Novel Ladder Polymers by the Platinum Complex-Catalyzed Dehydrogenative Double Silylation Reaction of 1,2,4,5-Tetrakis(dimethylsilyl)benzene with Cyclic Diynes

Shigeru Shimada,[†] Yuko Uchimaru,[†] and Masato Tanaka*[†,††]
[†]*National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305*
[††]*Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305*

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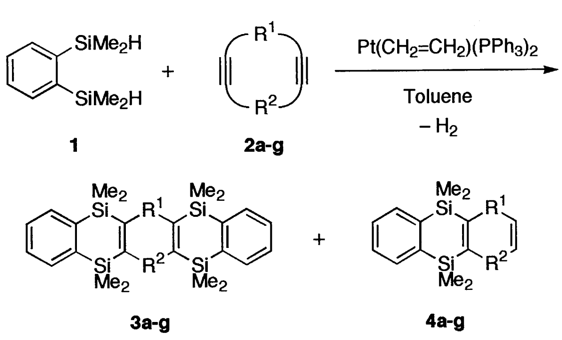
A platinum complex-catalyzed dehydrogenative double silylation reaction of 1,2,4,5-tetrakis(dimethylsilyl)benzene with cyclic diynes gave ladder polymers quantitatively.

Ladder polymers have attracted much attention because their unique structure will provide high performance materials in terms of thermal and chemical stability and mechanical strength.[1] Recently interests toward ladder polymers are again growing as electronic and nonlinear optical materials.[1b-c] However, the methods to prepare ladder polymers are limited.[1,2] Therefore, new synthetic methods for ladder polymers are desired. In the course of our study on the development of new synthetic methodologies for silicon-based materials, we found that the platinum complex-catalyzed dehydrogenative double silylation reaction of acetylenes[3] was a powerful tool to synthesize polycarbosilanes.[4] Now we applied this reaction for the synthesis of novel ladder polycarbosilanes.

A model reaction between 1,2-bis(dimethylsilyl)benzene **1** and cyclic diyne **2a**[5] (**1**/**2a** = 3/1) smoothly proceeded in the presence of a catalytic amount of $Pt(CH_2{=}CH_2)(PPh_3)_2$ in toluene at 110 °C with an evolution of H_2 to give the desired product **3a** in 85% yield (Table 1). The reaction seemed to have been completed within 10 min. Excess of **1** was recovered without any change. Under these conditions, a considerable amount of by-product **4a** (14%) was also formed. However, the amount of **4a** could be reduced to 2% by lowering the reaction temperature with a smaller amount of the catalyst. Under the new reaction conditions, the reaction of **1** with various alkylene-bridged diynes **2a-c**[5] and tricyclic diyne **2g**[6] gave the desired products **3a-c** and **3g** in excellent yields (Table 2). On the other hand, **3d** was obtained only in a low yield probably because of the instability of diyne **2d**[7] under the reaction conditions. Diynes **2e**[8] and **2f**[9] were reluctant to undergo the reaction; the former formed too stable platinum complexes[10] and the latter appeared too congested at the triple bond to react with **1**.



On the basis of the above results, polymerization of 1,2,4,5-tetrakis(dimethylsilyl)benzene **5** with diynes **2a-c** and **2g** was performed in the presence of 0.4 mol% of $Pt(CH_2{=}CH_2)(PPh_3)_2$ in toluene at 30 °C (12–24 h), 50 °C (4 h) and 110 °C (24 h). The results are summarized in Table 3. In all cases, the polymers were obtained in quantitative yields. In the reactions of diynes **2a-c**, the polymers **6a-c** completely precipitated after heating at 110 °C, and were almost insoluble in the common organic solvents. On the other hand, the polymer **6g** was soluble in toluene, $CHCl_3$, CH_2Cl_2, THF and insoluble in MeOH. The molecular weights of the insoluble polymers **6a-c** were estimated by the IR end group analysis,[11] while that of **6g** was determined by GPC based on the polystyrene standards.

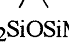
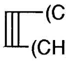
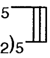
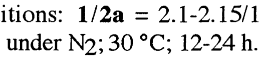
The structures of **6a-c** and **6g** were confirmed by comparing their ^{13}C and ^{29}Si CP/MAS NMR (for **6a-c**) or ^1H, ^{13}C, and ^{29}Si NMR ($CDCl_3$ solution, for **6g**) and IR spectra with those of **3a-c** and **3g**. The ^{13}C NMR spectrum of **3g** (Figure 1-(a)) displays five signals characteristic of 2-pyridone ring[2b,12] along with those of benzodisilacyclohexadiene rings.[3] The spectrum of

Table 1. The $Pt(CH_2{=}CH_2)(PPh_3)_2$-Catalyzed Reaction of **1** with **2a** (R^1 = $-(CH_2)_5-$, R^2 = $-(CH_2)_2O(CH_2)_2-$)[a]

cat / mol%	temp / °C	time / h	**3a** / %	**4a** / %
3	110	12	85[b]	14[b]
3	75	12	84[b]	15[b]
3	50	12	89[b]	10[b]
3	30	65	95[b]	3.6[b]
1[c]	30	12	94[d]	2[d]
0.2[c]	30	12	97[d]	2[d]

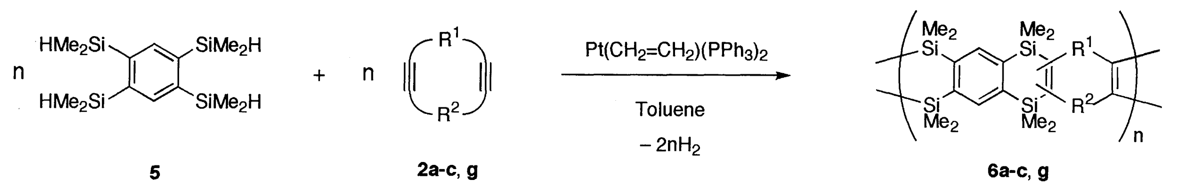
[a]Reaction conditions: **1**/**2a** = 3/1; solvent, toluene; under N_2. [b]Determined by GLC. [c]**1**/**2a** = 2.15/1. [d]**3a** and **4a** were isolated as a mixture. The ratio of **3a** to **4a** was determined by ^1H NMR.

Table 2. The $Pt(CH_2{=}CH_2)(PPh_3)_2$-Catalyzed Reaction of **1** with **2a-g**[a]

2	$-R^1-$	$-R^2-$	**3** / %[b]
2a	$-(CH_2)_5-$	$-(CH_2)_2O(CH_2)_2-$	94
2b	$-(CH_2)_5-$	$-(CH_2)_5-$	96
2c	$-(CH_2)_5-$	$-(CH_2)_6-$	91
2d[c]		$-CH_2OCH_2-$	18[d]
2e[c]			0
2f[c]	$-Me_2SiOSiMe_2-$	$-Me_2SiOSiMe_2-$	0
2g			91

[a]Reaction conditions: **1**/**2a** = 2.1-2.15/1; catalyst, 1 mol%; solvent, toluene; under N_2; 30 °C; 12-24 h. [b]Isolated yield as a mixture of **3** and **4**. The contents of **4** were ~2% in each case. [c]Catalyst, 3 mol%. [d]Isolated yield of **3d**.

Table 3. Platinum Complex-Catalyzed Polymerization of 1,2,4,5-Tetrakis(dimethylsilyl)benzene with Cyclic Diynes[a]



polymer	yield / %	$M_n/10^3$ (M_w/M_n)	Mp / °C	Td_5 / °C[b]	elemental analysis Calc C	Calc H	Found C	Found H
6a	99	3[c]	>300	390	65.25	8.92	65.44	8.93
6b	98	3[c]	>300	412	67.94	9.37	67.51	9.44
6c	98	—[c]	>300	403	68.43	9.50	68.44	9.57
6g	97	25(4.1)[d]	>300	402	74.85	10.61	74.01	10.57

[a] Reaction conditions: **5**/**2** = 1/1, 20-40 mM; catalyst, 0.4 mol%; under N_2; temperature and time, 30 °C (12 h), then 50 °C (4 h) and finally 110 °C (24 h). [b] Td_5 is 5 % weight loss temperature in TGA under He. [c] Estimated from IR spectra, see ref. 11. [d] Determined by GPC with the polystyrene standards in THF.

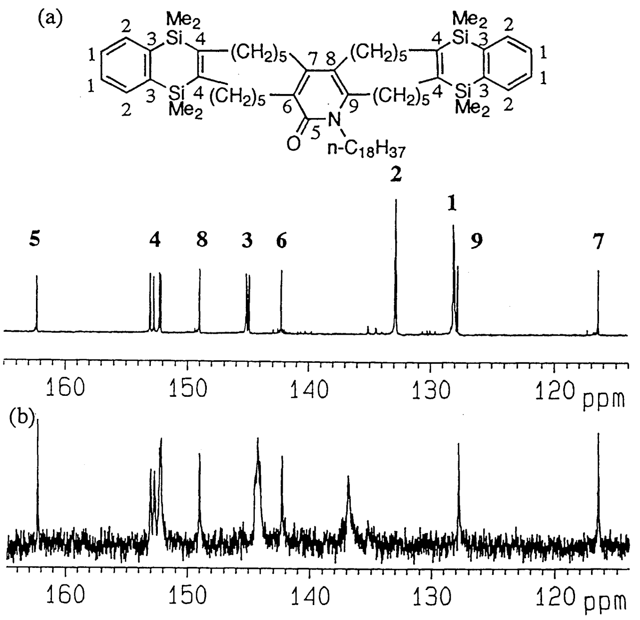


Figure 1. (a) ^{13}C NMR ($CDCl_3$) of the model compound **3g**. (b) ^{13}C NMR ($CDCl_3$) of the polymer **6g**.

6g (Figure 1-(b)) appears very similar to Figure 1-(a) except for the signals of carbons-1 and carbons-2 (the numbering are shown on the structure in Figure 1); in Figure 1-(b), there is no signal corresponding to carbons-1, and the signals corresponding to carbons-2 appears at lower field.

The present method provides a way to a variety of ladder polycarbosilanes by changing the structure of hydrosilane and cyclic diyne parts.

References and Notes

1 a) C. G. Overberger and J. A. Moore, *Adv. Polymer Sci.*, **7**, 113 (1970). b) L. Yu, M. Chen, and L. R. Dalton, *Chem. Mater.*, **2**, 649 (1990). c) A.-D. Schlüter, *Adv. Mater.*, **3**, 282 (1991).

2 Recent examples of ladder polymer synthesis: a) T. Tsuda, K. Maruta, and Y. Kitaike, *J. Am. Chem. Soc.*, **114**, 1498 (1992). b) T. Tsuda and H. Hokazono, *Macromolecules*, **26**, 5528 (1993). c) J. M. Tour and J. J. S. Lamba, *J. Am. Chem. Soc.*, **115**, 4935 (1993). d) M. Pollmann and K. Müllen, *J. Am. Chem. Soc.*, **116**, 2318 (1994).

3 M. Tanaka, Y. Uchimaru, and H.-J. Lautenschlager, *Organometallics*, **10**, 16 (1991); M. Tanaka and Y. Uchimaru, *Bull. Soc. Chim. Fr.*, **129**, 667 (1992).

4 Y. Uchimaru, P. Brandl, M. Tanaka, and M. Goto, *J. Chem. Soc., Chem. Commun.*, **1993**, 744.

5 J. Dale, A. J. Hubert, and G. S. D. King, *J. Chem. Soc.*, **1963**, 73.

6 Diyne **2g** was synthesized according to the procedure described in ref. 2b from diyne **2b** and octadecyl isocyanate.

7 A. Nissen and H. A. Staab, *Chem. Ber.*, **104**, 1191 (1971).

8 H. N. C. Wong and F. Sondheimer, *Tetrahedron*, **37**, 99 (1981).

9 H. Sakurai, K. Hirama, Y. Nakadaira, and C. Kabuto, *Chem. Lett.*, **1988**, 485.

10 To be published separately.

11 We assumed that the end groups of **6a-b** are consisted of mainly $Ar(SiMe_2H)_2$ groups and acetylene groups and that the ratio of the former and the latter was 1 to 1. Because the yields of **6a-b** were quantitative (≥98%), the average incorporation of **1** and **2** in **6a-b** should be near 1 to 1, and error arising from the above assumption is not so serious if the degree of polymerization is low. Upon the above assumption, the M_n was calculated through the estimation of the amount of the remaining $SiMe_2H$ groups by comparing the relative intensity of Si-*H* absorption (2150 cm^{-1}) to Si-*Me* absorption (1250 cm^{-1}) of **6a-b** with that of **5**. The M_n calculated for **6c** by this method is 8×10^3. But this value can contain a considerable error. For **6g**, the intensity of the Si-*H* absorption was too weak to apply this method.

12 L. E. Overman, S. Tsuboi, J. P. Roos, and G. F. Taylor, *J. Am. Chem. Soc.*, **102**, 747 (1980); J. H. Rigby and N. Balasubramanian, *J. Org. Chem.*, **54**, 224 (1989); T. Tsuda and H. Hokazono, *Macromolecules*, **26**, 1796 (1993).