# A Facile Preparation and Polymerization of 1,1-Difunctionalized Disiloxanes

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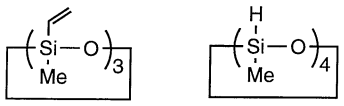
(Received March 11, 1996)

Novel 1,1-difunctionalized disiloxanes are synthesized by the alkylative cleavage of cyclic siloxane using several alkyllithiums followed by quenching with chlorosilanes. The prepared difunctionalized siloxanes are subjected to polyaddition through platinum catalyzed hydrosilylation.

Introduction of difunctionality onto the terminal silicon atom of oligo siloxanes has become of our considerable interest since the corresponding product would be converted, through polyaddition or polycondensation, to the polymers of novel structure with the terminal silicon atom incorporated into the polymer main chain.[1] Since we have been studying the syntheses and properties of the polymers containing siloxane moiety in the main chain as well as the side chain where the siloxane moiety has been used as the spacer or substituent,[2] incorporation of a part of silicon atom of the siloxane into the main chain of the polymer has been a center of our interest in connection with the properties of the resulting polymers. On the other hand, our recent synthetic study concerning the preparation of the functionalized siloxane compounds as monomers of the siloxane containing polymers has revealed that the cleavage of a cyclic dimethylsiloxane using several functionalized organolithium compounds leads to a variety of mono- or difunctionalized disiloxanes, tetrasiloxanes and oligosiloxanes respectively.[3] In addition, several functionalized cyclic siloxanes were also transformed to the corresponding disiloxanes through the similar cleavage reactions using an alkyllithium.[4] Therefore, the reaction of the functionalized organolithium reagent with the functionalized cyclic siloxane, if successful, would afford the disiloxane with 1,1-difunctionality after treatment of an appropriate silyl chloride and the resulting difunctionalized siloxane would be led to the corresponding polymer as illustrated in Scheme 1. Herein, we report the preparation of 1,1-difunctionalized disiloxanes and the polymerization of the compounds to give rise to the siloxane-containing polymers one of which silicon atom is incorporated into the polymer main chain.

When 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (**1a**)[5] is treated with 3 molar equivalents of vinyllithium, 1,1-divinylated disiloxane (**2a**) was obtained in 73% yield after quenching with chlorotrimetylsilane. The functionalized cyclic siloxane was similarly reacted with several functionalized organolithium reagents such as 2-furyl, 1-alkynyl, and allyl derivatives to yield the corresponding 1,1-difunctionalized disiloxanes after treatment with appropriate chlorosilanes respectively. It should be pointed out that the reaction of a cyclic siloxane bearing Si-H bond (**1b**)[5] also proceeded by vinyllithium[6] to give the 1,1-difunctionalized disiloxane (**2f**) bearing hydrido and vinyl groups. Results are summarized in Table 1.

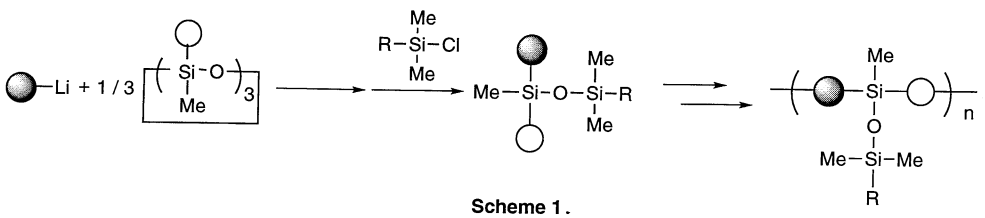


**1a** **1b**

The procedure for the synthesis of **2a** is representative: In order to prepare vinyllithium, butyllithium (10.0 mmol, as 2.5 M hexane solution) was added to a solution of tetravinyltin (2.5 mmol) in diethyl ether at 0 °C. After stirring the mixture at 0 °C for 30 min, the cyclic siloxane (**1a**, 3.3 mmol) was added to the resulting solution, and stirring was continued for 12 h at room temperature. The solvent was removed under reduced pressure to leave a crude oil to which diethyl ether (10 mL) and chlorotrimethylsilane (10.0 mmol) were successively added. White precipitates formed immediately, and the mixture was stirred at room temperature for 3 h. The precipitates were filtered, and the filtrate was concentrated to give an oily residue which was purified by trap to trap distillation under reduced pressure to afford the corresponding disiloxane in 73% yield.[7]

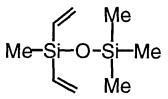
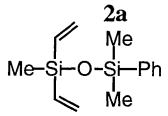
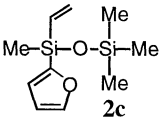
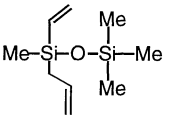
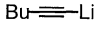
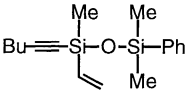
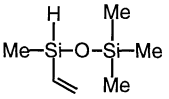
The disiloxanes modified with olefinic groups were subjected to polyaddition with a bifunctional hydrosilane. When the disiloxane (**2a**) was treated with 1,4-bis(dimethylsilyl)benzene (**3**) in the presence of a catalytic amount of the Lappert's platinum complex,[8] the polymer (**4**) was obtained after the reaction for 48 h at room temperature.[9] The molecular weight and the molecular weight distribution of **4** were found to be $Mn$ = 11000, $Mw/Mn$ = 3.9 respectively by GPC analysis.[10] Structure of this polymer is interesting in a sense that a half of the silicon atoms of the disiloxane was incorporated into the polymer main chain, hence the novel character including thermal properties may be anticipated. Details on the characterization of the polymer will be described in due course. The siloxane (**2f**) possessing an olefinic moiety as well as a hydrido group on the same silicon atom also polymerized in the presence of the platinum catalyst,[8] to yield the corresponding homopolymer (**5**) ($Mn$ = 1100, $Mw/Mn$ = 1.4).[10, 11]

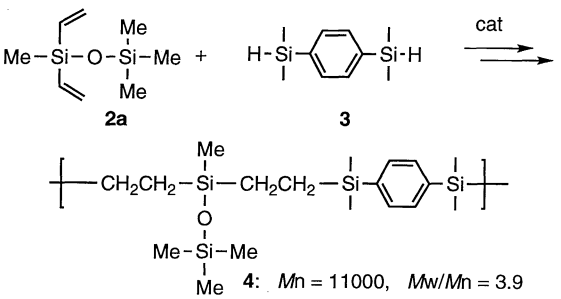
In short, the disiloxanes having two functional groups on one of the silicon atom were synthesized by the cleavage of functionalized cyclic siloxanes (**1a** and **1b**). The siloxanes,



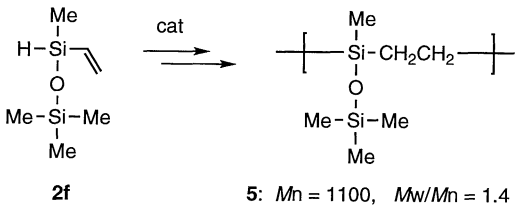
**Scheme 1.**

**Table 1.** Syntheses of 1,1-difunctionalized disiloxanes

| RLi | Siloxane | $RMe_2SiCl$ | Product | Yield (%) |
|---|---|---|---|---|
|  | **1a** | $Me_3SiCl$ |  **2a** | 73 |
| | | $PhMe_2SiCl$ |  **2b** | 89 |
|  | | $Me_3SiCl$ |  **2c** | 80 |
|  | | $Me_3SiCl$ |  **2d** | 75 |
|  | | $PhMe_2SiCl$ |  **2e** | 87 |
|  | **1b** | $Me_3SiCl$ |  **2f** | 65 |







thus obtained, homo- and copolymerized to afford the corresponding novel polymers.

This work was partially supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 07750968) from the Ministry of Education, Science, Sports and Culture, Japan.

## References and Notes

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4 K. Shintani, Y. Soga, A. Mori, and Y. Kawakami, unpublished results.

5 Available from ShinEtsu Chemical Co. Ltd. The authors are grateful for kind donation of these reagents.

6 *Four* molar equivalents of alkyllithium were required to cleave the cyclic *tetra*siloxane. The reaction was carried out at -30 °C to avoid undesireble side reaction.

7 $^1$H NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 9H), 0.21 (s, 3H), 5.76 (dd, 2H, $J$ = 5.5, 19.0 Hz), 5.99 (dd, 2H, $J$ = 5.5, 14.7 Hz), 6.14 (dd, 2H, $J$ = 19.0, 14.7 Hz); $^{13}$C NMR (50.3 MHz, $CDCl_3$): δ -1.3, 2.0, 132.8, 137.9; IR (neat): 3054, 2959, 1595, 1406, 1254, 1059, 843, 787, 754 cm$^{-1}$.

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9 M. Tsumura, T. Iwahara, and T. Hirose, *Polym., J.*, **27**, 1048 (1995); P. R. Dvornic and V. V. Gerov, *Macromolecules*, **27**, 1068 (1994); P. R. Dovornic, V. V. Gerov, and M. N. Goverdarica, *Macromolecules*, **27**, 7575 (1994).

10 Based on polystyrene standard. The consumpsion of the monomers and the structures of obtained polymers were confirmed by $^1$H and $^{13}$C NMR.

11 Although the polymerization condition was not fully optimized, the reaction of **5** (hydrosilylation between siloxy olefin and siloxy silane) seems less reactive. Hydrosilylation polymerizations using monomers bearing olefin and hydrosilane: K. Shintani, Y. Soga, A. Mori, and Y. Kawakami, Abstract: The Society of Polymer Science, Japan, Hokuriku regional meeting A-23 (1995); Y. Pang, S. Ijadi-Maghsoodi, and T. J. Barton, *Macromolecules*, **26**, 5671 (1993); T. Hayashi, S. Itsuno, K. Ito, and S. Yue, *Polym. Prepr., Jpn.*, **44**, 229 (1995).