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A New Method for Functionalization of Si-Si Bond-Containing Polymers by Insertion of Acetylenes into Polymer Backbones

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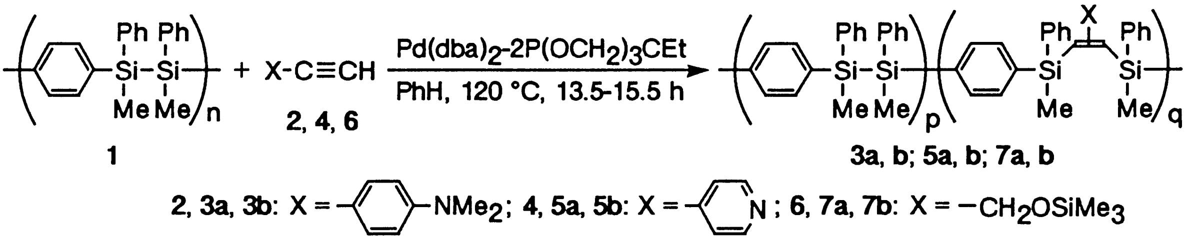
Partial insertion of functionalized acetylenes RC≡CH (R = 4-$Me_2NC_6H_4$, 4-pyridyl, Me_3SiOCH_2) into Si-Si bonds of a poly[p-(disilanylene)phenylene] (**1**) and poly(methylpropylsilylene) smoothly proceeded by $Pd(dba)_2$-$2P(OCH_2)_3CEt$ (dba = dibenzylideneacetone) catalyst. A modified polymer of **1** with a (4-dimethylaminophenyl)vinylene group showed higher conductivity than **1** when doped with iodine.

Recently increasing interests have been placed on organosilicon polymers for their intriguing physicochemical properties.[1)] To improve and/or control the properties, introduction of suitable functional groups has been recognized to be effective, although the methodology has been still limited to the side chains transformation.[2)] Meanwhile, we have recently disclosed that direct reconstruction of the backbones of Si-Si bond-containing polymers is achieved through insertion of acetylenes into Si-Si bonds by $Pd(dba)_2$-$2P(OCH_2)_3CEt$ catalyst.[3)] Here we report a successful application of the reaction to the introduction of functional groups into organosilicon polymers.

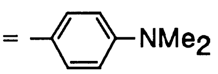
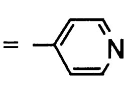
A mixture of poly[p-(1,2-dimethyl-1,2-diphenyldisilanylene)phenylene] (**1**, Mw 4.8 x 10^4, Mw/Mn 2.7, 0.2 mmol monomer unit),[4)] 4-ethynyl-N,N-dimethylaniline (**2**, 0.05 mmol), $Pd(dba)_2$-$2P(OCH_2)_3CEt$ (0.004 mmol Pd), and benzene (0.10 cm^3) was heated under nitrogen in a sealed tube at 120 °C for 13.5 h. The brown reaction mixture was dissolved in benzene, and a small amount of black insoluble powder, probably decomposed Pd catalyst, was removed by filtration. Addition of 2-propanol to the filtrate afforded a yellow solid. Washing with acetone and reprecipitation from benzene–2-propanol (twice) gave a pale yellow functionalized polymer (**3a**) with a [4-(N,N-dimethylamino)phenyl]vinylene group incorporated in the backbone (16% per a monomer unit) in 77% yield, Eq. 1 (Table 1).[5)]



(1)

The polymer **3a** showed almost the same shape of the GPC curve as **1**, and the average molecular weight of **3a** (Mw 4.4 x 10^4, Mw/Mn 2.7) was not so different from the predicted value (Mw 5.2 x 10^4, Mw/Mn 2.7), indicating no extensive degradation of the polymer having taken place during the reaction. In ^1H NMR of **3a**, the

Table 1. Reactions of poly[p-(1,2-dimethyl-1,2-diphenyldisilanylene)phenylene] (**1**) with acetylenes[a)]

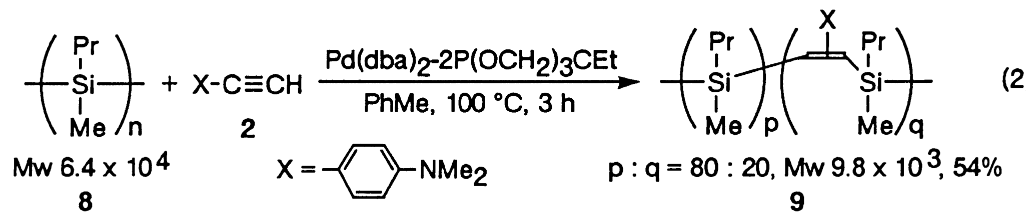
X-C≡CH	(mmol)	Modified polymers[b)] (p : q)	Yields[c)]/%	Mw (Mw/Mn)[d)]	Softening temp /°C
X = 	(0.05)	**3a** (16 : 84)	77	4.4×10^4 (2.7)	125-135
	(0.10)	**3b** (35 : 65)	79	3.9×10^4 (2.8)	130-145
X = 	(0.05)	**5a** (10 : 90)	88	4.2×10^4 (2.8)	125-140
	(0.10)	**5b** (19 : 81)	66	4.2×10^4 (3.0)	125-140
X = $-CH_2OSiMe_3$[e)]	(0.10)	**7a** (4 : 96)	90	3.6×10^4 (2.8)	105-125
	(0.80)	**7b** (62 : 38)	57	3.7×10^4 (2.3)	105-115

a) Reaction conditions: **1** 0.20 mmol monomer unit, acetylene 0.05-0.80 mmol, $Pd(dba)_2$-$2P(OCH_2)_3CEt$ 0.004 mmol Pd, PhH 0.10 cm^3, 120 °C, 13.5 h. b) Typical spectral data (**3a**, **5a**, **7a**) are listed in Ref. 5. c) Yields after purification by reprecipitations from PhH-2-PrOH or THF-2-PrOH. d) Determined by GPC with polystyrene standards. e) 15.5 h.

methyl proton signals of the =C-SiCH$_3$ moiety were observed at 0.05, 0.13, 0.34, and 0.39 ppm with almost equal intensity to each other. These chemical shift values indicate that the vinylene have cis geometry.[3)] In addition, the appearance of the four signals shows that both erythro and threo diastereomeric linkages are present to approximately the same extent (Fig. 1).[6)] Assignment of the four signals is based on the comparison of these chemical shift values with those of methyl signals of 1-phenyl-1,2-bis(methylsilyl)ethenes.[7)] On the other hand, the signal of the intact Si-SiCH$_3$ moiety appeared at 0.59 ppm (Fig. 2). Based on the integral ratio (B/A) of the former to the latter, the percentage of the modification of Si-Si bonds could be readily evaluated. In the present reaction, the extent of functionalization can be easily controlled by the amount of the charged acetylene; when a twice amount of **2** was used, the extent was approximately doubled to give **3b**.

The inserion of 4-ethynylpyridine (**4**) into the polymer **1** also proceeded to give modified polymers (**5a**, **b**)[5)] with incorporation of a (4-pyridyl)vinylene moiety (Table 1). Likewise, trimethylsiloxy substituent, which can be readily transformed to hydrophilic and reactive hydroxy group,[8)] could be introduced into **1** by using 3-trimethylsiloxy-1-propyne as an acetylene (**6**).

Furthermore, functionalization of a polysilane is also possible. Thus, when a toluene (0.2 cm^3) solution of poly(methylpropylsilylene) (**8**, Mw 6.4×10^4, Mw/Mn 3.1, 0.4 mmol monomer unit), **2** (0.2 mmol), and $Pd(dba)_2$-$2P(OCH_2)_3CEt$ (0.008 mmol Pd) was stirred under nitrogen at 100 °C for 3 h, a new polymer (**9**, Mw 9.8×10^3, Mw/Mn 3.0)[9)] with a [4-(N,N-dimethylamino)phenyl]vinylene group incorporated in the backbone (20% per a monomer unit) was obtained as a viscous oil after reprecipitation from benzene–2-propanol, Eq. 2.



(2)

Mw 6.4×10^4
8

p : q = 80 : 20, Mw 9.8×10^3, 54%
9

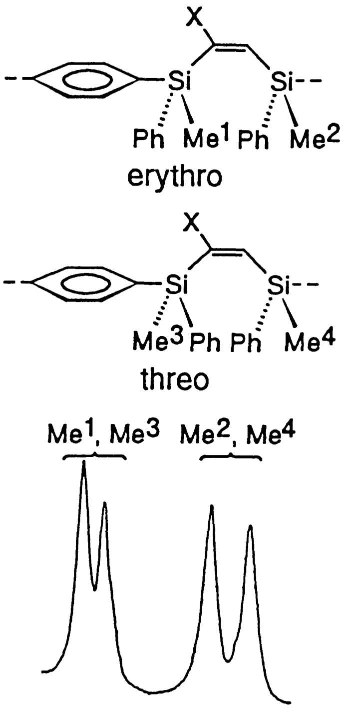


Fig. 1. Tentative assignment of =C-SiCH_3 in **3a**, **b**.

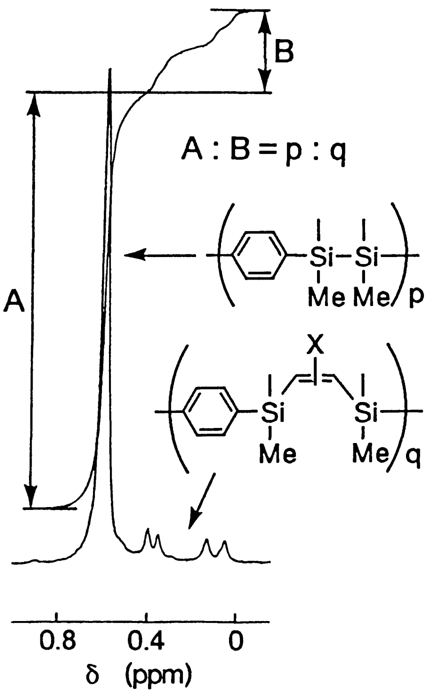


Fig. 2. Appearance of methyl proton signals of **3a**.

The modified polymer **9** showed UV absorption at nearly the same wavelength as the original polymer **8**, although with a little smaller ε value (in THF, λ_{max}, $\varepsilon_{monomer\ unit}$: **8**, 306 nm, 7.1 x 10^3; **9**, 304 nm, 4.6 x 10^3). Accordingly, **9** is supposed to retain characteristic properties similar to the starting polysilane.

Since Lewis basic functional groups are likely to interact with Lewis acidic compounds more preferably, the electric conductivities of the modified polymers **3** and **5** on exposure to acidic dopants are expected to be superior to that of the unmodified polymer **1**.[10)] Indeed, the conductivity of **3** doped with iodine proved to be about three times as high as that of **1**, although **5** showed almost the same conductivity as **1** (Table 2).

Table 2. Conductivity of modified polymers[a)]

Polymers	Conductivity/Scm^{-1}
1	3 x 10^{-4}
3a	1 x 10^{-3}
5b	4 x 10^{-4}

a) Conductivity of thin films (141-153 nm) doped with I_2 for 2.5-7 h in closed systems.

In conclusion, we demonstrate that the Pd(dba)$_2$-2P(OCH$_2$)$_3$CEt system-catalyzed insertion of functionalized acetylenes into Si-Si bonds provides a useful tool to introduce functional groups to, and hence, to control the properties of Si-Si bond-containing polymers. Further investigations on the extension to other polymers and unsaturated compounds as well as the detailed properties of the modified polymers are under way.

References

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

5) **3a**: ^{1}H NMR ($CDCl_3$): δ 0.05, 0.13, 0.34, 0.39 (each s, 6H, =C-$SiCH_3$), 0.59 (s, Si-$SiCH_3$), 2.69-2.90 (m, NCH_3), 6.37-6.59 and 6.88-7.06 (each m, NC_6H_4), 7.06-7.63 (m, SiC_6H_4, C_6H_5, =CH); IR (KBr): 1608 m, 1516 m, 1488 w, 1428 s, 1406 w, 1380 m, 1356 w, 1250 m, 1192 w, 1060 w, 1126 s, 1104 m, 1064 w, 1020 w, 1000 w, 948 w, 858 w, 784 s, 774 s, 736 s, 700 s, 676 m, 506 s, 468 m cm^{-1}; **5a**: ^{1}H NMR ($CDCl_3$): δ 0.12, 0.19, 0.34, 0.40 (each s, 6H, =C-$SiCH_3$), 0.59 (s, Si-$SiCH_3$), 6.80-6.92 and 8.19-8.33 (each m, NC_5H_4), 7.02-7.51 (m, C_6H_4, C_6H_5, =CH); IR (KBr): 1588 w, 1490 w, 1428 s, 1408 w, 1378 m, 1336 w, 1304 w, 1250 m, 1192 w, 1126 s, 1102 m, 1018 w, 998 w, 828 w, 784 s, 774 s, 736 s, 698 s, 676 m, 504 s, 470 m cm^{-1}; **7a**: ^{1}H NMR ($CDCl_3$): δ -0.09-0.00 (m, O-$SiCH_3$), 0.17-0.26 and 0.32-0.40 (each m, =C-$SiCH_3$), 0.59 (s, Si-$SiCH_3$), 4.02-4.13 (m, =C-CH_2), 7.07-7.42 (m, C_6H_4, C_6H_5, =CH); IR (KBr): 1488 w, 1428 s, 1406 w, 1378 m, 1336 w, 1302 w, 1250 m, 1192 w, 1126 s, 1102 s, 1064 w, 1018 w, 996 w, 878 w, 844 w, 784 s, 774 s, 734 s, 696 s, 684 m, 504 s, 470 m cm^{-1}.

6) The appearance of the rather wide-splitted four signals was previously postulated to originate from regioisomeric linkages of modified monomer units arising from non-selective insertion of arylacetylenes into neighboring Si-Si bonds.$^{3)}$ However, a modified polymer obtained by the insertion of phenylacetylene into poly[p-(*tetra*methyldisilanylene)phenylene], which does not have diastereomeric modified linkages, displayed a broad Si-Me signal within a narrow chemical shift range (0.17-0.29 ppm). This shows that the variance in chemical shift depending on the location of phenyl groups is rather small. Accordingly, we now consider that the appearance of the four signals is due to diastereoisomerism.

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9) **9**: Mw 9.8×10^3, Mw/Mn 3.0; ^{1}H NMR ($CDCl_3$): δ -0.05-0.46 (m br, $SiCH_3$), 0.53-1.15 (m br, $SiC\underline{H}_2CH_2C\underline{H}_3$), 1.15-1.60 (m br, $SiCH_2C\underline{H}_2$), 2.91 (br, NCH_3), 6.33-7.43 (m br, NC_6H_4, =CH); IR (neat): 1606 s, 1514 s, 1460 s, 1452 s, 1412 m, 1374 m, 1350 s, 1242 s, 1194 m, 1164 m, 1062 s, 998 m, 948 m, 816 s, 750 s, 714 m, 666 m cm^{-1}.

10) For the conductivity of **1** doped with SbF_5, M. Ishikawa, Y. Hasegawa, T. Hatano, A. Kunai, and T. Yamanaka, *Organometallics*, **8**, 2741 (1989); T. Hayashi, Y. Uchimaru, N. P. Reddy, and M. Tanaka, *Chem. Lett.*, **1992**, 647.

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