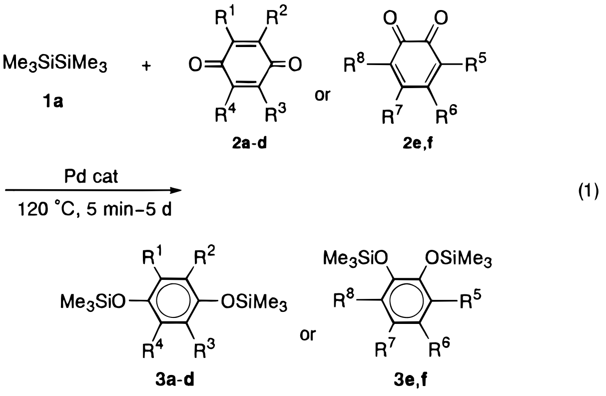
run no.	2	Pd cat. (mol % Pd[b])	time	product (yield,[c] %)
1	**2a**	$PdCl_2(PPh_3)_2$ (1)	5 min	**3a** (10)
2		$PdCl_2(P^iBu_3)_2$ (1)	5 min	**3a** (12)
3		$PdCl_2(PEt_3)_2$ (1)	5 min	**3a** ($\sim$100)
4		$PdCl_2(PMe_3)_2$ (1)	5 min	**3a** (17)
5		$PdCl_2(PPh_3)_2$ (2)	1 h	**3a** ($\sim$100 [95])
6		$PdCl_2(PhCN)_2$ (2)	1 h	**3a** (0.5), **4a** (0.5)
7		$PdCl_2(PhCN)_2-2PPh_3$ (2)	1 h	**3a** (96), **4a** (2)
8[d]		$Pd(dba)_2-2P(OCH_2)_3CEt$ (1)	12 h	**3a** (70), **4a** (9), **5a** (3), P1 ($\sim$4),[e] P2 ($\sim$1)[e]
9		$Pd(dba)_2-2PPh_3$ (2)	1 h	**3a** (47), **4a** (14), **5a** (trace[f]), P1 ($\sim$0.5),[e] P2 ($\sim$1)[e]
10		$Pd(dba)_2-4PPh_3$ (2)	1 h	**3a** (23), **4a** (9), **5a** (trace[f]), P1 (trace[f]),[e] P2 ($\sim$0.5)[e]
11		$Pd(PPh_3)_4$ (2)	1 h	**3a** (21), **4a** (8), **5a** (trace[f]), P1 (trace[f]),[e] P2 ($\sim$0.5)[e]
12	**2b**	$PdCl_2(PPh_3)_2$ (2)	24 h	**3b** (70 [$\sim$65][g]), P3 ($\sim$8),[e] P4 ($\sim$2)[e]
13		$PdCl_2(PEt_3)_2$ (2)	24 h	**3b** (83), P3 ($\sim$1),[e] P4 ($\sim$2)[e]
14	**2c**	$PdCl_2(PPh_3)_2$ (2)	1 h	**3c** (78 [80][h])
15		$PdCl_2(PEt_3)_2$ (2)	1 h	**3c** (87)
16		$Pd(dba)_2-2P(OCH_2)_3CEt$ (2)	1 h	**3c** (1)
17	**2d**	$PdCl_2(PPh_3)_2$ (2)	5 d	**3d** (2)
18		$PdCl_2(PEt_3)_2$ (2)	5 d	**3d** (5)
19[i]		$PdCl_2(PEt_3)_2$ (4)	5 d	**3d** (24)
20	**2e**	$PdCl_2(PPh_3)_2$ (2)	1 h	**3e** (27), **4e** (22)
21		$PdCl_2(PEt_3)_2$ (2)	1 h	**3e** (65), **4e** (22)
22		$PdCl_2(PMe_3)_2$ (2)	1 h	**3e** (56), **4e** (23)
23		$Pd(dba)_2-2P(OCH_2)_3CEt$ (2)	1 h	**3e** (11), **4e** (5)
24	**2f**	$PdCl_2(PPh_3)_2$ (2)	1 h	**3f** (78)
25		$PdCl_2(PEt)_2$ (2)	1 h	**3f** (99)
26		$Pd(dba)_2-2P(OCH_2)_3CEt$ (2)	1 h	**3f** ($\sim$100 [95])

[a] Conditions: **1a** (0.44 mmol), **2** (0.40 mmol), benzene (0.05 mL), 120 °C. [b] Based on **2**. [c] Estimated by GC based on **2**. Figures in brackets are isolated yields. [d] **1a** (3.52 mmol), **2a** (3.20 mmol), benzene (0.40 mL). [e] Figures in parentheses are approximate yields using the same GC (TCD) factors as those for **3**. [f] $\leq$0.2%. [g] $\sim$90% purity. [h] 6 h. [i] 140 °C.

lanes in the presence of some palladium catalysts to give the corresponding 1,2- and 1,4-bis(siloxy) aromatic compounds.[15,16] Herein are described full details of the novel catalysis, the reactivity of bis(silyl)platinum species in relation to the mechanism, and an application to the modification of organosilicon polymers.[17]

Results and Discussion

Catalysts. Heating a mixture of hexamethyldisilane (**1a**; 1.1 equiv), *p*-benzoquinone (**2a**), a palladium catalyst, and benzene at 120 °C gave a 1,6-double-silylation product, *p*-bis(trimethylsiloxy)benzene (**3a**) (eq 1; Table 1, runs 1−11). The activity of $PdCl_2L_2$ complexes



a: $R^1 = R^2 = R^3 = R^4 = H$
b: $R^1 = R^2 = R^3 = R^4 = Cl$
c: $(R^1, R^2) = -CH{=}CH-CH{=}CH-$, $R^3 = R^4 = H$
d: $(R^1, R^2) = (R^3, R^4) = -CH{=}CH-CH{=}CH-$
e: $(R^5, R^6) = -CH{=}CH-CH{=}CH-$, $R^7 = R^8 = H$
f : $(R^5, R^6) = (R^7, R^8) = -CH{=}CH-CH{=}CH-$

increased in the order $L = PPh_3 < P^iBu_3 < PMe_3 < PEt_3$,

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(13) For insertion of acetylenes into nonactivated Si−Si bonds, Ito et al. also reported an effective palladium catalyst system that contained a large amount of a tertiary alkyl isocyanide.[3k,s,t,w]

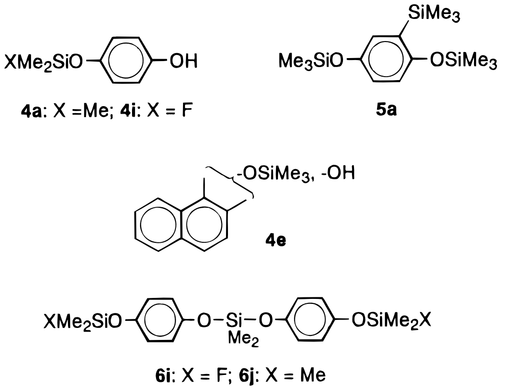
(14) For double silylation with nonactivated Si−Si bonds using iodine or fluoride anion as catalyst, see: (a) Matsumoto, H.; Koike, S.; Matsubara, I.; Nakano, T.; Nagai, Y. *Chem. Lett.* **1982**, 533. (b) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912. (c) Hiyama, T.; Obayashi, M. *Tetrahedron Lett.* **1983**, *24*, 4109.

(15) Insertion of *p*-benzoquinone into an activated disilane (1,2-difluoro-1,1,2,2-tetramethyldisilane) with the Pd−PPh_3 catalyst was previously reported.[5c] For iodine-catalyzed reactions of 1,4-quinones, see Ref 14a.

(16) The reaction is useful for protection of quinones. For instance, see: (a) Thompson, R. H. *Naturally Occurring Quinones*; Academic Press: New York, 1971. (b) Stewart, R. F.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 4999. (c) Willis, J. P.; Cogins, K. A. Z.; Miller, L. L. *J. Org. Chem.* **1981**, *46*, 3215.

(17) Preliminary results on polymer modification have already been published.[9b]

Chart 1



4a: X =Me; **4i**: X = F

5a

4e

6i: X = F; **6j**: X = Me

revealing $PdCl_2(PEt_3)_2$ to be most efficient (runs 1−4). With the $PdCl_2(PEt_3)_2$ catalyst (1 mol %) **3a** was obtained nearly quantitatively by heating only for 5 min. Palladium metal was essential in the reaction, and an attempt to run the reaction in the presence of PEt_3 (2 mol %) alone in place of $PdCl_2(PEt_3)_2$ did not result in the formation of **3a**. Although the activity of $PdCl_2(PPh_3)_2$ was lower, **3a** was formed in ∼100% yield by increasing the catalyst concentration (2 mol %) and prolonging the reaction time (1 h) (run 5). Phosphine ligands appear to be prerequisites for occurrence of the reaction; a palladium catalyst without phosphines, $PdCl_2(PhCN)_2$, was almost inactive, while the activity of the $PdCl_2(PhCN)_2$−$2PPh_3$ system was similar to that of $PdCl_2(PPh_3)_2$ (runs 6, 7). However, excess phosphine (P/Pd = 4) significantly slowed the reaction in Pd−PPh_3 systems such as $Pd(dba)_2$−$4PPh_3$ (dba = dibenzylideneacetone) and $Pd(PPh_3)_4$ (runs 10, 11). On the other hand, the $Pd(dba)_2$−$2P(OCH_2)_3CEt$ system, which was the catalyst of choice for insertion of acetylenes into Si−Si bonds,[3j,l] was less active and less selective in the present reaction (run 8); the formation of **3a** (70% yield, 12 h reaction time) was accompanied by the undesired formation of 4-(trimethylsiloxy)phenol (**4a**; Chart 1, 9%) and 1,4-bis(trimethylsiloxy)-2-(trimethylsilyl)benzene (**5a**; Chart 1, 3%).[18]

Besides the nature and the quantity of phosphorus ligands, the presence of chlorine in the reaction system affects the activity and selectivity. Thus, a chlorine-free Pd−PPh_3 system, $Pd(dba)_2$−$2PPh_3$, was much less active than $PdCl_2(PPh_3)_2$ and afforded a considerable amount of **4a** (run 9). Monitoring the progress of the reaction with the $PdCl_2(PPh_3)_2$ catalyst showed the presence of an induction period (2−3 min) (Figure 1), indicative of the conversion of $PdCl_2(PPh_3)_2$ into active species in the initial stage of the reaction. At the moment, however, the real structure of the catalytically active species and the mechanism detailing the favorable role of the chlorine atom are ambiguous.

Quinones. Besides **2a**, other 1,4-quinones such as chloranil (**2b**), 1,4-naphthoquinone (**2c**), and 9,10-anthraquinone (**2d**) also reacted with **1a** in the presence of palladium catalysts to give the corresponding 1,4-bis(siloxy) aromatic compounds (**3b**−**d**) in good to moderate yields (eq 1; Table 1, runs 12−19). In the series of 1,4-quinones, the reactivity decreases in the order **2a** > **2c** ≫ **2d**, presumably reflecting the steric hindrance of the quinones. As compared with **2a**, **2b** displays low reactivity, which can be considered in terms of steric and electronic factors. However, since 2,3,5,6-tetrafluoro-*p*-benzoquinone was more reactive than **2a**,[19] steric hindrance of the chlorine substituents appears to be the major factor for the low reactivity of **2b**. When 1,2-quinones were used in place of 1,4-quinones, 1,4-double silylation proceeded under similar conditions. Thus, 1,2-naphthoquinone (**2e**) and 9,10-phenanthraquinone (**2f**) reacted with **1a** to provide the corresponding 1,2-bis(siloxy) aromatics **3e** and **3f**, respectively (runs 20−26).[20] Noteworthy is the result that **3f** was obtained nearly quantitatively (run 26), since it was reported that **2f** did not form **3f** by the conventional double silylation using Me_3SiCl/K.[21]

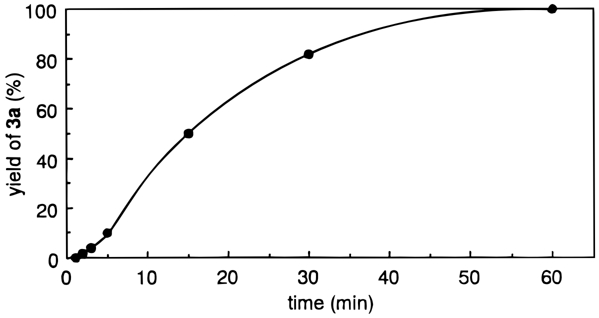


Figure 1. Time course of the yield of **3a** in the reaction of **1a** with **2a** catalyzed by $PdCl_2(PPh_3)_2$ (**1a**, 0.44 mmol; **2a**, 0.40 mmol; $PdCl_2(PPh_3)_2$, 0.004 mmol; benzene, 0.05 mL; 120 °C).

For almost all quinones, $PdCl_2(PEt_3)_2$ exhibited the highest activity among the catalysts examined, although the $Pd(dba)_2$−$2P(OCH_2)_3CEt$ system was also efficient in the reaction of **2f**. Usually the desired double silylation proceeded cleanly by using suitable palladium catalysts, and nearly pure products **3** were isolated by short-path distillation in excellent to good yields (runs 5, 14, and 26). However, in the reaction of **2b**, GC and GC−MS indicated formation of a dechlorinated byproduct (P3, ∼2−8% yield) that appeared to be 1,2,4-trichloro-3,6-bis(trimethylsiloxy)-5-(trimethylsilyl)benzene. The compound may be formed via substitution of the chlorine atom of **3b** by the trimethylsilyl group of **1a**.[22,23] On the other hand, the *o*-quinone **2e** gave a considerable amount of naphthol derivatives, 2-(trimethylsiloxy)-1-naphthol and 1-(trimethylsiloxy)-2-naphthol (**4e**; Chart 1, 5−23% yields). These are genuine products of the reaction and not secondary products coming from workup procedures.

Si−Si-Bonded Compounds. A phenylated disilane, 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**1b**), also re-

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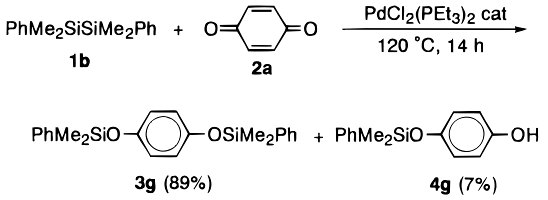
[18] Small amounts of other products (P1 and P2, total yields ∼5%) were also formed, although their structures have not been determined yet. GC-MS indicated *m*/*z* values for the parent ions of 254 (an isomer of **3a**) for P1 and 434 (**1a** + **2a** × 2 + Me_3Si − H) for P2 (see Experimental Section).

[19] (a) 2,3,5,6-Tetrafluoro-*p*-benzoquinone (TFBQ), which is sterically similar to **2a** but electronically more deficient than **2a**, showed higher reactivity than **2a**, although the products were not fully characterized;[19b] in the reaction with **1a** (**1a** 0.44 mmol, quinone 0.40 mmol, $PdCl_2(PPh_3)_2$ 0.004 mmol, benzene 0.05 mL, 120 °C, 10 min), the conversion of **1a** was 80% for TFBQ, while it was 34% for **2a**. The results indicate that electron-withdrawing substituents are likely to promote the reaction. (b) GC and GC-MS measurements indicated formation of p-$(Me_3SiO)_2C_6F_4$ (∼40% yield), Me_3SiF (∼20%), and an adduct (∼20%) that showed a GC-MS parent peak at *m*/*z* 560 which corresponded to **1a** + TFBQ × 2 + Me_3Si − F.

[20] The high reactivity of **2f** as compared with sterically less hindered **2e** suggests that the steric effect is not as crucial in the case of *o*-quinone.

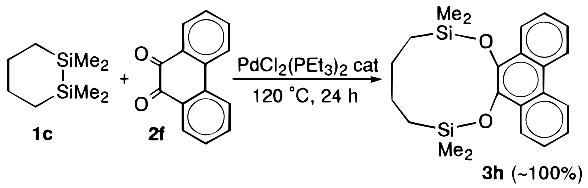
[21] Murakawa, T.; Fujii, K.; Murai, S.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2520.

acted with **2a** in the presence of the $PdCl_2(PEt_3)_2$ catalyst to give the *p*-bis(siloxy)benzene **3g** (89% yield) along with a small amount of the phenol derivative **4g** (7%) (eq 2).



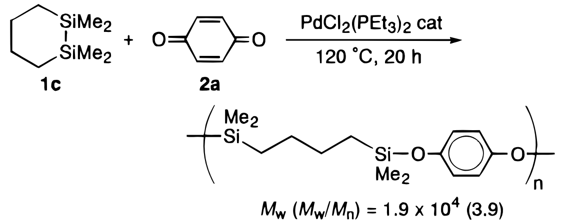
(2)

When a cyclic disilane, 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**1c**), was allowed to react with the *o*-quinone **2f**, the 10-membered cyclic product **3h** was obtained nearly quantitatively (eq 3).



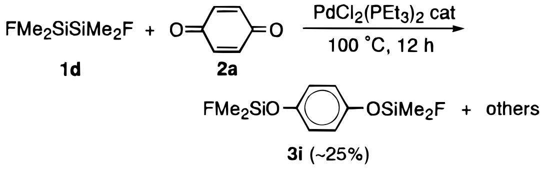
(3)

In contrast, we have found that treatment of **1c** with the *p*-quinone **2a** under similar reaction conditions resulted in ring-opening copolymerization to give a polymer consisting of alternating 1,6-disilahexylene and *p*-phenylenedioxy units (eq 4).[9a]



(4)

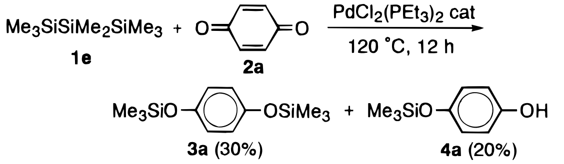
Different from **1a**,**b**, the activated disilane 1,2-difluoro-1,1,2,2-tetramethyldisilane (**1d**) did not undergo smooth addition to **2a** under the present conditions using the $PdCl_2(PEt_3)_2$ catalyst; the reaction formed the expected bis(siloxy)benzene **3i** in a much lower yield (~25%, eq 5), and gave byproducts (**4i**, **6i**, and P5, Chart 1) that appeared to be 4-(fluorodimethylsiloxy)phenol (**4i**), bis[4-(fluorodimethylsiloxy)phenoxy]dimethylsilane (**6i**), and difluorodimethylsilane (P5), respectively (GC (TCD) area ratio **3i**:**4i**:**6i**:P5 = 1:≤0.05:≤0.05:~1).



(5)

The formation of **6i** and P5 may suggest the involvement of (silylene)palladium species in the catalysis.[24]

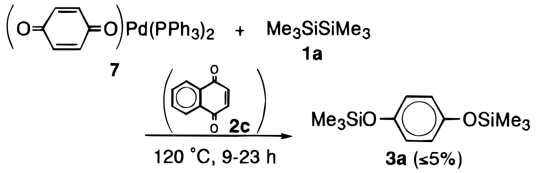
The reaction of octamethyltrisilane (**1e**) with **2a** unexpectedly gave **3a** (30%) and **4a** (20%) as the major volatile products (eq 6), via formal extrusion of a silylene unit from **1e**, along with a small quantity (≤10%) of a compound that was suggested by GC−MS to be a 1:2 adduct, dimethylbis[4-(trimethylsiloxy)phenoxy]silane (**6j**, Chart 1).



(6)

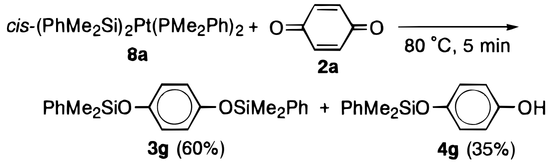
In the reaction of **1e** with phenylacetylene, formation of such degraded products was not observed, and a mixture of the regioisomeric 1:2 adducts was obtained cleanly.[3j,k]

Mechanism. Quinone **2a** is known to interact with $Pd(PPh_3)_4$ to give (*p*-benzoquinone)$Pd(PPh_3)_2$ (**7**).[25] Ugo et al. proposed that such a species was involved in the palladium-catalyzed addition of terminal olefins to **2a**.[26] Kumada et al. also assumed the possible participation of a similar intermediate in the addition of **1d** to **2a**.[5c] However, treatment of **7** with disilane **1a** (2 equiv) in the absence or presence of **2c** scarcely afforded **3a** (≤5% yield, ≥90% recovery of **7**) even after heating at 120 °C for 9−23 h (eq 7).



(7)

On the other hand, the reaction of *cis*-$(PhMe_2Si)_2Pt(PMe_2Ph)_2$[27] (**8a**) with **2a** (2 equiv) smoothly proceeded at 80 °C to form **3g** (60% yield) and **4g** (35%) (eq 8).[28]



(8)

Accordingly, the present catalysis seems to involve bis(silyl)palladium species, which are

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(22) For examples of palladium-catalyzed exchange reactions between C−X (X = Cl, Br, I) and Si−Si bonds giving C−Si and Si−X bonds, see: (a) Matsumoto, H.; Ohkawa, K.; Matsubara, I.; Kasahara, M.; Arai, T.; Nagai, Y. *J. Organomet. Chem.* **1984**, *264*, 29 and references cited therein. (b) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331 and references cited therein. (c) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974 and references cited therein. (d) Krafft, T. E.; Rich, J. D.; McDermott, P. J. *J. Org. Chem.* **1990**, *55*, 5430 and references cited therein.

(23) GC showed formation of another byproduct (P4, ~2%) whose GC-MS indicated the parent ion at *m*/*z* 356 (=$Me_3Si \times 2 + {}^{35}Cl \times 3 + C_6O_2H$).

(24) (Silylene)palladium species may be involved in the catalyses of a 1,2-dichlorodisilane and a 1,3-dichlorotrisilane under certain conditions as well. Thus, $Cl(SiMe_2)_2Cl$[24a] or $Cl(SiMe_2)_3Cl$[24b] respectively reacts with a diketone (benzil) or acetylenes (2 equiv) in the presence of a palladium catalyst to form a 4,5-diphenyl-1,3-dioxa-2-sila-4-cyclopentene or 1,4-disilacyclohexadienes, along with the coproduct Me_2SiCl_2. See: (a) Rich, J. D. *Organometallics* **1989**, *8*, 2609. (b) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530.

(25) Takahashi, S.; Hagihara, N. *Nippon Kagaku Zasshi* ***1967***, *88*, 1306.

(26) Roffia, P.; Conti, F.; Gregorio, G.; Pregaglia, G. F.; Ugo, R. *J. Organomet. Chem.* **1973**, *54*, 357.

(27) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411.

(28) Different from **8a**, a bis(fluorosilyl)platinum species, *cis*-$(FMe_2Si)_2Pt(PEt_3)_2$ (**8b**), that was prepared by oxidative addition of **1d** to $Pt(PEt_3)_3$[29] did not undergo smooth reaction with **2a** (see Experimental Section), which may be a reason for the nonselective catalytic reaction of **1d** with **2a**.

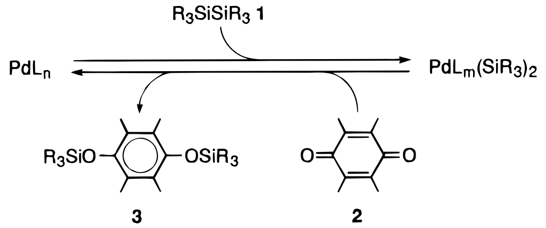
(29) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447.

Table 2. Reactions of Silicon Polymers (9) with Quinones (2)[a]

run no.	**9**[b]	**2** (amt, equiv)	Pd cat.[c]	time	product (yield,[d] %)	p:q[e]	M_w (M_w/M_n)[f] of **10**
1	**9a**	**2f** (1.05)	A	3 h	**10a** (90)	~100:~0	5.8×10^4 (3.0)
2[g]	**9a**	**2f** (0.30)	A	3 h	**10b** (86)	29:71	5.2×10^4 (2.9)
3	**9b**	**2f** (1.05)	A	1 h	**10c** (84)	~100:~0	5.0×10^4 (2.5)
4[h]	**9c**	**2f** (0.30)	A	40 min	**10d** (~100)	20:80	1.8×10^5 (2.4)
5[i]	**9b**	**2a** (1.05)	B	3 h	**10e** (83[j])	~100:~0	1.9×10^4 (2.4)[k]
6[h]	**9c**	**2a** (0.30)	B	15 min	**10f** (66)	21:79	1.1×10^5 (2.2)
7[h]	**9c**	**2a** (0.30)	C	40 min	**10f** (69)	21:79	2.5×10^5 (3.5)

[a] Conditions: **9** (0.20 mmol monomer unit), **2** (0.30 or 1.05 equiv/monomer unit of **9**), Pd catalyst (ca. 2 mol % Pd/**2**), benzene (0.10 mL), 120 °C. [b] **9a**, $M_w = 4.6 \times 10^4$ ($M_w/M_n = 2.6$); **9b**, $M_w = 2.5 \times 10^5$ ($M_w/M_n = 2.3$); **9c**, $M_w = 1.9 \times 10^5$ ($M_w/M_n = 2.3$). [c] Legend: A, $Pd(dba)_2-2P(OCH_2)_3CEt$; B, $PdCl_2(PEt_3)_2$; C, $PdCl_2(PPh_3)_2$. [d] Yield after purification. [e] Estimated by ^1H NMR and/or elemental analysis. [f] Measured by GPC using polystyrene standards. [g] Pd catalyst (4 mol % Pd/**2f**). [h] **9c** (0.50 mmol monomer unit). [i] **9b** (0.40 mmol monomer unit), benzene (0.20 mL). [j] A combined yield of two fractions with higher and lower molecular weights (see Experimental Section). [k] Before purification.

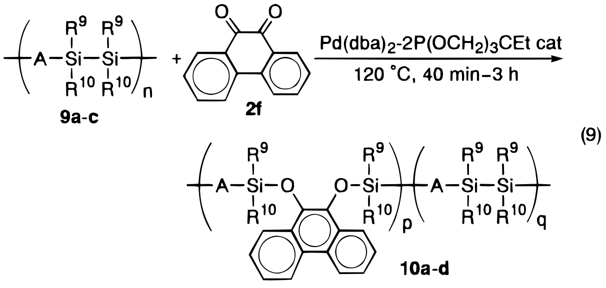
Scheme 1



formed by oxidative addition of Si−Si bonds to palladium species,[30] in the pathways leading to the formation of bis(siloxy) aromatics (Scheme 1). Analogous bis(silyl)metal species were previously proposed as intermediates for the double silylation of acetylenes, dienes, and olefins.[3o,u,29,31]

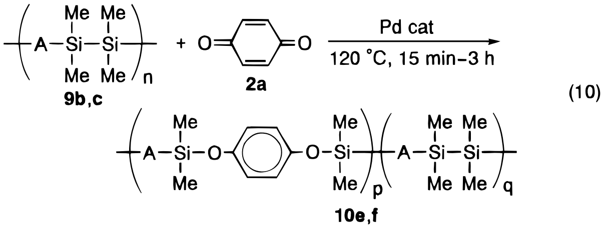
On the other hand, the phenol derivative **4a** was formed as a byproduct in the reaction of **1a** with **2a** under certain conditions. To get more information on the origin of the hydrogen atom of the hydroxy group, benzene-d_6 or $(D_3C)_3SiSi(CD_3)_3$ was used in place of benzene or **1a**, respectively ($Pd(dba)_2-2P(OCH_2)_3CEt$ catalyst). In each case, a mixture of compounds of types **3a** and **4a** was obtained as the major volatile product.[32] However, GC−MS and/or NMR measurements did not show deuterium incorporation into the hydroxy group of the type **4a** compound. The results indicate that the hydroxy hydrogen does not come from the solvent or from the disilane. Further studies are required to elucidate the mechanism of the formation of **4a** and other hydroxy-group-containing byproducts.

Modification of Silicon Polymers. The present catalysis was applicable to modification of Si−Si-bond-containing polymers by insertion of **2f** and **2a**, which could undergo double silylation with **1a** nearly quantitatively (eqs 9 and 10; Table 2).



(9)

9a, **10a**,**b**: A = p-C_6H_4, R^9 = Ph, R^{10} = Me
9b, **10c**: A = $(CH_2)_2$, $R^9 = R^{10}$ = Me
9c, **10d**: A = O, $R^9 = R^{10}$ = Me



(10)

9b, **10e**: A = $(CH_2)_2$; **9c**, **10f**: A = O

When a disilanylene-unit-containing polymer, poly[(1,2-dimethyl-1,2-diphenyldisilanylene)(p-phenylene)][33] (**9a**; $M_w = 4.6 \times 10^4$, $M_w/M_n = 2.6$), was treated with **2f** (1.05 equiv/monomer unit) in the presence of the $Pd(dba)_2-2P(OCH_2)_3CEt$ (ca. 2 mol % Pd/**2f**) catalyst at 120 °C for 3 h, insertion of **2f** into almost every Si−Si bond of **9a** cleanly took place to give the modified polymer **10a** (p:q = ~100:~0, $M_w = 5.8 \times 10^4$, $M_w/M_n = 3.0$) with 9,10-phenanthrylenedioxy units incorporated in the backbone (run 1). Analytically pure **10a** was readily obtained by precipitation from benzene−2-propyl alcohol. Since the reaction proceeds nearly quantitatively, the degree of the modification is easily controlled by varying the quantity of **2f** charged; the use of 0.30 equiv of **2f** per monomer unit of **9a** gave the modified polymer **10b** with 29% of the Si−Si bonds being converted (run 2). The molecular weight of **10b** ($M_w = 5.2 \times 10^4$, $M_w/M_n = 2.9$) was in reasonable agreement with the predicted value ($M_w = 5.5 \times 10^4$, $M_w/M_n = 2.7$) for 29% modification,[34] indicative of no extensive degradation having taken place during the reaction. Likewise, poly[(tetramethyldisilanylene)ethylene][4a] (**9b**; $M_w = 2.5 \times 10^5$, $M_w/M_n = 2.3$) could be exhaustively reconstructed by insertion of **2f** to give the new polymer **10c** ($M_w = 5.0 \times 10^4$, $M_w/M_n = 2.5$), albeit with a decrease in the molecular weight (run 3). A siloxane polymer, poly(tetramethyldisiloxane)[35] (**9c**; $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$), also reacted with **2f** (0.30 equiv) to give the

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(30) Although there has been no direct evidence, possible charge transfer from disilanes to quinones may assist oxidative addition of the disilanes to the palladium center by decreasing the electron density at the silicon atoms. For intramolecular charge transfer from a Si−Si bond to a quinone moiety, see: Sakamoto, K.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1466.

(31) (a) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (b) Murakami, M.; Yoshida, T.; Ito, Y. *Organometallics* **1994**, *13*, 2900.

(32) Compounds **3a** (64% yield) and **4a** (7%) were formed in the reaction run in benzene-d_6 (120 °C, 12 h), while the reaction of $(D_3C)_3SiSi(CD_3)_3$ gave $(D_3C)_3SiO$-p-C_6H_4-$OSi(CD_3)_3$ (~50%) and $(D_3C)_3SiO$-p-C_6H_4-OH (~3%), as analyzed by GC-MS and ^1H NMR.

(33) (a) Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673. (b) Nate, K.; Inoue, T.; Sugiyama, H.; Ishikawa, M. *J. Appl. Polym. Sci.* **1987**, *34*, 2445.

(34) Predicted M_w of **10b** = (M_w of **9a**) × (average formula weight per monomer unit with 29% modification of **10b**)/(formula weight per monomer unit of **9a**) = $(4.6 \times 10^4) \times (376.9/316.6) = 5.5 \times 10^4$.

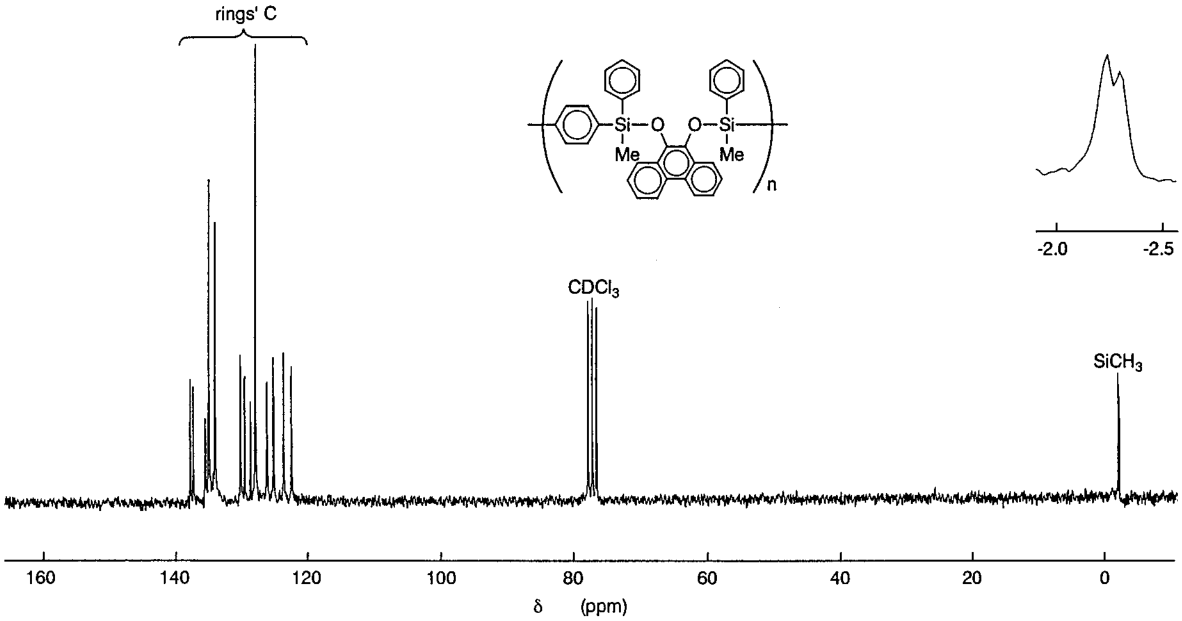
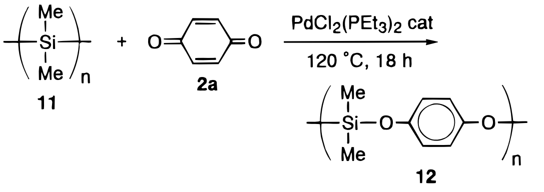


Figure 2. ^{13}C NMR spectrum of **10a** (in $CDCl_3$).

partially modified polymer **10d** ($M_w = 1.8 \times 10^5$, $M_w/M_n = 2.4$), with the degree of modification being 20% at 40 min reaction time (run 4).

Introduction of *p*-phenylenedioxy units was possible as well by using **2a**. Thus, the reaction of **9b** with **2a** (1.05 equiv) smoothly proceeded in the presence of the $PdCl_2(PEt_3)_2$ catalyst to give the exhaustively modified polymer **10e** ($M_w = 1.9 \times 10^4$, $M_w/M_n = 2.4$) (run 5). Polymer **9c** also underwent reaction with **2a** (0.30 equiv) to give the partially reconstructed polymer **10f** ($M_w = 1.1 \times 10^5$, $M_w/M_n = 2.2$) with 21% of the Si−Si bonds being transformed at 15 min reaction time (run 6). Modified polymers **10e**,**f** obtained with the $PdCl_2(PEt_3)_2$ catalyst showed lower molecular weights (GPC) than the original polymers, indicative of unfavorable degradation also having taken place. However, in the reaction of **9c**, a less active catalyst, $PdCl_2(PPh_3)_2$, was found to be able to reconstruct without the degradation; **10f** obtained with the $PdCl_2(PPh_3)_2$ catalyst exhibited an increased molecular weight ($M_w = 2.5 \times 10^5$) (run 7).

A polysilane also reacted with a quinone to provide an arylenedioxy-unit-containing polymer (eq 11). Thus,



(11)

upon heating of a mixture of poly(dimethylsilylene)[36] (**11**), **2a** (1.1 equiv/monomer unit), $PdCl_2(PEt_3)_2$ (ca. 1 mol %/**2a**), and benzene in a sealed tube at 120 °C, the originally insoluble **11** gradually dissolved to give a brown solution. After 18 h a small amount of an insoluble solid was removed by filtration. Concentration of the filtrate followed by washing with hexane gave the polymer **12** ($M_w = 1.5 \times 10^4$), consisting of alternating dimethylsilylene and *p*-phenylenedioxy units, in 85% yield. Reprecipitation with benzene−2-propyl alcohol provided a fraction with a higher molecular weight of $M_w = 2.3 \times 10^4$ ($M_w/M_n = 3.8$) in 46% yield. Polymer **12**, however, may be formed via interaction of dimethylsilylene with **2a** rather than via direct insertion of **2a** into the Si−Si bonds of **11**, judging from the result that the reaction of **1e** under similar reaction conditions involved formal extrusion of a dimethylsilylene unit (eq 6). In addition, we have observed that a cyclic oligosilane, dodecamethylcyclohexasilane, also underwent a palladium-catalyzed reaction with **2a**, possibly via silylene intermediates, to give the same polymer **12**.[9a]

Polymers **10a**−**c**,**e** possessed much higher chemical stability against hydrolysis than the monomeric compounds **3a**,**f** and could be purified by precipitation using 2-propanol without significant degradation. In contrast, siloxane polymers **10d**,**f** were not as stable, and attempted precipitation using 2-propanol or methanol resulted in a decrease in the molecular weight; the values of M_w before and after reprecipitation were respectively 1.7×10^5 and 1.2×10^5 for **10d** (precipitation with benzene−2-propyl alcohol) and 1.2×10^5 and 5.0×10^4 for **10f** (benzene−methanol). However, Florisil columns were found to be effective for purification of the polymers without extensive degradation; in separate experiments, the values of M_w before and after column chromatography (benzene eluent) were both 1.8×10^5 for **10d** and respectively 1.3×10^5 and 1.1×10^5 for **10f**.

Modified polymers **10** show satisfactory ^{1}H, ^{13}C, and/or ^{29}Si NMR, IR, and analytical data for the proposed structures. For instance, the ^{13}C NMR spectrum of **10a** cleanly displays 2 signals ascribable to the SiMe carbons at −2.3 and −2.2 ppm[37] and 13 signals for the ring carbons in the region 120−140 ppm (Figure 2). On the other hand, the partially modified polymer **10d** shows new $SiMe_2$ carbon signals A, B, and C at −0.2, 0.4, and

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[35] Chojnowski, J.; Kurjata, J.; Rubinsztajn, S. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 469.

[36] The molecular weight of **11** was measured by high-temperature GPC (ca. 210 °C) to be 4.7×10^3 for M_w ($M_w/M_n = 1.8$). See: Ohnaka, T. In *Synthesis and Applications of Organosilicon Polymers*; Sakurai, H. Ed.; CMC: Tokyo, 1989; p 99.

[37] The appearance of the two signals seems to originate from diastereoisomerism with respect to the placement of the substituents at the neighboring two silicon atoms.

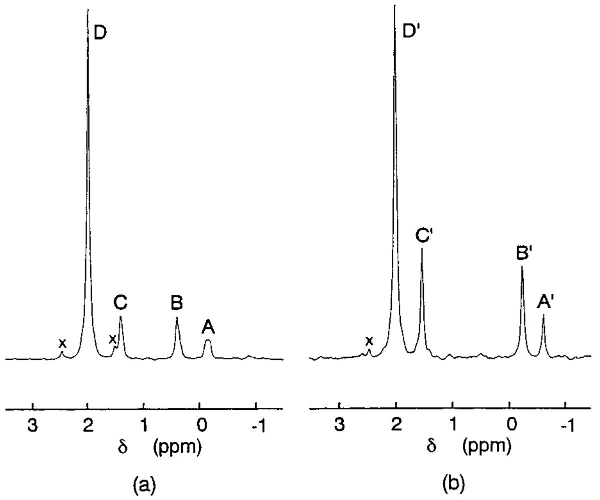

Figure 3. ^{13}C NMR signals of the $SiMe_2$ moieties of (a) **10d** and (b) **10f**. The signals marked with x are coupling satellites with ^{29}Si ($^1J_{SiC} \approx 48$ Hz). For assignment of the signals A−D and A′−D′, see Figure 4.

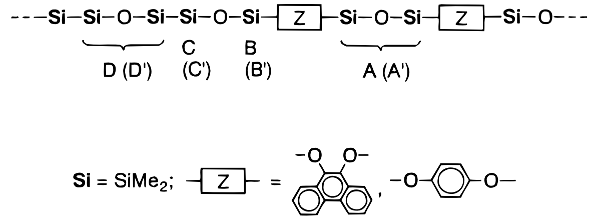

Figure 4. Possible classification of the $SiMe_2$ moieties in **10d** (**10f**) for the corresponding ^{13}C NMR signals (Figure 3).

1.4 ppm, respectively, along with an $SiMe_2$ signal D at the same chemical shift (2.0 ppm) as for the parent polymer **9c**, with the integral ratio A:B:C:D being 1:1.5: 1.4:9.5 (Figure 3a). Likewise, ^{13}C NMR of **10f** (run 7) displays new $SiMe_2$ signals A′, B′, and C′ at −0.7, −0.3, and 1.5 ppm, respectively, along with an intact signal D′ at 2.0 ppm with the ratio A′:B′:C′:D′ being 1:2.6:3.0: 11.4 (Figure 3 b). In view of the modified and/or intact diad linkages, the $SiMe_2$ moieties are classified into four groups, depending on the chemical shifts of the methyl carbons (Figure 4): those in two adjacent modified linkages for A and A′, those in modified linkages that are adjacent to unmodified linkages for B and B′, those in unmodified linkages for C and C′ (neighboring to B and B′, therefore the intensity of B ≈ C and B′ ≈ C′), and those in unmodified linkages for D and D′ (other than C and C′). On the basis of the assignment, the degrees of modification for **10d** and **10f** are respectively estimated at 19 and 20%, which are similar to those obtained from ^{1}H NMR and elemental analysis (20 and 21%, respectively). On the other hand, the order of the intensity, B (B′) > A (A′), indicates that modified linkages are separated rather than bonded to each other. Accordingly, the partially modified polymers **10d**,**f** seem to have random-type copolymeric structures.

Properties of the Modified Polymers. Polymers **10** exhibit new UV absorption bands arising from the introduced phenanthrene or benzene rings (ranges of λ_{max}: 297−299, 309−312, 348−350, and 365−367 nm for phenanthrene rings and 283−287 nm for benzene rings). In **10a**,**b** the value of the absorption coefficient is almost proportional to the degree of modification; the values at 299, 312, 348, and 366 nm are respectively 3.9×10^3, 4.0×10^3, 3.1×10^2, and 3.3×10^2 for the partially (29%) modified polymer **10b** and 1.4×10^4, 1.4×10^4, 1.5×10^3, and 1.6×10^3 for the exhaustively modified polymer **10a** (Figure 5). The existence of new absorption bands suggests the possibility that photoreactivities of these modified polymers are different from those of the starting polymers. Indeed, upon irradiation of a benzene solution of **10b** or **9a** (8×10^{-3} M) with a low-pressure mercury lamp, the modified polymer **10b** discontinued the decrease in molecular weight at about 40 min, while degradation of the unmodified polymer **9a** was still in progress[38] (Figure 6). In addition, **10b** gave a small amount of a fragment with a low molecular weight (8×10^2 at the peak top) in the early stage of the reaction (~10 min), whereas **9a** did not form such a fragment (Figure 7). The fragment, as well as the residual major fraction, showed a UV spectrum similar to that for **10b**, indicating that the phenanthrene rings still existed in the backbone (Figure 8).

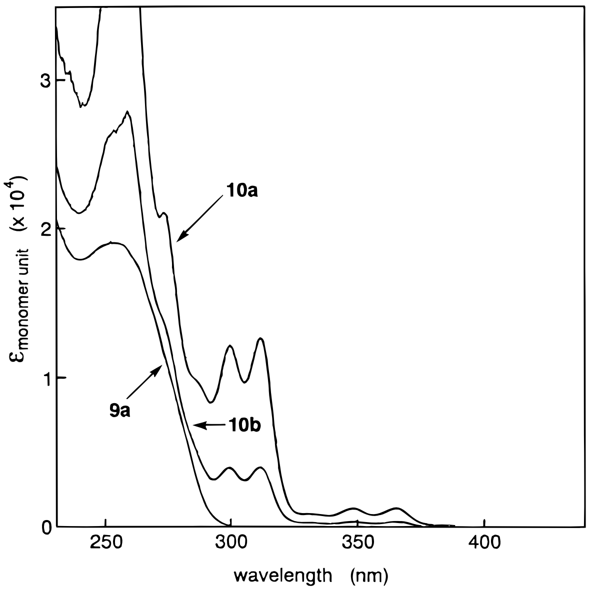

Figure 5. UV spectra of **10a**,**b** and **9a** (1×10^{-4} M THF solution).

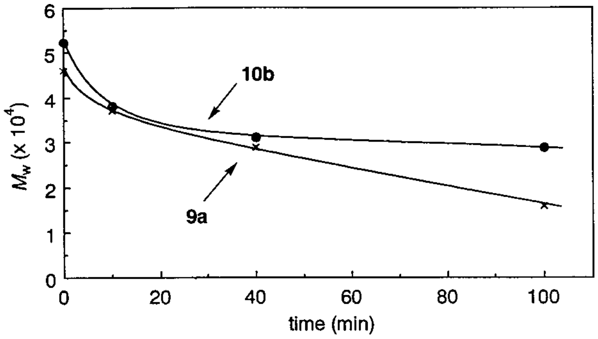

Figure 6. Time course of the molecular weights of **10b** and **9a** upon irradiation by UV light (8×10^{-3} M benzene solution, low-pressure mercury lamp, monitoring by GPC with an RI detector).

On the other hand, thermogravimetric analysis (TGA) of **10a** (100% modification), **10b** (29% modification), and **9a** (parent polymer; 0% modification) revealed that introduction of phenanthrene rings improved the thermal stability (Figure 9); the temperatures of 5 and 10%

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[38] Photoreactivity[33a] and thermal stability (TGA)[33b] for **9a** were previously examined.

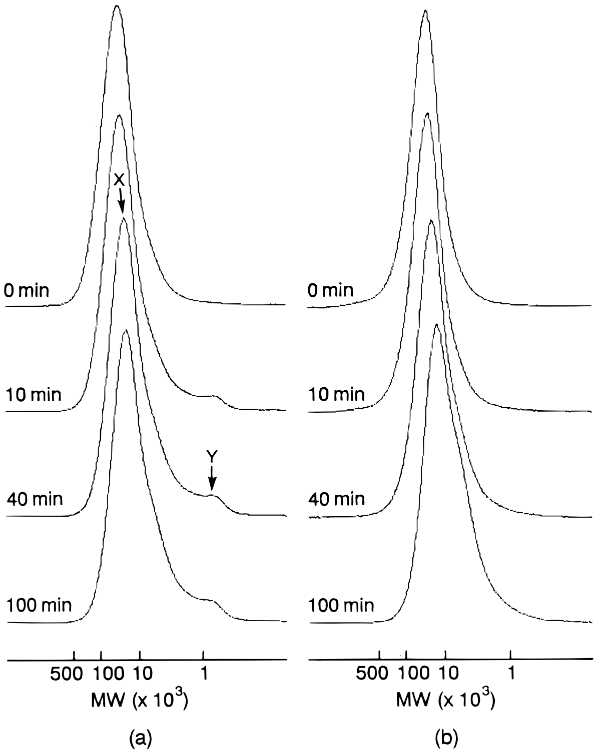

Figure 7. Time dependence of the GPC curves of (a) **10b** and (b) **9a** upon irradiation by UV light (8×10^{-3} M benzene solution, low-pressure mercury lamp, monitoring with a UV detector at 270 nm).

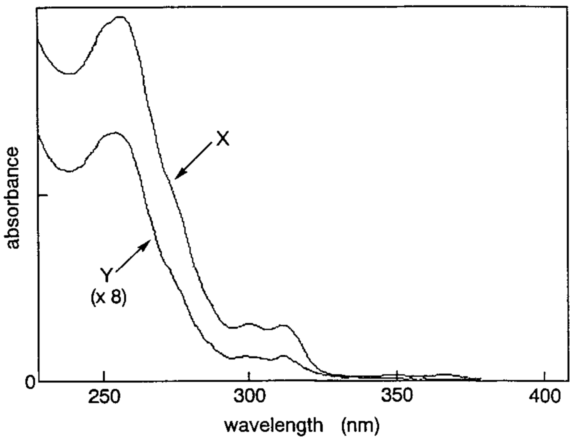

Figure 8. UV spectra of the degraded polymer of **10b** (UV irradiation for 40 min) at the molecular weights of 2.4×10^4 (X) and 8×10^2 (Y) (Figure 7; in GPC (THF eluent) using a UV detector with a photodiode array).

weight loss (modification degree, %) under helium at a 10 °C/min raising rate were respectively 455 and 465 °C (0), 470 and 485 °C (29), and 480 and 510 °C (~100). This indicates the possibility of offering a new class of heat-resistant materials by insertion of quinones having thermally stable aromatic rings.

In conclusion, insertion of 1,2- or 1,4-quinones into nonactivated Si−Si bonds proceeds in the presence of palladium catalysts such as $PdCl_2L_2$ (L = PEt_3, PPh_3, etc.) and $Pd(dba)_2-2P(OCH_2)_3CEt$ to give various 1,2- and 1,4-bis(siloxy) aromatic compounds. The process was successfully applied to the modification of Si−Si-bond-containing polymers by direct insertion of quinones into their backbones. Since the modified polymers exhibit unique photochemical and thermal properties, the present reaction provides a new methodology for controlling the physicochemical properties of Si−Si-bond-containing polymers.

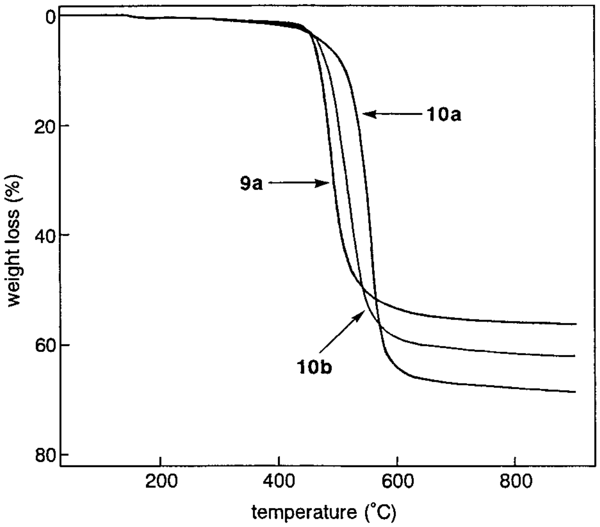

Figure 9. TGA of **10a**,**b** and **9a** (under helium, 10 °C/min raising rate).

Experimental Section

NMR spectra were measured on Bruker AC-200 (^{1}H and ^{13}C), Bruker ARX-300 (^{29}Si), and JEOL FX-90 (^{31}P) instruments (200 MHz for ^{1}H, 50.3 MHz for ^{13}C, 59.6 MHz for ^{29}Si, and 36.2 MHz for ^{31}P). The NMR solvent is $CDCl_3$ unless otherwise noted. Chemical shifts are referred to Me_4Si (0 ppm), $CHCl_3$ (7.25 ppm), C_6D_5H (7.16 ppm), or $C_6D_4HCD_3$ (6.97 ppm) for ^{1}H NMR, $CDCl_3$ (77.0 ppm) or C_6D_6 (128.0 ppm) for ^{13}C NMR, Me_4Si (0 ppm) for ^{29}Si NMR, and H_3PO_4 (85% solution in D_2O, 0 ppm) for ^{31}P NMR. IR spectra were recorded on JASCO A-302 and/or JASCO FT/IR-5000 spectrometers. UV spectra were measured on a Shimadzu UV-3100 spectrometer. GC−(HR)MS analyses (EI, 70 eV) were performed on Shimadzu QP-1000 and/or JEOL DX-303 spectrometers. Molecular weights of polymers were measured with a GPC system equipped with a high-pressure Shimadzu LC-6A pump, Shodex KF-80M, KF-802, and KF-801 columns, and Shimadzu RID-2A or Shodex SE-61 (RI) and/or Shimadzu SPD-M1A (UV) detectors using THF eluent and polystyrene standards. TGA was performed with a Shimadzu TG-30 system.

Every liquid starting material or solvent was dried with an appropriate agent (molecular sieves 4A, sodium, etc.) and distilled in vacuo or under nitrogen. 1,1,2,2-Tetramethyl-1,2-diphenyldisilane (**1b**) was purchased and distilled in vacuo. 1,1,2,2-Tetramethyl-1,2-disilacyclohexane[39] (**1c**), 1,2-difluoro-1,1,2,2-tetramethyldisilane[40] (**1d**), and octamethyltrisilane[41] (**1e**) were prepared according to the literature. *p*-Benzoquinone (**2a**) and 1,2-naphthoquinone (**2e**) were recrystallized from hexane. 1,4-Naphthoquinone (**2c**) was sublimed and subsequently recrystallized from benzene. Chloranil (**2b**), 9,10-anthraquinone (**2d**), and 9,10-phenanthraquinone (**2f**) were used as purchased. $PdCl_2(PPh_3)_2$,[42] $PdCl_2(PMe_3)_2$,[43] $PdCl_2(PhCN)_2$,[44] $Pd(dba)_2$,[45] $Pd(PPh_3)_4$,[46] (*p*-benzoquinone)Pd-

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$(PPh_3)_2$[25] (**7**), *cis*-$(PhMe_2Si)_2Pt(PMe_2Ph)_2$[27] (**8a**), and *cis*-$(FMe_2Si)_2Pt(PEt_3)_2$[29] (**8b**) were synthesized by the literature reactions. $PdCl_2(P^iBu_3)_2$[47] and $PdCl_2(PEt_3)_2$[48] were prepared by treatment of $PdCl_2(PhCN)_2$ with 2 equiv of the corresponding phosphines according to the reported procedure.[49] PPh_3 was recrystallized from ethanol. $P(OCH_2)_3CEt$ was distilled and subsequently recrystallized from hexane. Poly[(1,2-dimethyl-1,2-diphenyldisilanylene)(*p*-phenylene)][33a] (**9a**), poly[(tetramethyldisilanylene)ethylene][4a] (**9b**), and poly(tetramethyldisiloxane)[35] (**9c**) were prepared according to the literature. Poly(dimethylsilylene) (**11**) was obtained from Nippon Soda Co. Ltd.

Catalytic Reactions. Each reaction of a Si−Si-bonded compound with a quinone was carried out at 120 or 100 °C under nitrogen in a sealed glass tube (6 mm i.d.).

Reactions of 1a with 2a−f. A typical procedure is as follows (Table 1, run 5). A mixture of **1a** (0.44 mmol), **2a** (0.40 mmol), $PdCl_2(PPh_3)_2$ (0.008 mmol), and benzene (0.05 mL) was heated at 120 °C for 1 h. GC and GC−MS analyses showed almost complete consumption of **2a** and formation of *p*-bis(trimethylsiloxy)benzene (**3a**; ∼0.40 mmol, ∼100% yield). In a separate reaction under the same conditions, concentration of the reaction mixture followed by Kugelrohr distillation gave **3a** (0.38 mmol, 95% yield).

Similarly, 1,2,4,5-tetrachloro-3,6-bis(trimethylsiloxy)benzene (**3b**; ∼65% yield, ∼90% purity), 1,4-bis(trimethylsiloxy)naphthalene (**3c**; 80% yield), and 9,10-bis(trimethylsiloxy)phenanthrene (**3f**; 95% yield) were respectively isolated in the reactions of **1a** with **2b** ($PdCl_2(PPh_3)_2$ catalyst, 24 h; run 12), **2c** ($PdCl_2(PPh_3)_2$ catalyst, 6 h; run 14), and **2f** ($Pd(dba)_2$−$2P(OCH_2)_3CEt$ catalyst, 1 h; run 26). Preparative GC was used to purify 1,2-bis(trimethylsiloxy)naphthalene (**3e**) (vide infra). Compounds **3a**,[14a,16b] **3b**,[50] **3c**,[14a,50] **3d**,[50] **3e**,[50] and **3f**[51] were identified by NMR, IR, and GC−(HR)MS spectra or by comparison with the authentic samples.

The reaction of **2a** using the $Pd(dba)_2$−$2P(OCH_2)_3CEt$ catalyst (run 8) gave **3a** (70% yield) and other products (**4a**, **5a**, P1, and P2) whose GC−(HR)MS parent ions respectively corresponded to 4-(trimethylsiloxy)phenol, 1,4-bis(trimethylsiloxy)-2-(trimethylsilyl)benzene,[52] an isomer of **3a** with $M^+ = m/z$ 254, and a compound with $M^+ = m/z$ 434 (**1a** + **2a** × 2 + Me_3Si − H) (GC (TCD) area ratio **3a**:**4a**:**5a**:P1:P2 = 100:10:5:5:3). Preparative GC gave relatively pure **4a** (∼60% purity, a mixture with **3a**) and **5a** (∼95% purity). Their NMR spectra were consistent with the proposed structures.

On the other hand, the reaction of **2b** (run 12) gave **3b** (70% yield) and other products (P3 and P4) (GC (TCD) area ratio **3b**:P3:P4 = 100:13:2). GC−MS showed the parent ion for P3 at *m/z* 428 (for ^{35}Cl), which corresponded to 1,2,4-trichloro-3,6-bis(trimethylsiloxy)-5-(trimethylsilyl)benzene, while the parent ion for P4 was *m/z* 356 (=$Me_3Si \times 2 + {}^{35}Cl \times 3 + C_6O_2H$).

In the reaction of **2e** (run 20), GC−(HR)MS showed formation of **3e** (27% yield) and 2-(trimethylsiloxy)-1-naphthol and 1-(trimethylsiloxy)-2-naphthol (**4e**; 22%). Preparative GC gave relatively pure **3e** (∼85% purity, a mixture with **4e**) and **4e** (∼60% purity, a mixture with **3e**).

Spectral data for **3b**, **3f**, **4a**, **4e**, **5a**, P1, P2, P3, and P4 are as follows.

3b: ^1H NMR δ 0.33 (s, 18H, $SiCH_3$); ^{13}C NMR δ 0.8 (SiC), 124.5 (4C), 144.6 (2C); GC−MS *m/z* (relative intensity) 390 (28, M^+ for ^{35}Cl), 375 (35), 340 (29), 325 (17), 267 (30), 93 (35), 73 (100), 45 (38); GC−HRMS calcd for $C_{12}H_{18}Cl_4O_2Si_2$ 389.9598, found 389.9614.

3f: ^1H NMR δ 0.28 (s, 18H, $SiCH_3$), 7.50−7.66 (m, 4H, ring 2,3,6,7-H), 8.05−8.17 (m, 2H, ring 1,8-H), 8.58−8.69 (m, 2H, ring 4,5-H); ^{13}C NMR δ 0.1 (SiC), 120.5 (4C), 149.4 (2C); GC−MS *m/z* (relative intensity) 366 (100, M^+), 266 (38), 73 (74), 45 (20); GC−HRMS calcd for $C_{20}H_{26}O_2Si_2$ 354.1471, found 354.1470.

4a: ^1H NMR δ 0.22 (s, 9H, $SiCH_3$), 4.37 (s, 1H, OH), 6.70 (s, 4H, C_6H_4) (addition of D_2O diminished the signal at 4.38 ppm); MS *m/z* (relative intensity) 182 (46, M^+), 167 (100); GC−HRMS calcd for $C_9H_{14}O_2Si$ 182.0763, found 182.0758.

4e: a mixture of 2-(trimethylsiloxy)-1-naphthol and 1-(trimethylsiloxy)-2-naphthol (ratio of the two regioisomers A:B ≈ 1:4); ^1H NMR δ 0.33 (isomer A) and 0.36 (B) (each s, 9H, $SiCH_3$), 5.23 (A) and 5.83 (B) (each s, 1H, OH), 7.08−8.19 (m, 6H, ring protons) (addition of D_2O diminished the signals at 5.23 and 5.83 ppm); GC−MS *m/z* (relative intensity) 232 (49, M^+), 216 (100), 201 (44), 186 (43), 75 (41); GC−HRMS calcd for $C_{13}H_{16}O_2Si$ 232.0920, found 232.0917.

5a: ^1H NMR δ 0.24 (s, 18H, $SiCH_3$), 0.29 (s, 9H, $SiCH_3$), 6.61 (d, J = 8.6 Hz, 1H, ring H), 6.69 (dd, J = 8.6, 2.9 Hz, 1H, ring H), 6.82 (d, J = 2.9 Hz, 1H, ring H); ^{13}C NMR δ −1.0, 0.2, and 0.6 ($SiCH_3$), 116.9, 121.1, and 126.2 (aromatic CH), 130.9, 148.6, and 154.6 (quaternary C); IR (neat) 1472 (s), 1260 (s), 1216 (s), 924 (s), 842 (s) cm^{-1}; GC−MS *m/z* (relative intensity) 326 (100, M^+), 311 (27), 295 (14), 73 (50); GC−HRMS calcd for $C_{15}H_{30}O_2Si_3$ 326.1553, found 326.1560.

P1: GC−MS *m/z* (relative intensity) 254 (28, M^+), 238 (100), 223 (88), 179 (14), 133 (13), 73 (32), 45 (16); GC−HRMS calcd for $C_{12}H_{22}O_2Si_2$ 254.1158, found 254.1169.

P2: GC−MS *m/z* (relative intensity) 434 (100, M^+), 419 (30), 223 (88), 355 (14), 254 (14), 73 (50); GC−HRMS calcd for $C_{21}H_{34}O_4Si_3$ 434.1765, found 434.1766.

P3: GC−MS *m/z* (relative intensity) 428 (19, M^+ for ^{35}Cl), 413 (9), 270 (16), 93 (16), 73 (100), 45 (23).

P4: GC−MS *m/z* (relative intensity) 356 (5, M^+ for ^{35}Cl), 269 (100), 267 (95), 113 (44), 93 (26), 73 (19), 63 (27).

Reaction of 1b with 2a. A mixture of **1b** (0.80 mmol), **2a** (0.88 mmol), $PdCl_2(PEt_3)_2$ (0.016 mmol), and benzene (0.20 mL) was heated at 120 °C for 14 h. GC and GC−MS showed formation of *p*-bis(dimethylphenylsiloxy)benzene (**3g**, 0.71 mmol, 89% yield) and 4-(dimethylphenylsiloxy)phenol (**4g**, 0.055 mmol, 7%). Florisil column chromatography with benzene eluent gave pure **3g** and relatively pure **4g** (∼80% purity, a mixture with **3g**) as colorless oils.

3g: ^1H NMR δ 0.49 (s, 12H, $SiCH_3$), 6.64 (s, 4H, OC_6H_4O), 7.37−7.49 and 7.61−7.72 (each m, 6H and 4H, C_6H_5); ^{13}C NMR δ −1.2 ($SiCH_3$), 120.5 (OC_6H_4O), 127.9 (*m*-C of C_6H_5), 129.8 (*p*-C of C_6H_5), 133.4 (*o*-C of C_6H_5), 137.3 (*ipso*-C of C_6H_5), 149.3 (SiOC); IR (neat) 1506 (s), 1430 (m), 1256 (s), 1238 (s), 1222 (s), 1122 (s), 920 (s), 840 (s), 810 (s), 792 (s), 742 (m), 730 (m), 702 (s), 666 (m); GC−MS *m/z* (relative intensity) 378 (100, M^+), 363 (63), 285 (75), 135 (87), 43 (22). Anal. Calcd for $C_{22}H_{26}O_2Si_2$: C, 69.79; H, 6.92. Found: C, 69.73; H, 6.90.

4g: ^1H NMR (C_6D_6) δ 0.38 (s, 6H, $SiCH_3$), 3.70 (br s, 1H, OH), 6.32−6.42 and 6.67−6.77 (each m, each 2H, OC_6H_4O), 7.12−7.24 and 7.53−7.63 (each m, 3H and 2H, C_6H_5); GC−MS *m/z* (relative intensity) 244 (100, M^+), 229 (91), 151 (32), 135 (66), 43 (23); GC−HRMS calcd for $C_{14}H_{16}O_2Si$ 244.0919, found 244.0929.

Reaction of 1c with 2f. A mixture of **1c** (0.60 mmol), **2f** (0.66 mmol), $PdCl_2(PEt_3)_2$ (0.008 mmol), and benzene (0.15 mL) was heated at 120 °C for 24 h. ^1H NMR showed formation of **3h** in ∼100% yield. Florisil column chromatography with benzene eluent gave nearly pure **3h** (0.555 mmol, 93% yield) as a colorless viscous oil.

3h: ^1H NMR δ 0.16 (s, 9H, $SiCH_3$), 0.92−1.07 and 1.83−2.00 (each m, each 4H, CH_2), 7.50−7.67 (m, 4H, ring H), 8.06−8.17 and 8.58−8.79 (each m, each 2H, ring H); ^{13}C NMR δ −1.5 ($SiCH_3$), 15.7 and 23.6 (CH_2), 122.4, 124.8, 126.4, and 128.3 (ring CH), 127.6, 129.9, and 137.8 (ring quaternary C); IR

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(47) $PdCl_2(P^iBu_3)_2$: mp 150.2−151.5 °C. Anal. Calcd for $C_{24}H_{54}Cl_2P_2Pd$: C, 49.53; H, 9.35. Found: C, 49.54; H, 9.35.

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(neat) 1600 (s), 1492 (m), 1450 (s), 1420 (m), 1374 (s), 1356 (s), 1340 (s), 1282 (m), 1252 (s, SiMe), 1228 (m), 1178 (s), 1118 (s), 1064 (s), 1036 (s), 926 (s), 882 (s), 866 (s), 838 (s), 820 (s), 794 (s), 758 (s), 726 (s), 698 (m), 676 (m), 664 (m), 642 (m); GC−MS *m/z* (relative intensity) 380 (66, M^+), 266 (100), 236 (33), 99 (13), 59 (30); GC−HRMS calcd for $C_{22}H_{28}O_2Si_2$ 380.1628, found 380.1646.

Reaction of 1d with 2a. A mixture of **1d** (0.40 mmol), **2a** (0.44 mmol), $PdCl_2(PEt_3)_2$ (0.004 mmol), and benzene (0.05 mL) was heated at 100 °C for 12 h. GC and GC−MS showed formation of *p*-bis(fluorodimethylsiloxy)benzene (**3i**; ~0.1 mmol, ~25% yield) and other products (**4i**, **6i**, and P5) whose GC−(HR)MS parent ions corresponded to those of 4-(fluorodimethylsiloxy)phenol, bis[4-(fluorodimethylsiloxy)phenoxy]dimethylsilane, and difluorodimethylsilane (GC (TCD) area ratio **3i**:**4i**:**6i**:P5 = 100:5:2:95). NMR spectral data for **3i** were in agreement with the reported values.[5c]

4i: GC−MS *m/z* (relative intensity) 186 (100, M^+), 171 (73), 79 (33), 77 (55), 49 (19), 47 (31); GC−HRMS calcd for $C_8H_{11}FO_2Si$ 186.0512, found 186.0511.

6i: GC−MS *m/z* (relative intensity) 428 (100, M^+), 395 (33), 243 (34), 77 (21); GC−HRMS calcd for $C_{18}H_{26}F_2O_4Si_3$ 428.1107, found 428.1121.

P5: GC−MS *m/z* (relative intensity) 96 (74, M^+), 81 (100).

Reaction of 1e with 2a. A mixture of **1e** (0.40 mmol), **2a** (0.88 mmol), $PdCl_2(PEt_3)_2$ (0.016 mmol), and benzene (0.10 mL) was heated at 120 °C for 12 h. GC and GC−MS showed formation of **3a** (0.12 mmol, 30%), **4a** (0.08 mmol, 20%), and a compound (**6j**) whose GC−(HR)MS parent ion corresponded to dimethylbis[4-(trimethylsiloxy)phenoxy]silane (GC area ratio **3a**:**6j** = 5:≤2). GPC of the reaction mixture showed a peak with $M_w \approx 8 \times 10^2$ ($M_w/M_n \approx 1$).

6j: GC−MS *m/z* (relative intensity) 420 (100, M^+), 195 (14), 73 (64); GC−HRMS calcd for $C_{20}H_{32}O_4Si_3$ 420.1608, found 420.1593.

Reaction of 7 with 1a. A mixture of **7** (0.0215 mmol), **1a** (0.043 mmol), and benzene-d_6 (0.25 mL) was heated under nitrogen in a sealed NMR tube at 120 °C for 23 h. ^{1}H NMR showed almost no reactions taking place (yield of **3a** ≤1%, ≥90% recovery of **7**). When a mixture of **7** (0.021 mmol), **1a** (0.042 mmol), **2c** (0.021 mmol), and benzene-d_6 (0.25 mL) was heated at 120 °C for 9 h, ^{1}H NMR and GC showed formation of a small amount of **3a** (~4% yield) with recovery of **7** (≥90%).

Reaction of 8a with 2a. A mixture of **8a** (0.0075 mmol), **2a** (0.015 mmol), and benzene-d_6 (0.30 mL) was heated under nitrogen in a sealed NMR tube at 80 °C for 5 min. NMR and GC showed almost complete consumption of **8a** and formation of **3g** (60% yield), **4g** (35%), and a platinum complex that appeared to be (*p*-benzoquinone)$Pt(PMe_2Ph)_2$:[53] ^{1}H NMR δ 1.24 (d, $J_{PH} = 9.8$ Hz, $J_{PtH} = 34.0$ Hz, 12 H, PCH_3), 5.44 (t, $J_{PH} = 2.4$ Hz, $J_{PtH} = 24.5$ Hz, 4H, OC_6H_4O); ^{31}P NMR δ −13.0 (s, $^1J_{PtP} = 3745$ Hz).

Reaction of 8b with 2a. To a toluene-d_8 (0.70 mL) solution of **8b** (0.061 mmol) placed in a Schlenk tube cooled to −50 °C was added **2a** (0.061 mmol) under nitrogen. The suspension was warmed to room temperature over ~3 h. ^{1}H NMR of the supernatant solution displayed the SiMe signals of **8b**, **3i**, and other unidentified species in the region 0−0.3 ppm (integral ratio of the SiMe protons **8b**:**3i**:others ≈ 18:1:3). GC and GC−MS showed formation of **3i** as the major volatile product. When the reaction was carried out in benzene-d_6 from room temperature to 120 °C, NMR and GC−MS showed formation of a complex mixture, and **3i** was not detected.

Reactions of 9a−c and 11 with 2a,f. A typical procedure is as follows. A mixture of **9a** ($M_w = 4.6 \times 10^4$, $M_w/M_n = 2.6$, 0.20 mmol monomer unit), **2f** (0.21 mmol), $Pd(dba)_2$ (0.004 mmol), $P(OCH_2)_3CEt$ (0.008 mmol), and benzene (0.10 mL) was heated at 120 °C for 3 h. Benzene (4 mL) was added to the reaction mixture, and the solution was filtered. The filtrate was concentrated (~1 mL) and was added dropwise to 2-propanol (~4 mL). The precipitated solid was separated and dried in vacuo to give **10a** (0.18 mmol monomer unit, 90% yield) with $M_w = 5.8 \times 10^4$ ($M_w/M_n = 3.0$).

Similarly, **10b**,**c** were obtained in the reactions of **9a**,**b** with **2f**. The reaction conditions and the yields and the molecular weights of the polymers after precipitation are shown in Table 2. In the reaction of **9b** with **2a**, precipitation with benzene−2-propyl alcohol from the reaction mixture ($M_w = 1.9 \times 10^4$, $M_w/M_n = 2.4$) gave a fraction **10e** (A) (0.18 mmol monomer unit, 46% yield) with a higher molecular weight, $M_w = 3.6 \times 10^4$ ($M_w/M_n = 2.6$). Concentration of the mother liquor yielded another fraction **10e** (B) (37%) with a lower molecular weight, $M_w = 1.2 \times 10^4$ ($M_w/M_n = 2.0$). When **9c** was used, the produced polymers **10d**,**f** were purified by passage of the reaction mixtures through short-path Florisil columns (benzene eluent).

In the reaction of **11**, a mixture of **11** (1.0 mmol monomer unit), **2a** (1.1 mmol), $PdCl_2(PEt_3)_2$ (0.01 mmol), and benzene (0.50 mL) was magnetically stirred at 120 °C for 18 h. Benzene (~5 mL) was added to the reaction mixture, and the solution was filtered. Concentration of the filtrate in vacuo followed by washing of the residual solid with hexane gave **12** (0.85 mmol monomer unit, 85% yield, $M_w = 1.5 \times 10^4$, $M_w/M_n \approx 6$). Reprecipitation with benzene−2-propyl alcohol and slight evaporation of the solvents provided the fraction **12** (A) (46%) with a higher molecular weight, $M_w = 2.3 \times 10^4$ ($M_w/M_n = 3.8$).

Appearance and physical, spectral, and analytical data for **10a−f** and **12** are as follows.

10a: off-white solid; softening temperature 177−195 °C; ^{1}H NMR δ 0.47 (br s, 6H, $SiCH_3$), 7.03−7.63 (m, 18H, benzene and phenanthrene ring H), 7.73−7.95 and 8.37−8.60 (each m, 4H, phenanthrene ring H); ^{13}C NMR δ −2.3 and −2.2 (2C, $SiCH_3$), 122.1 (2C), 123.3 (2C), 124.8 (2C), 125.8 (2C), 127.6 (4C), 128.3 (2C), 129.2 (2C), 129.8 (2C), 133.7 (4C), 134.6 (4C), 135.2 (2C), 137.0 (2C), 137.4 (2C); IR (KBr) 1600 (m), 1492 (m), 1450 (m), 1426 (m), 1370 (m), 1340 (m), 1256 (m), 1176 (m), 1136 (s), 1114 (s), 1064 (m), 1034 (m), 924 (m), 840 (m), 784 (s), 756 (s), 736 (m), 724 (m), 698 (m), 516 (m) cm^{-1}; 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), 366 (1.6×10^3) nm. Anal. Calcd for $C_{34}H_{28}O_2Si_2$: C, 77.82; H, 5.38. Found: C, 77.25; H, 5.31.

10b: off-white solid; softening temperature 145−155 °C; ^{1}H NMR δ 0.40−0.88 (m, $SiCH_3$), 7.03−7.76 (m, benzene and phenanthrene ring H), 7.76−7.91 and 8.35−8.58 (each m, phenanthrene ring H); IR (KBr) 1600 (m), 1496 (m), 1454 (m), 1430 (s), 1374 (m), 1340 (m), 1248 (m), 1178 (m), 1114 (s), 1066 (m), 1038 (m), 928 (m), 840 (m), 784 (s), 772 (s), 758 (s), 736 (s), 696 (s), 500 (s) cm^{-1}; 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. Anal. Calcd for $(C_{34}H_{28}O_2Si_2)_{0.29}(C_{20}H_{20}Si_2)_{0.71}$: C, 76.67; H, 5.97. Found: C, 76.68; H, 5.95.

10c: off-white solid; softening temperature 82−90 °C; ^{1}H NMR δ 0.08 (s, 12H, $SiCH_3$), 0.61 (s, 4H, $SiCH_2CH_2$), 7.37−7.52, 7.92−8.04, and 8.44−8.59 (each m, ring H, 8H); ^{13}C NMR δ −1.7 (4C, $SiCH_3$), 8.6 (2C, CH_2), 122.3 (2C), 122.6 (2C), 124.8 (2C), 126.1 (2C), 127.5 (2C), 129.7 (2C), 137.2 (2C); IR (KBr) 1601 (m), 1491 (m), 1452 (m), 1423 (m), 1373 (m), 1357 (m), 1340 (m), 1253 (m), 1180 (m), 1137 (m), 1118 (m), 1065 (m), 1035 (m), 926 (m), 820 (s), 793 (m), 754 (s), 725 (m) cm^{-1}; 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. Anal. Calcd for $C_{20}H_{24}O_2Si_2$: C, 68.13; H, 6.86. Found: C, 68.08; H, 6.66.

10d: off-white gummy solid; softening temperature 50−59 °C; ^{1}H NMR δ −0.10−0.36 (m, $SiCH_3$), 7.10−7.67, 8.01−8.30, and 8.44−8.71 (each m, ring H); ^{13}C NMR δ −0.2, 0.4, 1.4, and 2.0 ($SiCH_3$), 122.2, 123.1, 123.4, 124.8, 126.2, 127.6, 129.5, 129.8, 136.4, and 136.7 (ring C); IR (neat) 1620 (m), 1603 (m), 1493 (m), 1456 (m), 1425 (m), 1404 (m), 1375 (m), 1357 (m),

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(53) For some (*p*-quinone)$Pt(PPh_3)_2$ complexes, see: Cenini, S.; Ugo, R.; Monica, G. L. *J. Chem. Soc. A* **1971**, 416.

1342 (m), 1251 (s), 1183 (m), 1116 (m), 1063 (s), 1036 (s), 932 (m), 843 (s), 804 (s), 766 (s), 725 (m), 681 (m), 646 (m) cm^{-1}; 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. Anal. Calcd for $(C_{18}H_{20}O_3Si_2)_{0.20}(C_4H_{12}OSi_2)_{0.80}$: C, 46.95; H, 7.88. Found: C, 46.89; H, 7.68.

10e (A): off-white solid; softening temperature 76−79 °C; ^{1}H NMR δ 0.20 (s, 12H, $SiCH_3$), 0.67 (s, 4H, $SiCH_2CH_2$), 6.67 (s, 4H, ring H); ^{13}C NMR δ −2.1 (4C, $SiCH_3$), 7.8 (2C, CH_2), 120.5 (4C), 149.4 (2C); IR (KBr) 1506 (s), 1470 (m), 1367 (m), 1253 (s), 1226 (s), 1131 (m), 1052 (m), 922 (s), 835 (s), 785 (s), 756 (m), 717 (m), 526 (m) cm^{-1}; UV (THF) λ_{max} ($\epsilon_{monomer\ unit}$) 287 (2.4×10^3) nm. Anal. Calcd for $C_{12}H_{20}O_2Si_2$: C, 57.09; H, 7.98. Found: C, 56.80; H, 7.87.

10f: pale brown viscous oil; ^{1}H NMR δ 0.11−0.24 (m, $SiCH_3$), 6.72 (br s, ring H); ^{13}C NMR δ −0.7, −0.3, 1.5, 2.0 ($SiCH_3$), 120.36 and 120.42 (*o*-C), 148.6 and 149.1 (*ipso*-C); IR (KBr) 1506 (s), 1404 (m), 1251 (s), 1054 (s), 932 (s), 835 (s), 816 (s), 799 (s), 766 (s), 681 (m), 646 (m) cm^{-1}; UV (THF) λ_{max} ($\epsilon_{monomer\ unit}$) 283 (5.2×10^2) nm. Anal. Calcd for $(C_{10}H_{16}O_3Si_2)_{0.21}(C_4H_{12}OSi_2)_{0.79}$: C, 40.76; H, 8.35. Found: C, 40.74; H, 8.05.

12 (A): sticky brown solid; ^{1}H NMR (C_6D_6) δ 0.22 (br s, 6H, $SiCH_3$), 6.91 (br s, 4H, ring H); ^{13}C NMR (C_6D_6) δ −2.5 (2C, SiC), 120.9 (4C), 149.5 (2C); ^{29}Si NMR (C_6D_6) δ −5.2; IR (KBr) 1502 (s), 1263 (m), 1234 (m), 1214 (s), 936 (s), 839 (s), 806 (m) cm^{-1}. Anal. Calcd for $C_8H_{10}O_2Si$: C, 57.80; H, 6.06. Found: C, 58.45; H, 5.43.

Photoreactivities of 10b and 9a. A stirred benzene (1 mL) solution of **10b** or **9a** (0.008 mmol monomer unit) under nitrogen in a quartz cell was irradiated with a low-pressure mercury lamp (EIKOHSHA, EL-S-SQ 30W) that was placed at a distance of 15 cm from the cell. At reaction times of 10, 40, and 100 min, irradiation was discontinued, and a portion (20 μL) of the solution was taken out by a syringe. The solution was concentrated by nitrogen stream, and the residue was analyzed by GPC. The values of M_w (irradiation time, min) were 5.2×10^4 (0), 3.8×10^4 (10), 3.1×10^4 (40), and 2.9×10^4 (100) for **10b** and 4.6×10^4 (0), 3.7×10^4 (10), 2.9×10^4 (40), and 1.6×10^4 (100) for **9a** (Figures 6−8).

Thermogravimetric Analyses of 10a,b and 9a. The measurements were carried out under helium in the range of room temperature to 900 °C at a raising rate of 10 °C/min. The temperatures of 5 and 10% weight loss were 480 and 510 °C for **10a**, 470 and 485 °C for **10b**, and 455 and 465 °C for **9a** (Figure 9). The weights of the residues after heating to 900 °C were 32, 38, and 44% for **10a**,**b** and **9a**, respectively.

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