Ring-Opening Polymerization of 1,1,2,2-Tetramethyl-1,2-disilacyclopentane *via* Palladium Complex-Catalyzed Si-Si Bond Metathesis

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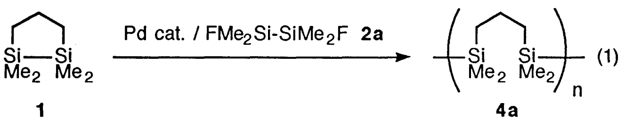
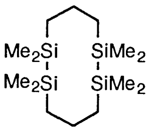
Ring-opening metathesis polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane was found to proceed in the presence of catalytic amounts of a Pd complex ($PdCl_2(dppb)$ or $PdCl_2(dbpb)$) and 1,2-difluoro-1,1,2,2-tetramethyldisilane to effectively give a high molecular weight polymer ($Mw > 3 \times 10^5$).

Current interest has been focused on Si-Si bond-containing polymers because of their unique physicochemical properties.[1] In this respect, development of new methodologies for their synthesis is highly desired. The metathesis reaction of Si-Si bonds has been long known.[2,3] To the best of our knowledge, however, the transition metal complex-catalyzed ring-opening metathesis polymerization (ROMP) of cyclic disilanes and cyclopolysilanes has not been well studied[4,5] despite its great potential. We now report that the transition metal complex-catalyzed ROMP of a cyclic disilane is highly promoted by addition of a catalytic amount of activated disilanes.

A mixture of 1,1,2,2-tetramethyl-1,2-disilacyclopentane **1** (0.5 mmol), 1,2-difluoro-1,1,2,2-tetramethyldisilane **2a** (0.05 mmol), and $PdCl_2(dppb)$ (0.005 mmol, dppb = 1,4-bis(diphenylphosphino)butane) was heated in a sealed glass tube at 100 °C for 15 h (Eq. 1). GPC analysis (polystyrene standards) of the reaction mixture revealed the formation of a polymer (monomodal, $Mw = 3.4 \times 10^5$, $Mw/Mn = 3.4$). By GC and GC-MS analyses for volatiles, the dimer **3** was detected in 5% GC yield (80% conversion of **1**; throughout the paper, yields are based on the conversion) along with 6% combined yield of several unidentified products and 70% recovery of **2a**. After removal of the Pd complex by means of a short Florisil column chromatography followed by evaporation of volatiles, the polymer **4a** was isolated in 85% yield (colorless gel, $Mw = 2.8 \times 10^5$, $Mw/Mn = 3.6$). The structure of **4a** was confirmed by ^1H-, ^{13}C-, and ^{29}Si-NMR, and IR. The use of $PdCl_2(dbpb)$ (dbpb = 1,4-bis(dibutylphosphino)butane) also gave a similar result (4% of **3**, 90% of **4a** ($Mw = 4.6 \times 10^5$, $Mw/Mn = 5.4$), 76% conversion of **1**). On the other hand, in the absence of the difluorodisilane **2a**, dimerization of **1** (89% yield of **3**, 44% conversion of **1**) mainly proceeded and only a trace of a polymer was formed ($Mw = 1.2 \times 10^6$, $Mw/Mn = 1.8$).

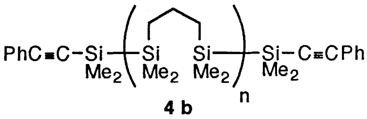


(1)

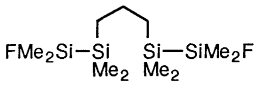


3

When 1,2-bis(phenylethynyl)-1,1,2,2-tetramethyldisilane **2b** was used[6] instead of **2a**, oligomers **4b**[7] and cyclic dimer **3** were obtained (61% and 37% yields, respectively, 56% conversion of **1**) along with a trace of a polymer ($Mw = 3.1 \times 10^5$, $Mw/Mn = 5.6$).



4 b



5 a

$PdCl_2(PPh_3)_2$ is known to catalyze the cross-metathesis between **1** and **2a** to give **5a**.[2,8] We believe that **5a** is the initial product in our reaction, and that the successive reactions between the resulting Si-Si bond activated by the fluorine substituent and the Si-Si bond of **1** take place to afford the polymer **4a**.

Further extension of the present procedure featured with the use of fluorodisilanes as promoters to polysilane synthesis is in progress.

References and Notes

1 For example, "Silicon-Based Polymer Science," ed by J. M. Zeigler and F. W. G. Fearon, Advances in Chemistry Series **224**, American Chemical Society, Washington, DC (1990).

2 K. Tamao, T. Hayashi, and M. Kumada, *J. Organomet. Chem.*, **114**, C19 (1976).

3 H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *J. Organomet. Chem.*, **131**, 147 (1977).

4 Kumada et al. very briefly reported that the treatment of 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane with a catalytic amount of $PdCl_2(PPh_3)_2$ formed non-volatile polymers without any characterization of the products; see ref. 2.

5 M. Suzuki, *Yuki Gosei Kagaku Kyokaishi*, **51**, 141 (1993), and the references cited therein.

6 The Pd-catalyzed Si-Si bonds metathesis between **1** and vinyl- or ethynyl-substituted disilanes was reported; see, ref. 3.

7 Oligomers **4b** displayed satisfactory ^1H-, ^{13}C-, and ^{29}Si-NMR, and IR spectral data. The Mn value based on ^1H-NMR was 1.2×10^3 while GPC indicated $Mn = 1.25 \times 10^3$ and $Mw/Mn = 1.4$. These Mn values correspond to the hexamer (n = 6); calcd $Mn = 1.21 \times 10^3$.

8 When $PdCl_2(PPh_3)_2$ was used under the present reaction conditions, dimer **3** was the main product.