A Facile Synthesis of Disiloxanes with Functional Groups

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A facile synthetic method to obtain mono and difunctionalized disiloxanes, which can be used as various monomers for speciality polymers is described. The ring-opening of cyclic siloxanes with functionalized organometallic reagents followed by quenching with a variety of silyl chlorides gives the functionalized disiloxanes in good to excellent yields.

Disiloxane segment in main chain or side chain of macromolecular compound has been shown to play an important role in the field of materials science. In a gas permeable membrane based on polystyrene derivative as well as a sidechain liquid crystalline polymers, for example, introduction of the siloxane segment to these molecular structures exhibited striking effects.[1, 2] Despite considerable significance of the introduction of siloxane segment into such polymeric compounds, chemistry of siloxane has rarely been studied. A facile synthetic method for the disiloxanes with functional group(s) is of great interest and importance in the aspect of not only polymer chemistry but also synthetic organic chemistry. Cyclic trisiloxanes and tetrasiloxanes are known to be cleaved by excess alkyllithiums to give the corresponding lithium trialkylsilanolate.[3] The reaction of hexamethylcyclotrisiloxane (D_3) with 3 equiv of methyllithium, for example, affords lithium trimehylsilanolate, which can be converted to hexamethyldisiloxane after treatment with trimethylsilyl chloride.[3] Thus, we intrigued that ring-opening of a cyclic siloxanes with a functionalized organometallic reagent could afford the silanolate, which was lead to the corresponding difunctionalized disiloxanes via a treatment of the silyl chlorides with a second functional group as illustrated in Scheme 1. We herewith wish to report a facile synthesis of disiloxanes with functional groups by the way described above, which can be used as a monomers to construct a variety of macromolecular structures.

A representative synthetic procedure for the difunctionalized disiloxane is described as a synthesis of 1-hexynylpentamethyldisiloxane. To a solution of 1-hexynyllithium (30 mmol), which was prepared by the reaction of 1-hexyne with butyllithium, in 19 mL of THF was added a THF solution of D_3 (10 mmol / 5 mL) at 0 °C. The mixture was then stirred under reflux for 4 h. After cooling to room temperature, the reaction was quenched by the addition of Me_3SiCl (60 mmol). Removal of excess Me_3SiCl and THF left a colorless oil along with lithium chloride as a white precipitate which was removed by filtration. After the solid was washed with hexane repeatedly, concentration of the combined filtrate under reduced pressure left an oil which was distilled to yield the disiloxane (70%) as a colorless liquid.[4] As shown in Table 1, the corresponding alkynyl dimethylsilanolate was quenched using several silyl chlorides such as trimethylsilyl, phenyldimethylsilyl, t-butyldimethylsilyl and dimethylsilyl to give a variety of disiloxanes with (a) functional group(s). Although the yields represented in the Table were dispersed because of the efficiency during the distillation procedure, most reactions proceeded quantitatively to give the corresponding functionalized disiloxanes irrespective of the organolithium species employed.

Several organolithium compounds were similarly allowed to react with D_3 to give the corresponding lithium silanolate, followed by treatment with silyl chlorides to yield the disiloxanes in good yields, which were also shown in Table 1. It should be pointed out that the reaction of D_3 with lithiated biphenyl derivative which can be a mesogenic group of liquid crystalline materials followed by quench of silyl chlorides with polymerizable functional groups afforded the disiloxanes. The compounds can be polymerized to give the side chain liquid crystalline polymers.

In short, the reaction of cyclic siloxanes by organometallic reagents with a functional group led to lithium silanolate, which was quenched with various silyl chlorides to yield a wide variety of disiloxanes. The method, reported here, opened a facile synthetic route to disiloxanes with functional groups, which could be useful as monomers to introduce siloxane segment into macromolecular architecture.[5] The syntheses of the polymers by these disiloxane compounds will be described elsewhere in due course. And studies to elucidate the mechanism are now in progress.

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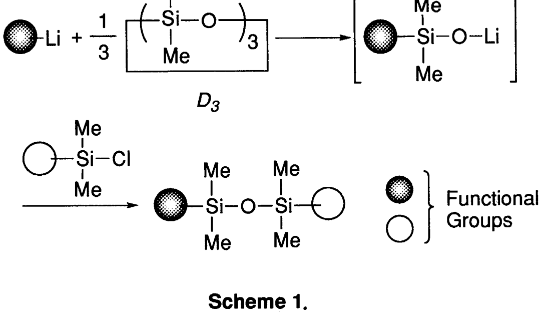


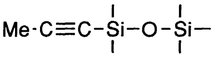
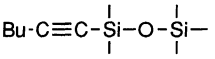
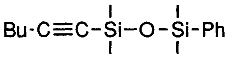
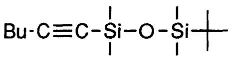
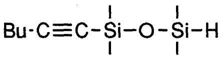
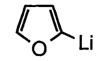
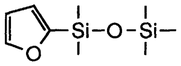
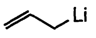
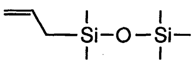
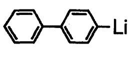
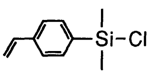
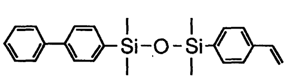
Scheme 1.

References and Notes

1 For gas permeable membranes: (a) Y. Kawakami, T. Aoki, H. Hisada, Y. Yamamura, and Y. Yamashita, *Polym. Comm.*, **26**, 133 (1985); (b) Y. Kawakami, H. Karasawa, T. Aoki, Y. Yamamura, H. Hisada, and Y. Yamashita, *Polymer J.*, **17**, 1159 (1985); (c) Y. Kawakami and T. Sugisaka, *J. Memb. Sci.*, **50**, 189 (1990).

2 For side chain liquid crystalline polymers: H. Inoue, Y. Soga, A. Mori, and Y. Kawakami, *Polym. Prep. Jpn.*, **43**, 1132 (1994); Y. Kawakami, K. Toida and Y. Ito, *Macromolecules*, **26**, 1177 (1993); Y. Nagase, T. Saito, H.

Table 1. Synthesis of disiloxanes by functionalized alkyllithiums, D_3 and silylchlorides[a]

R^1Li	Silylchloride	Product	Yield (%)[b]
Me-C≡C-Li	Me_3SiCl	 $\mathrm{Me{-}C{\equiv}C{-}Si{-}O{-}Si{-}}$	59
Bu-C≡C-Li	Me_3SiCl	 $\mathrm{Bu{-}C{\equiv}C{-}Si{-}O{-}Si{-}}$	70
Bu-C≡C-Li	$PhMe_2SiCl$	 $\mathrm{Bu{-}C{\equiv}C{-}Si{-}O{-}Si{-}Ph}$	91
Bu-C≡C-Li	t-$BuMe_2SiCl$		45
Bu-C≡C-Li	HMe_2SiCl	 $\mathrm{Bu{-}C{\equiv}C{-}Si{-}O{-}Si{-}H}$	71
	Me_3SiCl		82
	Me_3SiCl		77
			>99[c]

[a]Reactions were carried out 1.0 equiv of a lithium reagent, 0.33 equiv of D_3 amd 1.0-2.0 equiv of a silylchloride. [b]Isolated yield by distillation unless specified. [c]Purified by column chromatography on silica gel.

Abe., Y. Takamura, *Macromol. Chem. Phys.*, **195**, 263 (1994); Y. Nagase and Y. Takamura, *Makromol. Chem.*, **193**, 1225 (1992).

3 J. G. Frye, R. M. Salinger, F. W. Fearon, J. M. Klosowski, T. Deyoung, *J. Org. Chem.*, **35**, 1308 (1970). See also: ref. 1(a); S. M. Sieburth and L. Fensterbank, *J. Org. Chem.*, **58**, 6314 (1993); S. M. Sieburth and W. Mu, *J. Org. Chem.*. **58**, 7584 (1993).

4 Bp 170 °C (760 Torr); IR (neat) 2961, 2936, 2904, 2876, 2177, 1595, 1255, 1055 cm^{-1}; ^1H NMR (300 MHz, CDCl3) d = 2.23 (2H, t, J = 6.9 Hz), 1.35-1.57 (4H, m), 0.92 (3H, t, J = 7.2 Hz), 0.19 (6H, s, $Si(CH_3)_2$), 0.12 (9H, s, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 106.56, 84.39, 30.56, 21.88, 19.36, 13.53, 2.47, 1.76.

5 For example: T. Masuda and T. Higashimura, *Adv. Polym. Sci.*, **81**, 121 (1986); R. Asami, J.-i. Oku, M. Takeuchi, K. Nakamura and M. Takaki, *Polym. J.*, **20**, 699 (1988) and references therein.