A New Polycondensation Process for the Preparation of Polysiloxane Copolymers

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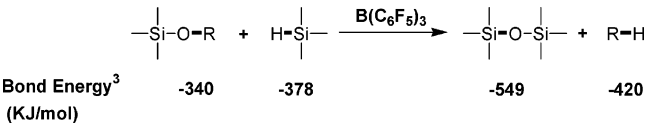
Introduction. Linear siloxane polymers and copolymers are prepared by two general methods: ring-opening polymerization of cyclic organosiloxanes and polycondensation of difunctional organosilanes or oligosiloxanes.[1−3] The ring-opening polymerization is very efficient and widely used to produce siloxane homopolymers and random copolymers.[1,2] The polycondensation is more suitable for preparation of well-defined copolymers. Dehydrogenative coupling of organosilanols with organohydrosilanes is particularly convenient due to its high selectivity. In addition, the byproduct, hydrogen, is easily removed from the reaction mixture. The dehydrogenative coupling is catalyzed by transition metal complexes such as platinum, rhodium, ruthenium, and palladium and has been employed in the synthesis of several well-defined copolymers.[4−7] Unfortunately, this reaction requires relatively high concentration of precious metals (0.1 mol %), and only moderate molecular weight copolymers have been obtained. Moreover, silanol self-condensation may accompany this process, leading to disruption of the desirable perfectly alternating architecture.

Tris(pentafluorophenyl)borane, $[B(C_6F_5)_3]$ (**1**), has been known since the early 1960s,[8] but its importance in organic synthesis has been recognized in the past two decades. It is a remarkably stable Lewis acid with strength comparable to BF_3.[9] Compound **1** has found many important applications; as a coactivator of metallocene initiators in olefin polymerization,[10] as a catalyst for allylstannylation of aldehydes,[11] and for Diels−Alder reactions.[12] Recently, **1** has been described as a catalyst for a number of reactions involving organohydrosilanes including reduction of oxygenated compounds.[13−15] Borane **1** has been also employed as a catalyst for the condensation of silanol-stopped polysiloxanes and organohydrosiloxanes.[16] The patented process leads to a rapid formation of a siloxane network and release of hydrogen as the byproduct.

In this paper we report the facile condensation reaction between organohydrosilanes and organoalkoxysilanes that leads to the formation of siloxane bond and releases alkane as an inert byproduct (Scheme 1). This reaction requires catalytic amounts of **1** and takes place under mild conditions (ambient temperature or below). As such, the new process provides a versatile tool for preparation siloxane polymers and copolymers.

Experimental Section. a. Materials. All reagents were used as received. 1,4-Bis(dimethylsilyl)benzene (**2**), diphenyldimethoxysilane (**3**), and anhydrous toluene were purchased from Aldrich. 4,4′-Bis(dimethylsilyl)-diphenyl ether (**4**), methylphenyldimethoxysilane (**5**), diphenylsilane (**6**), and dimethyldimethoxysilane (**7**) were purchased from Gelest. 1,4-Bis(dimethylmethoxysilyl)benzene (**8**) was prepared from **2** and methanolic sodium methoxide. Tris(pentafluorophenyl)borane (**1**) was purchased from Aldrich or Boulder Scientific Co.

Scheme 1. Condensation Reaction of Alkoxysilanes and Organohydrosilanes



b. Instrumentation. ^{1}H NMR spectra were acquired on a Bruker Avance 400 spectrometer; ^{29}Si NMR spectra were acquired on Omega 500 spectrometer operating at 99.35 MHz. Gel permeation chromatography was carried out on a MetaGel 300 × 7.8 linear column eluted with chloroform containing 1% isopropyl alcohol at a flow rate of 1.0 mL/min. Molecular weights were calibrated against polystyrene standards. Nonisothermal DSC experiments were performed with a TA Instruments Q100 using heating cycle from −80 to 100 °C at 10 °C/min.

Typical polycondensation reactions were carried out as follows:

Polycondensation of 1,4-Bis(dimethylsilyl)benzene with Diphenyldimethoxysilane. A dry 50 mL three-neck flask equipped with stir bar, condenser, thermometer, and rubber septum seal was evacuated and then filled back with nitrogen. The flask was charged via a glass syringe with 10 mL of toluene, 2.04 g (10.5 mmol) of 1,4-bis-(dimethylsilyl)benzene, and 2.3 × 10^{-3}g (4.28 × 10^{-4} mmol) of $B(C_6F_5)_3$. The flask was chilled in an ice water bath, and 2.56 g (10.5 mmol) of diphenyldimethoxysilane was added dropwise via a glass syringe over a period of 2 h. The condensation reaction started after addition of few drops of diphenyldimethoxysilane. The start of reaction was indicated by an exotherm and release of a gaseous byproduct.

When addition of diphenyldimethoxysilane was complete, the reaction mixture was heated to 50 °C to complete the polymerization. After 1 h of heating at 50 °C the reaction mixture was poured into 100 mL of methanol. Solvent was decanted from the precipitated polymer, and the residue was dissolved in methylene chloride. The polymer solution was filtered through anhydrous $CaSO_4$, solvent was removed under vacuum, and the polymer was dried on the vacuum line to yield of 3.54 g (83%) of a viscous liquid. GPC analysis indicated M_w = 30 292 and M_w/M_n = 2.78. DSC T_g = −7.7 °C. ^{1}H NMR: δ 0.29 ppm (s 12H, CH_3) and δ 7.2−7.65 ppm (m, 14H, C_6H_5 and C_6H_4); ^{29}Si NMR δ −2.27 ppm (s, 2Si, **Si**$(CH_3)_2$) and δ −48.32 ppm (s, 1Si, **Si**$(C_6H_5)_2$).

Caution: In some cases, particularly when the organohydrosilane is added to the alkoxysilane, an induction period is observed, and the reaction does not start after addition of the first few drops. The reaction may start suddenly after a significant amount of organohydrosilane is added with very high exotherm and rapid gas evolution. In that situation it is important to run experiments on a small scale and in a large enough flask so significant volume is available for expansion of the reaction mixture. It is preferable to add the dialkoxysilane to a mixture of the hydrosilane plus catalyst.

Results and Discussion. Several catalysts such as transition metal complexes, palladium on carbon, and

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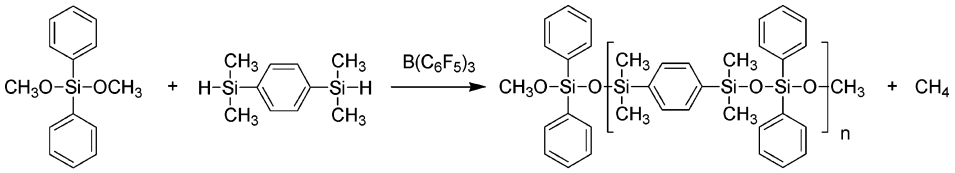
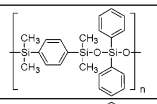
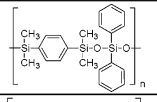
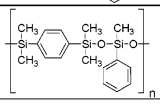
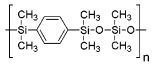
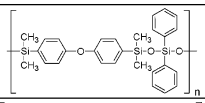
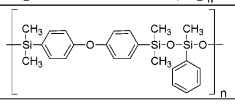
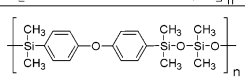
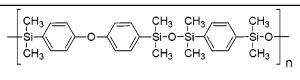
Scheme 2. Polycondensation of 1,4-Bis(dimethylsilyl)benzene (2) with Diphenyldimethoxysilane (3)



3 **2**

Table 1. Polycondensations of Dihydrosilanes with Dialkoxysilanes in the Presence of $B(C_6F_5)_3$[a]

Hydrosilane + alkoxy silanes[b]	Polymer	$[B(C_6F_5)_3]$ (mol/l)	M_w (K)	M_w/M_n	T_g (°C)	% yield
2 + 3		2.90×10^{-4}	30.3	2.78	-7.7	83
6 + 8		1.04×10^{-2}	25.8	2.69	-6.4	74
2 + 5		6.39×10^{-4}	11.7	1.65	-35.5	80
2 + 7		6.10×10^{-4}	49.1	2.24	-59.5	92
4 + 3		1.95×10^{-3}	53.0	6.30	-3	58
4 + 7		1.95×10^{-3}	15.9	2.20	-23.8	89
4 + 7		1.95×10^{-3}	26.1	2.38	-22.8	90
4 + 8		9.76×10^{-4}	29.6	2.34	-12.5	95

[a] All reactions were carried out with equimolar amounts of dihydro- and dialkoxysilanes. [b] 1,4-Bis(dimethylsilyl)benzene (**2**), diphenyldimethoxysilane (**3**), 4,4′-bis(dimethylsilyl)diphenyl ether (**4**), methylphenyldimethoxysilane (**5**), diphenylsilane (**6**), dimethyldimethoxysilane (**7**), 1,4-bis(dimethylmethoxysilyl)benzene (**8**).

$B(C_6F_5)_3$ are used to promote heterocondensation process between organohydrosilane and organosilanol. However, the dehydrocondensation process has some synthetic limitations such as low solubility of certain siloxane diols, e.g. diphenylsilanediol, propensity of many organosilanols and organosiloxanols toward self-condensation, e.g. dimethylsilanediol, and synthetic difficulties in preparation of various organosilanols, e.g. methylsilanetriol. For these reasons, replacement of the silanol functionality with an alkoxy group would significantly broaden the spectrum of available monomers and oligomers that can be used to prepare siloxane copolymers.

Recently, we reported a new polycondensation reaction between organoalkoxysilanes and organohydrosilanes.[17] The new process involves cleavage of C−O and Si−H bonds and formation Si−O and C−H bonds (Scheme 1). This process is extremely exothermic due to a very large enthalpy of reaction, $\Delta H \approx -250$ kJ/mol.

An exemplary polycondensation is depicted in Scheme 2. Kawakami has prepared the same copolymer by a dehydrocoupling process of diphenylsilanediol with **2**.[5]

This new polycondensation reaction takes place at or below room temperature in the presence of very low levels of $B(C_6F_5)_3$. The rate of the reaction can be controlled by the rate of addition of reagents. The reaction is completed over a period of 2−3 h, and high molecular weight (M_w = 10K−50K) materials are obtained. A variety of dihydrosilanes and dialkoxysilanes have been combined in a similar fashion to obtain polysiloxanes, as presented in Table 1.

The ^{29}Si NMR spectra of these polymers indicate, for the most part, a perfectly alternating structure is obtained. However, in the case of the polymers made from dialkoxysilane **7**, significant scrambling of the backbone is observed which gives rise to a more random distribution of the siloxane segments. The observed disturbance may be due to the exchange of hydrogen and alkoxy group at reacting silicon centers. The mechanistic aspects of the reaction that lead to this scrambling are under investigation in our laboratory and will be reported in a separate publication.

Conclusions. A new, very efficient heterocondensation process between dihydrosilanes and dialkoxysilanes leads to the formation of polysiloxanes with elimination of a hydrocarbon as a byproduct. The broad generality of this process will serve as a very useful tool in synthesis of novel siloxane oligomers and polymers.

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References and Notes

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