Polysilane Synthesis by Catalytic Disproportionation of Alkoxydisilanes with Organolithium Reagents

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(Received September 21, 1994)

Network polysilanes with various substituents have been prepared by a disproportionation reaction of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane with a small amount of organolithium reagents. Aromatic dilithio compounds lead to incorporation of aromatic bridges into the network polysilanes, which show relatively higher electroconductivity by iodine doping. It seems that lithium ethoxide catalyzes the polymerization.

Polysilanes are interesting research targets due to their unusual electronic and optical properties. They are expected to be used as ceramic precursor, photoinitiator, photoconducter, photoresist, nonlinear optical material, *etc.*[1] Although the Wurtz-type coupling of organohalosilanes is usually applied to preparation of polysilanes, it has some limitations: *i.e.* difficulty in a control of the polymer molecular weight distribution, restriction of bearing substituents, difficulty in substituents sequence control, formation of great mass of salt, *etc.* So, many alternative methods were investigated: *i.e.* dehydrogenative coupling of hydrosilanes,[2] ring-opening polymerization of cyclic oligosilanes,[3] anionic polymerization of masked disilenes,[4] *etc.*

For practical use of polysilanes as functional materials, not only structural optimization but also economical preparation of them is required. We are investigating low cost preparation methods of functional polysilanes. Catalytic disproportionation reaction of disilanes is one of candidates for them. The disilanes are readily available from by-products in the industrially operated direct synthesis of chloromethylsilanes.

Baney, *et al.* obtained polycyclic polysilanes by disproportionation of chloromethyldisilanes catalyzed by Bu_4PCl at 250 °C.[5] Disproportionation of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane catalyzed by sodium methoxide was studied by Nagai, *et al.* to give cyclic or linear oligosilanes at moderate temperature.[6] Watanabe, *et al.* recently published a synthesis of network methyl polysilanes by this method.[7]

Previously, we reported incorporation of substituents into network methyl polysilanes, by the disproportionation reaction of alkoxymethyldisilanes, in the presence of organoalkoxysilanes.[8] Here, we present an alternative method of substituents incorporation into network polysilanes by the disproportionation reaction of alkoxymethyldisilanes with a small amount of organolithium reagents (Eq. 1). By this method, substituents are introduced from organic halides by one-pot reactions.

$$\underset{\mathbf{1}}{Me(EtO)_2SiSi(OEt)_2Me} \xrightarrow{RLi} \underset{\mathbf{2}}{(Me, EtO, R)\ \text{polysilane}} \qquad (1)$$

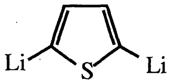
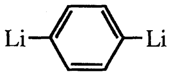
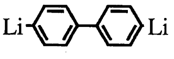
Disproportionation reaction of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane (**1**) was carried out to give phenylated ethoxymethylpolysilane in the presence of a catalytic amount of phenyllithium. In a typical experiment, 0.42 ml of 1.78 M phenyllithium solution in cyclohexane / diethyl ether (7/3) (0.75 mmol) was added into 2 g of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane (**1**, 7.5 mmol) in THF (5 ml) at room temperature. Then the reaction mixture was heated to 100 °C and maintained the condition for 20 h under nitrogen atmosphere. The reaction mixture turned yellow with the heating. After the complete disappearance of the disilane was confirmed by GC, insoluble lithium salt was filtered off and the filtrate was added to 100 ml of absolute methanol. Subsequent filtration of precipitated solid and drying in vacuo gave 180 mg of white powder. ^{29}Si NMR ($CDCl_3$, δ) -70.1, -65.9, -57.9, -21.9. ^{1}H NMR ($CDCl_3$, δ) -0.1 – -0.9 (broad s), 1.2 (t), 3.7 (q), 7.3 (m). IR (neat, cm^{-1}) 2980, 2900, 1400, 1232, 1065, 1015, 760. In cases that solids were not precipitated, the methanol solutions were concentrated at 150 °C under reduced pressure to give polymeric products by removing by-produced

Table 1. Disproportionation Reactions Initiated by Organolithium Reagents

RLi	Amount (mol eq.)	Reaction Temp./°C	Reaction Time/h	Yield/mg[a]	Mw (Mw/Mn)[b]	Me/EtO/R[c]
PhLi	0.1	100	20	180	72000 (1.29), 11000 (2.08)[d]	66/29/5
PhLi	0.3	100	20	220	18000 (3.74)	78/12/10
PhLi	0.5	100	20	500	12000 (2.51)	75/13/12
MeLi	0.02	100	10	167	12800 (3.51)	80/20
MeLi	0.10	100	10	140	3500 (1.18)	86/14
MeLi	0.15	100	10	710	1220 (1.24)	75/25
BuLi	0.1	100	10	280	2100 (1.27)	61-a/39/a[e]
Ph_3SiLi	0.1	100	20	400	14400 (3.96)	91/8/1

[a] Isolated yield starting from 2.0 g of **1**. [b] Measured by GPC (vs. polystyrene standards). [c] Ratios of substituents on the silicon atom determined by ^{1}H NMR. [d] Two peaks were observed. [e] Signals of Me and Bu could not be separated in the ^{1}H NMR.

Table 2. Disproportionation Reactions Initiated by Dilithio Compounds

RLi	Amount (mol eq.)	Yield/mg[a]	Mw (Mw/Mn)[b]	Me/EtO/R[c]
	0.05	240	79800 (1.28), 11600 (2.17)[d]	85/13/2
	0.1	640	4000 (1.89)	75/18/7
	0.1	600	75800 (1.24), 10600 (3.15)[d]	80/14/6

Reactions were carried out at 100 °C for 20 h after the addition of **1** into the dilithio reagents.
[a] Isolated yield starting from 2.0 g of **1**. [b] Measured by GPC (vs. polystyrene standards). [c] Ratios of substituents on the silicon atom determined by ^{1}H NMR. [d] Two peaks were observed.

ethoxymethylsilanes.

The reactions also proceeded by using other organolithium reagents to give substituted methylpolysilanes. The results are shown in Table 1. Molecular weights of obtained polysilanes were decreased with the increase of added organolithium reagent. UV-VIS absorption spectra of those polysilanes tailed to 380 - 400 nm and indicated a network polysilane framework.[9]

By the use of dilithio reagents prepared from appropriate organic dibromides and butyllithium, network polysilanes with aromatic bridges were obtained. The results are listed in Table 2. Remarkable shifts of the UV-VIS absorption bands were not observed by the introduction of an aromatic bridge into the polysilanes.

Thin films were prepared from those network polysilanes by the use of spin coating technique. After iodine doping, films prepared from network polysilanes with the aromatic bridges indicated three orders higher electroconductivity, 10^{-4} S/cm, compared with those of network polysilanes without the bridges.

It seems that the disproportionation is catalyzed by lithium ethoxide, which is formed by the reaction of organolithium reagents with ethoxydisilanes. Only methylation of disilane was observed during the reaction of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane (**1**) with methyllithium at low temperature (-78 °C), as shown by the GC measurement. In that time, polysilanes were not obtained.

As a result, we describe that the disproportionation reaction of alkoxydisilanes by a small amount of organolithium reagents is a very convenient method for introduction of substituents into network methylpolysilanes, especially aromatic bridges. We also showed that molecular weight of network polysilane can be controlled easily by the amount of added organolithium reagents in the reaction. This preparation method is useful for practical manufacturing of polysilane materials.

This work was performed by Toshiba Silicone Co., Ltd. under the management of Japan High Polymer Center as a part of Industrial Science and Technology Frontier Program supported by New Energy and Industrial Technology Development Organization.

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