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Dehydrogenative Condensation of Hydrosilanes Catalyzed by an Organoneodymium Complex

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Dehydrogenative condensation of trihydrosilanes is catalyzed by $(C_5Me_5)_2NdCH(SiMe_3)_2$ to give polysilanes in high yields. In the polymerization of $PhSiH_3$, molecular weight of the polymer becomes higher with an increase of the reaction temperature. Cyclic structures are indicated for oligomers larger than pentamers by FD-MS spectroscopy.

Polysilanes represent a new class of polymers with the Si-Si backbone. They are expected to be utilized as preceramics, photoresists, conducting polymers, photoconductors, nonlinear optical materials, photopolymerization catalysts, thermochromic materials, *etc.*[1)] However, since the synthetic method for polysilanes is almost limited to the Wurtz-type coupling of organodichlorosilanes with sodium metal, an alternative and controllable process for polysilanes under mild conditions has been strongly desired. Anionic polymerization of masked disilenes,[2)] electroreductive condensation of dichlorosilanes,[3)] and dehydrogenative condensation of polyhydrosilanes catalyzed by metal complexes[4)] are examples of promising approaches. Here we wish to report a condensation of trihydrosilanes catalyzed by an organoneodymium complex.

Recently, we have reported the hydrosilylation of olefins with polyhydrosilanes catalyzed by an alkyl- or hydridoneodymium complex.[5)] In the hydrosilylation of styrene with phenylsilane, a small amount of trisilane, $PhH_2SiSiPhHSiPhH_2$, was formed as a by-product. Hence, we investigated the dehydrogenative condensation of hydrosilanes utilizing $(C_5Me_5)_2NdCH(SiMe_3)_2$ as a catalyst (Eq. 1). In a typical experiment, $PhSiH_3$ (1 cm^3, 8.1 mmol) was added to the catalyst (0.01 mmol) in a glass autoclave and was heated at 80 °C for 48 h. Remaining $PhSiH_3$ was analyzed by GC using an internal standard after the dissolution of the reaction mixture in THF. The polymers were characterized by GPC, IR, NMR, and MS.

$$\mathrm{RSiH_3} \xrightarrow{\mathrm{Cp^*{}_2NdCH(SiMe_3)_2}} \mathrm{Polysilane} + \mathrm{H_2} \qquad (1)$$

The results are summarized in Table 1. Although the polymerization of phenylsilane took place even at room temperature, the reaction was slow and the product was oily after 15 d. The polymerization was effectively accelerated by heating. The reaction at 80 °C for 2 d gave a sticky gum.[6] GPC revealed a monomodal molecular weight distribution (Mw = 780 relative to polystyrene standards). The ^{1}H NMR spectrum (C_6D_6) showed complicated broad Si-H signals consisting of major signal tops at δ 4.47, 4.71, 4.95, and 5.02 ppm. Although it is premature to assign the each signal top, Harrod et al. has proposed that the higher field massif is due to $-SiH_2Ph$ moieties and that the lower is arising from -SiHPh- units for the poly(phenylsilane) formed with Cp_2TiMe_2.[7] The intensity ratio of the total Si-H to the phenyl protons was close to 5 (5.6, uncorrected for $C_6H_nD_{n-6}$ contaminants in the NMR solvent), indicative of major components of the product polymer being cyclic (*vide infra*). The reaction at 130 °C yielded a solid which melted at 60-70 °C. The absorbance ratio of SiH_2 bending (910 cm^{-1}) to Si-H stretching (2090 cm^{-1}) is reported to be diagnostic of polysilanes structures.[7] The ratio for the present solid polymer was 0.38 which was smaller than 0.47 reported for the linear octamer. This is in good agreement with the Mw being 16.0×10^2. However, the lower ratio is also explainable by the cyclic structure. The GPC analysis of the product exhibited a bimodal distribution; the molecular weight at the peak tops were 870 and 560. A polymer of still higher Mw (4830) was obtained by further raising the reaction temperature to 160 °C. The polymer was also bimodal with a larger proportion of the higher Mw component as compared with the product formed at 130 °C.

The polymerization of *n*-hexylsilane was slower as compared with that of phenylsilane. The molecular weight of the resulting oil was 530 after 2 d at 80 °C. The structures of the oligomers, $n\text{-}C_6H_{13}SiH_2\text{-}((n\text{-}C_6H_{13})SiH)_n\text{-}SiH_2(n\text{-}C_6H_{13})$ (n = 0, 1, 2), were confirmed by high resolution GC-MS. The tetramer consists of two isomers which presumably correspond to the *meso*- and *dl*-forms resulting from the two chiral silicon atoms.[8] The molecular weight did not become so high even at 160 °C (Mw = 950), although the catalyst was still alive as judged from the characteristic green color of organoneodymium complexes.

Table 1. Neodymium-catalyzed polymerization of hydrosilanes[a)]

Silane	Cat.[b)]	Conditions	Product	Mw/10^2 [c)]	Mw/Mn[c)]
$PhSiH_3$	NdR	room temp, 15 d	oil	5.2	1.26
$PhSiH_3$	NdR	80 °C, 2 d	gum	7.8	1.37
$PhSiH_3$	NdCl	80 °C, 2 d	no reaction		
$PhSiH_3$	NdR	100 °C, 2 d	gum	9.9	1.54
$PhSiH_3$	NdR	130 °C, 2 d	solid	16.0	1.91
$PhSiH_3$	NdR	130 °C, 2 d			
		and 160 °C, 7 d	solid	48.3	3.09
n-$C_6H_{13}SiH_3$	NdR	80 °C, 2 d	oil	5.3	-
n-$C_6H_{13}SiH_3$	NdR	160 °C, 13 d	oil	9.5	1.25

a)Reaction conditions: silane 1.0 cm^3, catalyst 0.01 mmol. Except the reaction with NdCl, conversions of the starting silanes were almost 100%. b)NdR: $(C_5Me_5)_2NdCH(SiMe_3)_2$. NdCl: $[(C_5Me_5)_2NdCl_2]Li\text{-}(Et_2O)_2$. c)Determined by GPC using polystyrenes as standards.

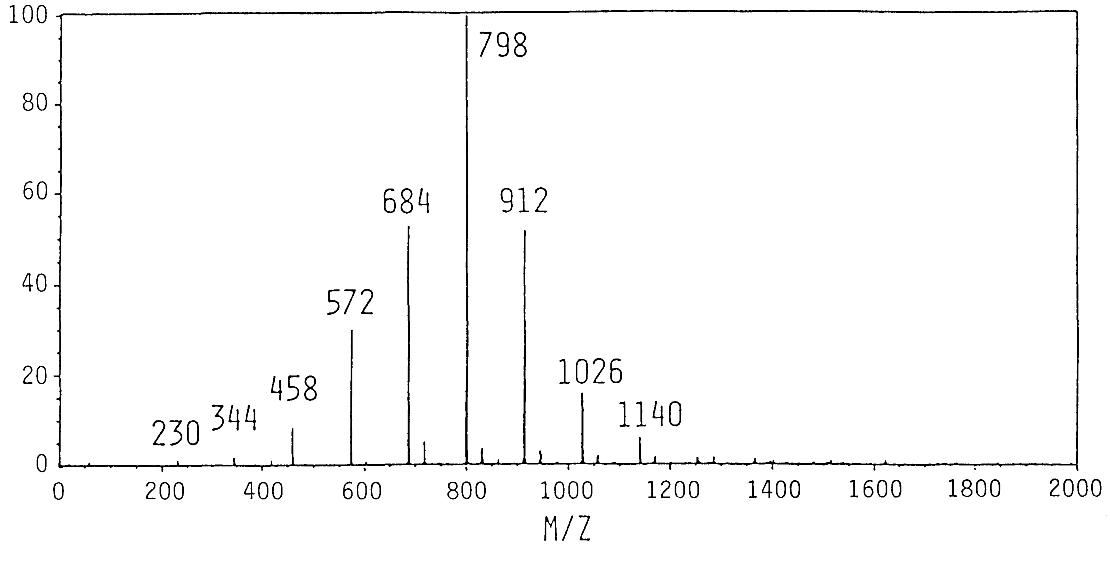

Fig. 1. Field desorption mass spectrum of poly(*n*-hexylsilane) synthesized *via* neodymium-catalyzed dehydrogenation of *n*-hexylsilane at 160 °C. Mass numbers were omitted below decimal points.

FD-MS spectra of the polysilanes obtained from phenyl- or *n*-hexylsilane suggested cyclic structures for the oligomers larger than pentamer (Fig. 1), while the molecular weights of the dimer to the pentamer corresponded with the linear structures. Cyclic structures were also reported for poly(*n*-butylsilane)s synthesized from *n*-$C_4H_9SiH_3$ by the catalysis of Cp_2ZrMe_2.[8,9]

In summary, this paper discloses the first example of lanthanoid-catalyzed dehydrogenative condensation of hydrosilanes. Utilization of other organolanthanoid complexes and other hydrosilanes are now in progress.

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