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Siloxane Coupling Agents

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ABSTRACT: New siloxane coupling agents have been prepared by the platinum-catalyzed addition of $CH_2{=}CHSi(OR)_3$ silanes ($R = CH_3$ or $CH_2CH_2OCH_3$) to four different siloxanes, poly[(methylhydrogen)-siloxane-*co*-dimethylsiloxane], poly[(methylhydrogen)siloxane] (dp = 33), tetramethyldisiloxane, and tetramethylcyclotetrasiloxane. These new hydrophobic materials offer a distinct alternative to conventional silane coupling agents, prevalent in many industrial applications. The new preparations allow for control of molecular weight, the extent of coupling functionality, and the distribution of coupling groups on the siloxane backbone. The use of 2D NMR experiments, COSY, and HETCOR indicated two modes of addition to the Si−H groups had occurred, Markovnikov and anti-Markovnikov. GPC, FTIR, and ^1H and ^{13}C NMR were used to thoroughly characterize all the reaction products.

Introduction

Silane coupling agents are commonly applied to fibers to improve the overall performance of reinforced composite materials by generating a water-resistant surface between an organic polymer and an inorganic substrate. The disastrous effects of water on the mechanical properties of glass-reinforced composites are well documented.[1−4] To overcome such problems, coupling agents are used that are able to react or interact with both the glass surface and the polymer. Coupling agents are applied either from dilute aqueous solutions, as partial hydrolyzates, or from organic solvents (generally an alcohol),[4−12] and most have undergone initial hydrolyzation and oligomerization prior to interacting with the chosen substrate.[9,10] The resultant siloxane films which form deposit on the glass fiber surface, and over time multiple layers develop.[4,7,11,12] Even though alkylsilane coupling agents are bonded to oxide surfaces through thermally stable siloxane bonds, such bonds are hydrolyzable, and the rate of hydrolysis increases dramatically with increasing temperature and pH.

Functional siloxanes, like silanes, are also capable of adhering to a variety of surfaces.[13−15] Siloxanes, that function as hydrophobic coupling agents, offer not only a distinct alternative but also significant advantages over their corresponding silane coupling agents. They are strongly water-resistant polymers[16−20] and should, in principle, also be able to give water-resistant interfaces between glass fibers and organic resins in composite materials. The investigation of siloxanes bearing the appropriate functional groups will therefore lead to a whole new class of coupling agents, with all the advantages of silanes but with greater control and reproducibility in surface modification. The characterization and synthesis of such siloxanes containing pendant trialkoxysilyl groups has proved elusive, as increasing the amounts of trialkoxy substituents has increased the sensitivity of the siloxanes toward hydrolysis.

Hydrosilylation allows the attachment of a wide variety of functional groups to the siloxane backbone. The reaction involves the addition of one or more Si−H moiety to unsaturated organic reagents (Figure 1). All nine Group VIII transition metals display some catalytic activity in hydrosilylation, with platinum being the most active and therefore the most widely used catalyst. Speier's catalyst, comprised of an isopropyl alcohol solution of chloroplatinic acid hydrate ($H_2PtCl_6{\cdot}xH_2O$), is widely used in both industrial and academic laboratories to affect the addition of a Si−H moiety to an unsaturated compound. Hydrosilylation reactions generate two adducts, α and β (major product), along with some minor products from side reactions (Figure 1).[21−25] Thus, functionalization of siloxanes with trialkoxy substituents should be possible by the hydrosilylation of unsaturated groups to pendant Si−H groups on a siloxane backbone.

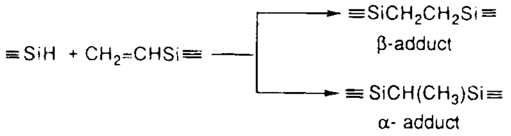

Figure 1. Hydrosilylation reaction.

Platinum complexes can also catalyze the formation of a Si−Si bond during hydrosilylation.[21] Such side reactions are explained by using the hydrosilylation mechanism proposed by Lewis et al.[26] (Figure 2). Bis(divinyltetramethyldisiloxane)Pt^0,[27] commonly referred to as Karstedt's catalyst, undergoes an induction period, where the bonding of dioxygen forms colloidal platinum complex **1**. The formation of the colloidal platinum complex **1**, which subsequently acts as the actual hydrosilylation promoter, explains why most hydrosilylations need a trace of oxygen to get started.[26,28,29] Oxidative addition of $HSiR_3$ to complex **1** completes the first half of the catalytic cycle, generating intermediate **2**. This intermediate is susceptible to nucleophilic attack by an olefin, which generates the hydrosilylation product and regenerates the platinum catalyst **1** (Figure 2). Likewise, nucleophilic attack of complex **2** by trace amounts of water or alcohols in the hydrosilylation reaction similarly regenerates complex **1**, with hydrogen production in a side reaction that also generates alkoxysilanes (Figure 2). Hydrogen is also produced by the slow attack on complex **2** of further $HSiR_3$, a side reaction that deactivates the hydrosilylation catalysts and generates products containing Si−Si bonds.

Increasing the catalyst concentration increases the hydrogen evolved. Boileau et al.[24] modeled such side reactions, by heating pentamethyldisiloxane in toluene

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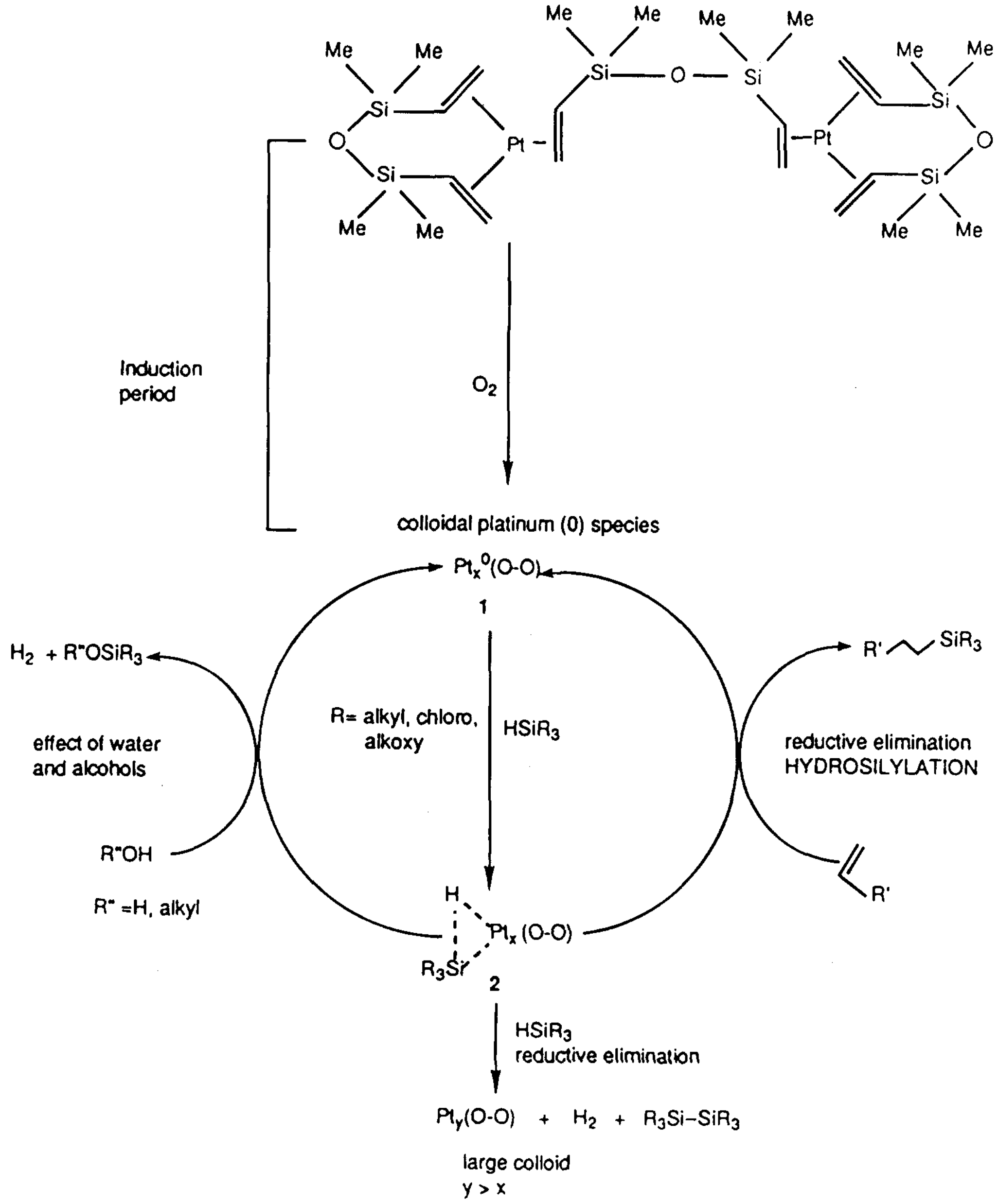


Figure 2. Hydrosilylation mechanism.

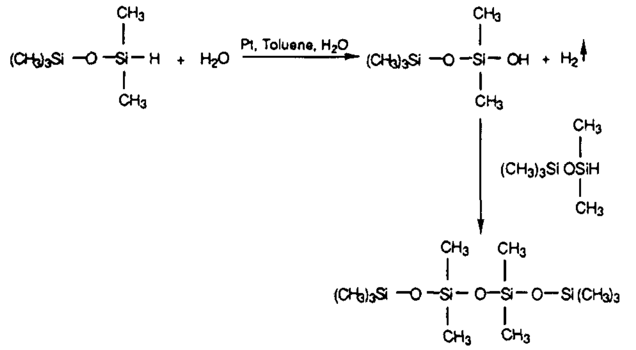


Figure 3. Reaction of pentamethyldisiloxane with water.

that had previously been saturated with water, in the presence of the platinum hydrosilylation catalyst (Figure 3). A silanol initially forms followed by a condensation reaction with excess siloxane to form decamethyltetrasiloxane. Importantly, the researchers established that strict exclusion of water (or alcohols) from hydrosilylation reactions will minimize hydrogenation side reactions.

The synthetic and catalytic aspects associated with the hydrosilylation of vinyltrimethoxysilane and vinyltris(2-methoxyethoxy)silane to various hydrogenalkoxysilanes, such as $HSi(OEt)_3$, have been investigated by Marciniec et al.[30,31] Hydrosilylation of vinyltrimethoxysilane or vinyltris(2-methoxyethoxy)silane onto polymeric siloxane backbones has not been widely studied. We have reported on the application of various functionalized polymers to glass fibers.[32] Crespy et al.[33] synthesized a polysiloxane containing pendant trimethoxysilane and glycidic groups via hydrosilylation with vinyltrimethoxysilane and 1-(allyloxy)-2,3-epoxypropane in the presence of Speier's catalyst, H_2PtCl_6. No apparent α-adduct was formed.

This paper details the synthesis and characterization of novel siloxane coupling agents. It describes how to monitor the reaction (and its side reactions) effectively and then how to identify the reaction products.

Experimental Section

Materials. Octamethylcyclotetrasiloxane (Toshiba), poly[(methylhydrogen)siloxane] (siloxane **2a**; Dow Corning; degree

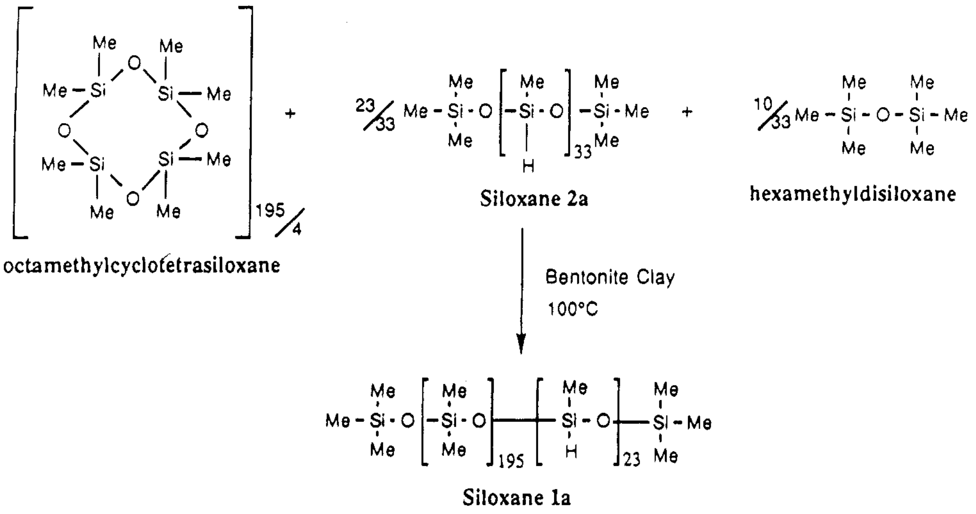


Figure 4. Preparation of siloxane **1a**.

of polymerization = 33), hexamethyldisiloxane (General Electric), 1,1,4,4-tetramethyldisiloxane (Aldrich, 99%), acid-treated bentonite clay (Ace Chemicals), and tetramethylcyclotetrasiloxane (Petrarch) were used as supplied.

Vinyltris(2-methoxyethoxy)silane (Union Carbide, A 172) and vinyltrimethoxysilane (Shin Etsu) were distilled under vacuo and stored under nitrogen.

Toluene (Ace chemicals) was acid washed and distilled over sodium.

Hydrogen hexachloroplatinate(IV) ($H_2PtCl_6{\cdot}xH_2O$; Aldrich) was made up to a 1% solution in dry tetrahydrofuran (distilled from sodium benzophenone).

NMR Spectroscopic Analysis. Samples were analyzed with a Varian Gemini Fourier transform NMR spectrometer (200 MHz) and associated software. Both ^{13}C and ^{1}H NMR spectra were obtained on this instrument using a $CDCl_3$ solvent (Cambridge Isotope Laboratories) unless stated otherwise. The delay between successive pulse sequences was 1–10 s. The number of transients for ^{1}H and ^{13}C NMR was generally 32 and 2000, respectively. The attached proton test (APT), heteronuclear correlation spectroscopy (HETCOR), and correlated spectroscopy (COSY) experiments were obtained by conventional methods.[34]

Fourier Transform Infrared Spectroscopy (FTIR). Analysis was performed with a Biorad Model FTS 65 FTIR spectrometer using NaCl plates. Spectra were obtained over the wavenumber range from 450 to 4000 cm^{-1} at a resolution of 2 cm^{-1} using a MCT detector with coaddition of 64 scans.

Gel Permeation Chromatography (GPC). The molecular weight M_w was determined using a Waters Model GPC with a differential refractometer Model R401 detector. The column series consisted of 500 and 10^3 Å Ultrastyragel columns from Waters Associates.

Synthesis of a Poly[(methylhydrogen)siloxane-*co*-dimethylsiloxane] (Siloxane 1a). A multinecked 1-L glass reactor vessel was equipped with a reflux condenser and a mechanical stirrer. The flask was charged with octamethylcyclotetrasiloxane (1000 g, 3.38 mol), siloxane **2** (103.51 g, 0.05 mol), hexamethyldisiloxane (3.40 g, 0.02 mol), and acid-treated Bentonite clay (17 g, 1.5% w/w reagents/clay). The mixture was stirred at 100 °C for 16 h, and the clay was allowed to settle before the reaction mixture was decanted through a 10-μm filter. The filtrate was heated under reduced pressure (0.5 kPa, 100 °C) to remove mixed cyclic species. The product was characterized by NMR, FTIR, and GPC. Yields of product routinely exceed 95%.

NMR data (ppm): δ 0.07–0.16 ($SiMe_3$), 4.69 (SiH). FTIR data (cm^{-1}; (s = strong, m = medium, w = weak): ν 800 (s, $SiCH_3$), 877 (s, SiH), 1020 and 1090 (s, SiOSi), 1260 (s, $SiCH_3$), 1460 (m, CH_3), 2160 (s, SiH), 2964 (s, CH_3). GPC data: M_w = 15 900.

Preparation of Siloxane Coupling Agents. All reaction flasks were flame dried under vacuo. Siloxanes **1a** and **2a** were dried (0.5 kPa, 120 °C) for 3 h before use. NMR data are collected in Table 2 (vide infra). Yields of product routinely exceed 90%.

Siloxane 1b. Siloxane **1a** (1.00 g, 0.06 mmol), vinyltrimethoxysilane (0.21 g, 1.45 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) were mixed at 70 °C under nitrogen until no Si–H absorption (2160 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed under vacuo (0.5 kPa, 50 °C).

FTIR data (cm^{-1}): ν 800 (s, SiC), 1020–1093 (s, SiOSi, CO), 1143 (m, $SiCH_2CH_2Si$), 1191 (m, $SiOCH_3$), 1260 (s, $SiCH_3$), 1411 (m, CH_3), 1466 (w, OCH_3), 2837 (m, OCH_3), 2961 (s, CH_3). GPC data: M_w = 28 400.

Siloxane 1c. Siloxane **1a** (1.00 g, 0.06 mmol), vinyltris(2-methoxyethoxy)silane (0.41 g, 1.45 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) were mixed at 70 °C under nitrogen until no Si–H absorption (2160 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed under vacuo (0.5 kPa, 50 °C).

FTIR data (cm^{-1}): ν 794 (s, SiC), 960 (m, $SiOCH_2-$), 1014–1124 (s, SiOSi, CO), 1143 (m, $SiCH_2CH_2Si$, $SiOCH_2-$), 1200 (m, $SiOCH_2-$), 1262 (s, $SiCH_3$), 1292 (w, $SiOCH_2-$), 1370 (w, $SiOCH_2-$), 1411 (m, $SiCH_3$), 1454 (m, OCH_3), 2725 (w, $SiOCH_2-$), 2819 (m, OCH_3), 2881 (m, CH_3), 2935 (m, CH_2), 2964 (s, CH_3). GPC data: M_w = 32 600.

Siloxane 2b. Siloxane **2a** (1.00 g, 0.47 mmol), vinyltrimethoxysilane (2.28 g, 15.41 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) mixed at 70 °C under nitrogen until no Si–H absorption (2160 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed in vacuo (0.5 kPa, 100 °C).

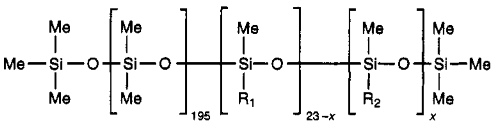
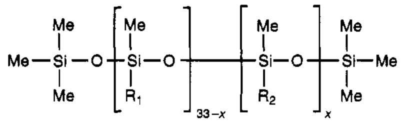
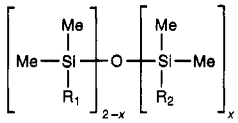
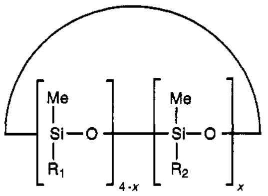
FTIR data (cm^{-1}): ν 771 (m, $SiCH_3$), 848 (m, $SiCH_3$), 1023–1091 (s, SiOSi, CO), 1141 (m, $SiCH_2CH_2Si$), 1192 (m, $SiOCH_3$), 1259 (m, $SiCH_3$), 1410 (w, $SiCH_3$), 1479 (w, OCH_3), 2837 (m, OCH_3), 2950 (m, CH_3). GPC data: M_w = 10 200.

Siloxane 2c. Siloxane **2a** (0.50 g, 0.233 mmol, dried as described above), vinyltris(2-methoxyethoxy)silane (2.16 g, 7.70 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) were mixed at 70 °C under nitrogen until no Si–H absorption (2160 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed in vacuo (0.5 kPa, 50 °C).

FTIR data (cm^{-1}): ν 845 (s, SiC), 962 (m, $SiOCH_2-$), 1023–1100 (s, SiOSi, CO), 1141 (m, $SiCH_2CH_2Si$, $SiOCH_2$), 1201 (m, $SiOCH_2$), 1259 (m, $SiCH_3$), 1295 w, $SiOCH_2$), 1370 (w, $SiOCH_2$), 1405 (w, $SiCH_3$), 1452 (m, OCH_3), 2724 (w, $SiOCH_2$), 2821 (s, OCH_3), 2877 (s, CH_3), 2933 (s, CH_2). GPC data: M_w = 12 500.

Siloxane 3b. Tetramethyldisiloxane (2.00 g, 14.89 mmol), vinyltrimethoxysilane (4.41 g, 29.75 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) were mixed at 70 °C under

Table 1. Structure of Siloxanes

siloxane backbone	siloxane no.	x	R_1	R_2
	**1a**	$x = 0$	H	
	1b	$x \le 23$	$CH_2CH_2Si(OCH_3)_3$	$CH(CH_3)Si(OCH_3)_3$
	1c	$x \le 23$	$CH_2CH_2Si(OCH_2CH_2OCH_3)_3$	$CH(CH_3)Si(OCH_2CH_2OCH_3)_3$
	**2a**	$x = 0$	H	
	2b	$x \le 33$	$CH_2CH_2Si(OCH_3)_3$	$CH(CH_3)Si(OCH_3)_3$
	2c	$x \le 33$	$CH_2CH_2Si(OCH_2CH_2OCH_3)_3$	$CH(CH_3)Si(OCH_2CH_2OCH_3)_3$
	**3a**	$x = 0$	H	
	3b	$x \le 2$	$CH_2CH_2Si(OCH_3)_3$	$CH(CH_3)Si(OCH_3)_3$
	3c	$x \le 2$	$CH_2CH_2Si(OCH_2CH_2OCH_3)_3$	$CH(CH_3)Si(OCH_2CH_2OCH_3)_3$
	**4a**	$x = 0$	H	
	4b	$x \le 4$	$CH_2CH_2Si(OCH_3)_3$	$CH(CH_3)Si(OCH_3)_3$
	4c	$x \le 4$	$CH_2CH_2Si(OCH_2CH_2OCH_3)_3$	$CH(CH_3)Si(OCH_2CH_2OCH_3)_3$

nitrogen until no Si−H absorption (2100 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed in vacuo (0.5 kPa, 50 °C).

FTIR data (cm^{-1}): ν 796 (s, $SiCH_3$), 1088 (s, SiOSi, CO), 1141 (m, $SiCH_2CH_2Si$), 1192 (m, $SiOCH_3$), 1253 (m, $SiCH_3$), 1410 (w, $SiCH_3$), 1461 (w, OCH_3), 2837 (m, OCH_3), 2954 (m, CH_3). GPC data: $M_w = 360$.

Siloxane 3c. Tetramethyldisiloxane (1.50 g, 2.28 mmol), vinyltris(2-methoxyethoxy)silane (6.25 g, 11.16 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) were mixed at 70 °C under nitrogen until no Si−H absorption (2100 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed in vacuo (0.5 kPa, 50 °C).

FTIR data (cm^{-1}): ν 792 (s, $SiCH_3$), 962 (m, $SiOCH_2$), 1029–1100 (s, SiOSi, CO), 1137 (m, $SiCH_2CH_2Si$, $SiOCH_2-$), 1200 (m, $SiOCH_2-$), 1255 (m, $SiCH_3$), 1294 (w, $SiOCH_2-$), 1370 (w, $SiOCH_2-$), 1409 (w, $SiCH_3$), 1460 (w, OCH_3), 2725 (w, $SiOCH_2-$), 2819 (w, OCH_3), 2881 (s, CH_3), 2927 (s, CH_2). GPC data: $M_w = 580$.

Siloxane 4b. Tetramethylcyclotetrasiloxane (2.00 g, 8.32 mmol), vinyltrimethoxysilane (4.93 g, 21.00 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) were mixed at 70 °C under nitrogen until no Si−H absorption (2160 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed in vacuo (0.5 kPa, 50 °C).

FTIR data (cm^{-1}): ν 776 (s, $SiCH_3$), 1089 (s, SiOSi, CO), 1141 (m, $SiCH_2CH_2Si$), 1195 (m, $SiOCH_3$), 1260 (m, $SiCH_3$), 1410 (w, $SiCH_3$), 1461 (w, OCH_3), 2837 (m, OCH_3), 2954 (m, $SiCH_3$). GPC data: $M_w = 500$.

Siloxane 4c. Tetramethylcyclotetrasiloxane (1.50 g, 6.24 mmol), vinyltris(2-methoxyethoxy)silane (6.99 g, 25.00 mmol), toluene (10 mL), and a H_2PtCl_6 solution (0.1 mL) were mixed at 70 °C under nitrogen until no Si−H absorption (2160 cm^{-1}) was detectable by FTIR spectroscopy. Toluene and excess silane were removed in vacuo (0.5 kPa, 50 °C).

FTIR data (cm^{-1}): ν 776 (s, $SiCH_3$), 840 (s, $SiCH_3$), 959 (m, $SiOCH_2-$), 1090 (s, SiOSi, CO), 1135 (m, $SiCH_2CH_2Si$, $SiOCH_2-$), 1191 (m, $SiOCH_2-$), 1255 (m, $SiCH_3$), 1291 (w, $SiOCH_2-$), 1370 (w, $SiOCH_2-$), 1409 (w, $SiCH_3$), 1460 (w, OCH_3), 2725 (w, $SiOCH_2-$), 2819 (w, OCH_3), 2881 (s, CH_3), 2927 (s, CH_2). GPC data: $M_w = 940$.

Results and Discussion

In contrast to the active investigations in organosilicon chemistry, concerning the reactions of silicon−silicon or silicon−carbon linkages, the reactions of organosiloxanes, which are of great industrial importance, have aroused relatively little interest among chemists. In this paper, we describe a convenient method for the preparation of pendant trialkoxysilyl-substituted siloxanes. The aim of this project was to prepare, characterize, and compare the reaction products from the hydrosilylation of two commonly used silane coupling agents, vinyltrimethoxysilane and vinyltris(2-methoxyethoxy)silane, with (methylhydrogen)siloxanes of varying chain length and structure. Four different siloxanes were chosen for this research, a poly[(methylhydrogen)siloxane-*co*-dimethylsiloxane] (siloxane **1a**), poly(methylhydrogen)siloxane (dp = 33) (siloxane **2a**), tetramethyldisiloxane, and tetramethylcyclotetrasiloxane. Of these, tetramethyldisiloxane represents a terminal Si−H siloxane, available as a pure fine chemical which permits detailed reaction pathway and product analysis. Similarly, tetramethylcyclotetrasiloxane is also available as a pure fine chemical, also allowing detailed reaction pathways and products to be determined, but in this case pendant Si−H groups are being reacted. Siloxane **2a** contains a large sequenceof pendant Si−H groups and will give an indication of the hydrosilylation efficiency and whether steric restraints prohibit complete reaction of all Si−H groups with vinyltrialkoxysilanes. Last, siloxane **1a** is illustrative of a range of siloxane copolymers, which permit the controlled incorporation of pendant trialkoxysilyl groups to a siloxane backbone. These copolymers are larger than the other siloxanes used and so will reflect the efficiency of the hydrosilylation reaction with high molecular weight, hydrophobic materials, where access to the Si−H functionality is likely to be very solvent dependent.

Siloxane **1a** was prepared by heating a mixture of hexamethyldisiloxane, siloxane **2a**, and octamethylcyclotetrasiloxane together with acid-treated clay (Figure 4). This process involves ring-opening copolymerization of the cyclic monomer with a hydride siloxane and a chain-terminating agent (hexamethyldisiloxane),[16] which gives rise to a distribution of dimethylsiloxy and (methylhydrogen)siloxy units in the final product. The ratio

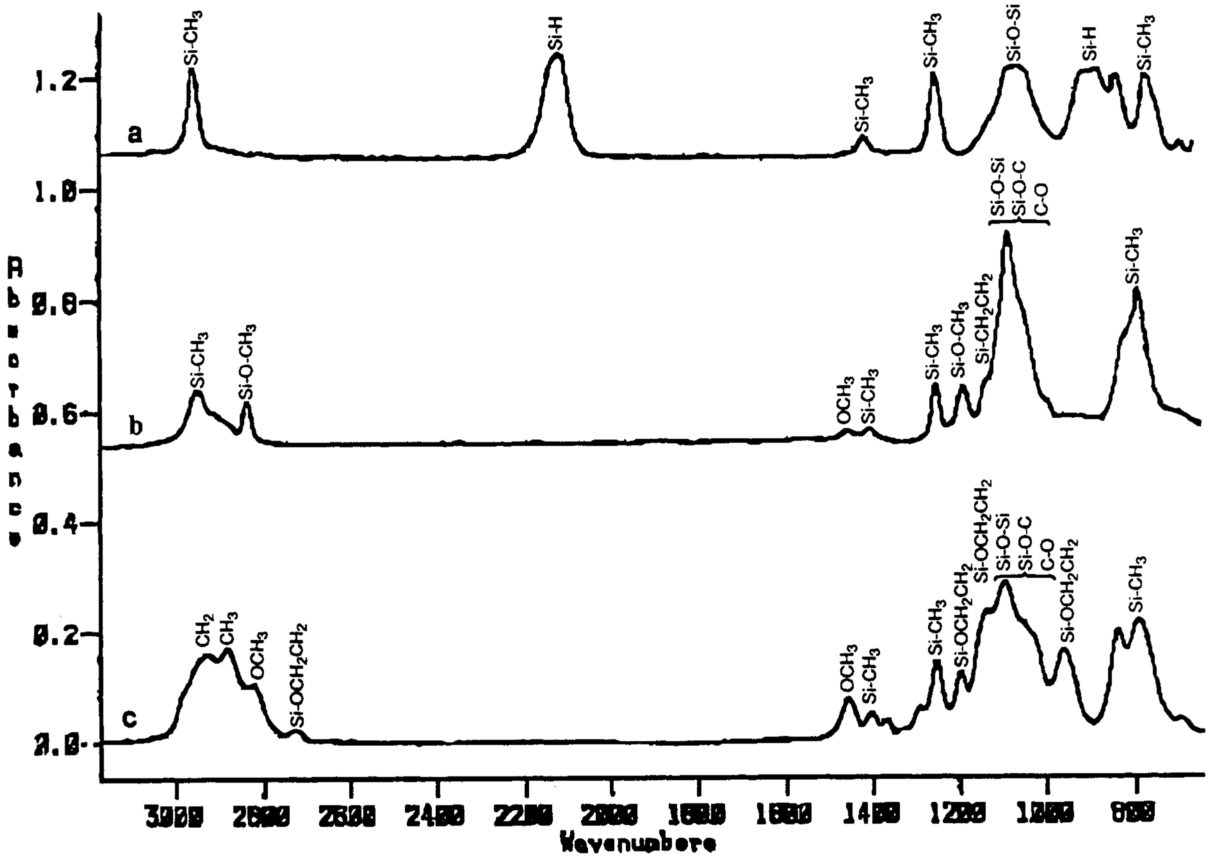
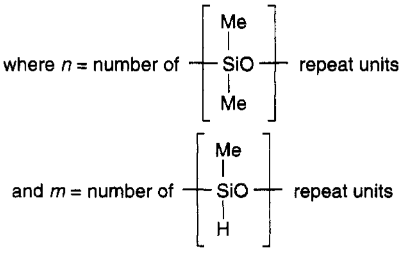


Figure 5. FTIR spectra of (a) tetramethyldisiloxane (siloxane **3a**), (b) siloxane **3b**, and (c) siloxane **3c**.

of the cyclic Me_2SiO groups and the Si–H groups of the siloxane oligomer to the hexamethyldisiloxane terminating groups determines the molecular weight of the final siloxane product. The number of Si–H groups in the final polymer can therefore be controlled by adjusting the stoichiometry of the reagents. To determine the frequency of the Si–H and methylsiloxy groups, both ^{1}H NMR and GPC data were used in solving eqs 1 and 2.[35]

$$162 + 74n + 60m = \text{molecular weight} \quad (1)$$

$$\frac{18 + 6n + 3m}{m} = \frac{\int \text{SiMe protons}}{\int \text{SiH protons}} \quad (2)$$



where n = number of $\left[-\overset{\text{Me}}{\underset{\text{Me}}{\text{SiO}}}- \right]$ repeat units

and m = number of $\left[-\overset{\text{Me}}{\underset{\text{H}}{\text{SiO}}}- \right]$ repeat units

Hydrosilylation remains one of the best ways to form Si–C bonds. Therefore, to prepare siloxane coupling agents, vinyltrimethoxysilane and vinyltris(2-methoxyethoxy)silane were hydrosilylated onto the four different siloxanes containing Si–H groups (using H_2PtCl_6 as the catalyst). Table 1 shows the starting siloxane and the hydrosilylated products formed. For ready identification, the siloxanes have been numbered as **1a**–**4c** where **a** refers to the starting siloxane, **b** refers to hydrosilylations with vinyltrimethoxysilane, and **c** refers to hydrosilylations with vinyltris(2-methoxyethoxy)silane. Note x refers to the number of $SiCH(CH_3)$ groups.

The progress of the hydrosilylation reaction was monitored in the ^{1}H NMR spectra, by the disappearance of the Si–H resonance at 4.7 ppm and the disappearance of the vinyl resonances at 5.9 and 6.05 ppm indicating the alkene has reacted with Si–H groups on the siloxane backbone. The disappearance of an absorption band at 2100–2160 cm^{-1} (varies with siloxane) in the FTIR also indicates that the Si–H groups of the siloxane have reacted. The absence of this band and the C=C resonance at 1600 cm^{-1} due to the vinylsilane were an indication that the reaction had gone to completion. The C–O resonance (1100 cm^{-1}) is not seen in the spectra as it is subject to interference by the Si–O–Si band of the siloxane backbone (Figure 5 shows the FTIR spectra of siloxanes **3a**–**c**). However, for siloxanes **1c**, **2c**, **3c**, and **4c** the $-SiOCH_2CH_2-$ group also has resonances at 960 and 1140 cm^{-1}. The resonance at 1140 cm^{-1} may also be attributed to $-SiCH_2CH_2Si-$ as reported by Lipp et al.[36] For siloxanes **1b**, **2b**, **3b**, and **4b** this resonance appears and is not in the spectrum of the starting siloxane or vinyltrimethoxysilane. Therefore, for these siloxanes the resonance at 1140 cm^{-1} can be assigned as $SiCH_2CH_2Si$. The $SiOCH_3$ resonance is at 2839 cm^{-1} for siloxanes **1b**, **2b**, **3b**, and **4b**. FTIR can be used to monitor the disappearance of Si–H and give a quick indication when the reaction is finished. However, for more detailed analysis several techniques need to be used.

At the beginning of each hydrosilylation reaction hydrogen was evolved. The formation of hydrogen suggests that either Si–Si or Si–O–Si bonds are formed.[21,24] When the Si–H peak disappears in the FTIR spectrum, the ^{1}H NMR spectrum still indicates a

Table 2. NMR Data for Siloxane Coupling Agents

siloxane no.	X	$-\mathrm{SiC^{\alpha}H_2C^{\beta}H_2Si(OX)_3}$		$-\mathrm{SiC^{\alpha'}H(C^{\beta'}H_3)}-$	
		^{1}H	^{13}C	^{1}H	^{13}C
1b	$\mathrm{C^1H_3}$	0.0 ($\mathrm{SiMe_3}$) 0.5 (α,β) 3.5 (**1**)	1.0 ($\mathrm{SiMe_3}$) 1.8 (α) 8.2 (β) 50.4 (**1**)		
1c	$\mathrm{-C^2H_2C^3H_2OC^4H_3}$	0.0 ($\mathrm{SiMe_3}$) 0.5 (α,β) 3.3 (**4**) 3.4 (**3**) 3.8 (**2**)	1.0 ($\mathrm{SiMe_3}$) 1.5 (α) 8.2 (β) 58.8 (**4**) 62.1 (**2**) 73.6 (**3**)		
2b	$\mathrm{C^1H_3}$	0.1 ($\mathrm{SiMe_3}$) 0.5 (α,β) 3.3 (**1**)	−1.0 ($\mathrm{SiMe_3}$) 1.0 (α) 8.0 (β) 50.0 (**1**)	0.4 (α′) 1.3 (β′)	5.0 (α′) 7.0 (β′)
2c	$\mathrm{-C^2H_2C^3H_2OC^4H_3}$	0.1 ($\mathrm{SiMe_3}$) 0.6 (α,β) 3.4 (**4**) 3.5 (**2**) 4.0 (**3**)	−1.3 ($\mathrm{SiMe_3}$) 1.7 (α) 8.3 (β) 58.7 (**4**) 61.7 (**3**) 73.4 (**2**)	0.2 (α′) 1.1 (β′)	5.6 (α′) 7.5 (β′)
3b	$\mathrm{C^1H_3}$	0.2 ($\mathrm{SiMe_3}$) 0.6 (α,β) 3.6 (**1**)	−0.5 ($\mathrm{SiMe_3}$) 0.6 (α) 9.1 (β) 50.6 (**1**)	0.2 (α′) 1.3 (β′)	5.4 (α′) 7.6 (β′)
3c	$\mathrm{-C^2H_2C^3H_2OC^4H_3}$	0.1 ($\mathrm{SiMe_3}$) 0.6 (α,β) 3.4 (**4**) 3.5 (**2**) 4.0 (**3**)	−1.3 ($\mathrm{SiMe_3}$) 1.7 (α) 8.3 (β) 58.7 (**4**) 61.7 (**3**) 73.4 (**2**)	0.2 (α′) 1.3 (β′)	5.6 (α′) 7.5 (β′)
4b	$\mathrm{C^1H_3}$	0.1 ($\mathrm{SiMe_3}$) 0.5 (α,β) 3.6 (**1**)	−1.0 ($\mathrm{SiMe_3}$) 1.0 (α) 8.0 (β)	0.2 (α′) 1.3 (β′)	5.4 (α′) 7.6 (β′)
4c	$\mathrm{-C^2H_2C^3H_2OC^4H_3}$	0.1 ($\mathrm{SiMe_3}$) 0.5 (α,β) 3.4 (**4**) 3.5 (**2**) 4.0 (**3**)	−1.6 ($\mathrm{SiMe_3}$) 1.4 (α) 7.8 (β) 58.8 (**4**) 62.0 (**3**) 73.6 (**2**)	0.1 (α′) 1.0 (β′)	5.3 (α′) 7.4 (β′)

small amount of vinylsilane is present, which is consistent with the interpretation that a small number of the Si−H groups react to form Si−Si bonds. It is likely Si−Si bonds are forming, as water was carefully excluded from the reaction (water reacts with Si−H groups to form Si−O−Si bonds). Any residual vinylsilane is finally removed in vacuo with the solvent (toluene), at the end of the reaction. To complete product characterization, several NMR techniques were used.

Complete assignment of the resonances observed in the ^{13}C and ^{1}H NMR spectra is possible using APT, COSY, and HETCOR NMR pulse sequences. Table 2 provides complete structural assignments for all siloxane coupling agents synthesized. Siloxane **3c** will be analyzed in detail to illustrate how structural assignments to specific spectral resonances can be made. For siloxane **3c**, the APT ^{13}C NMR spectrum displays positive signals for the $\mathrm{CH_2}$ group and inverted or negative signals for the CH and $\mathrm{CH_3}$ groups (Figure 6). The two negative signals present at 5.6 (C2) and 7.5 ppm (C3) indicate that some α adduct was formed. The signals at 1.7 (C7) and 8.3 ppm (C8) belong to the β adduct. The APT ^{13}C NMR spectrum for a typical hydrosilylation reaction (Figure 1) would have positive resonances for the major peaks associated with the β adduct, while the minor product, the α adduct, would have its resonances inverted. Therefore, the APT experiment allows a quick determination of the extent of stereochemical specificity in a hydrosilylation reaction.

To establish the ^{1}H NMR assignments, a COSY experiment was completed (Figure 7, siloxane **3c**). The COSY spectrum shows six signals along the diagonal, which correspond to the six signals in the conventional ^{1}H NMR spectrum. The signals off the diagonal, the cross peaks, indicate two coupled nuclei. Therefore, linking the diagonal peaks to their associated cross peaks (Figure 7) establishes which multiplets belong to mutually coupled protons.[31] For instance, Figure 7 shows coupling between protons at 0.2 and 1.3 ppm, assigned to C2 and C3, respectively. The COSY experiment allowed the C3 resonance to be assigned, though it appears near the $\mathrm{SiMe_3}$ resonances. Similarly, coupling between C4 and C5 is clearly seen. Both the $\mathrm{SiCH_2CH_2Si}$ resonances are at 0.6 ppm (vide infra). The COSY experiment allows for easy identification of coupling between (^{1}H−^{1}H) homonuclear systems, and in hydrosilylation reaction products both COSY and APT identify the resonances associated with the α and β adducts.

A HETCOR experiment was completed (Figure 8) to remove the remaining ambiguities associated with ^{1}H NMR spectral assignments and allow complete assignment of ^{13}C NMR resonances. In Figure 8 (siloxane **3c**), the one-dimensional ^{1}H NMR spectrum is shown on top and the ^{13}C NMR one-dimensional spectrum on the left-hand side. By starting from the ^{13}C NMR signals we have already assigned, the correlation peaks can be used to identify the corresponding ^{1}H NMR signals. The HETCOR experiment reveals that the ^{1}H NMR signals associated with C7 and C8 are equivalent (0.6 ppm) yet

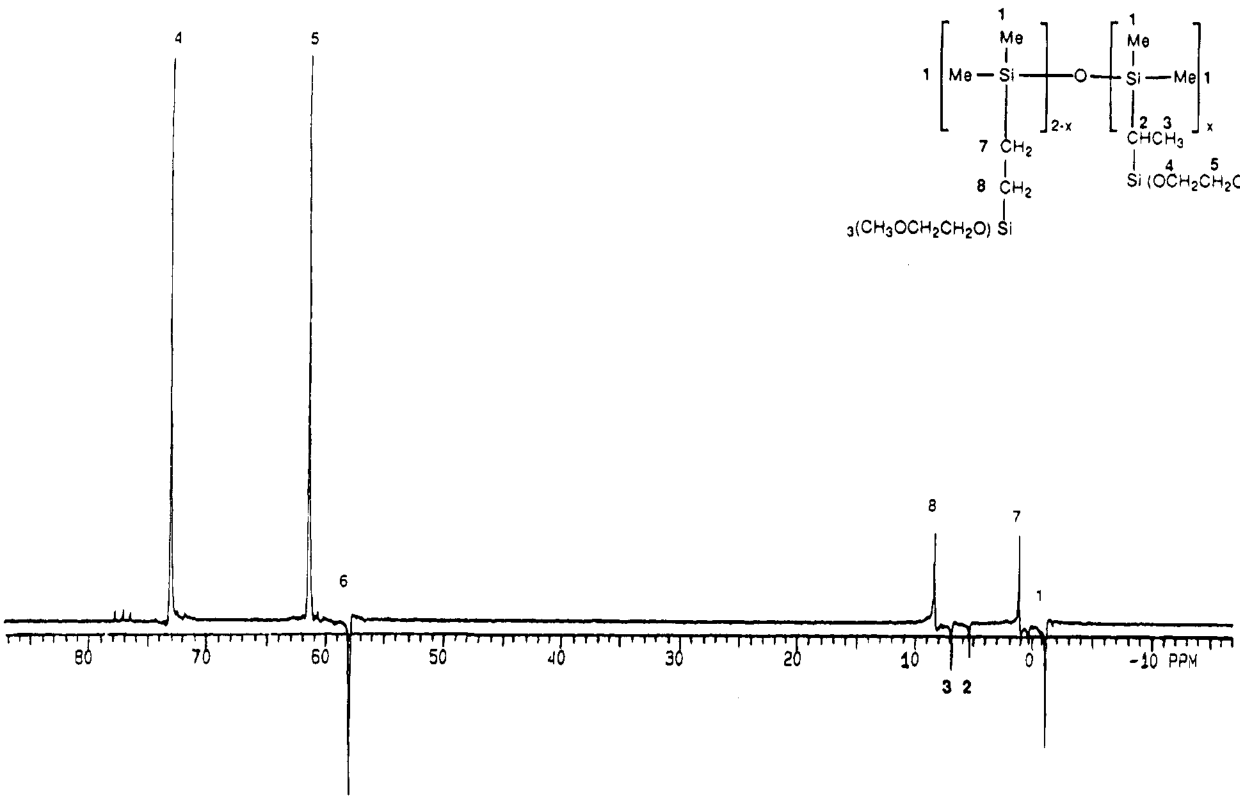


Figure 6. APT spectrum of siloxane **3c**.

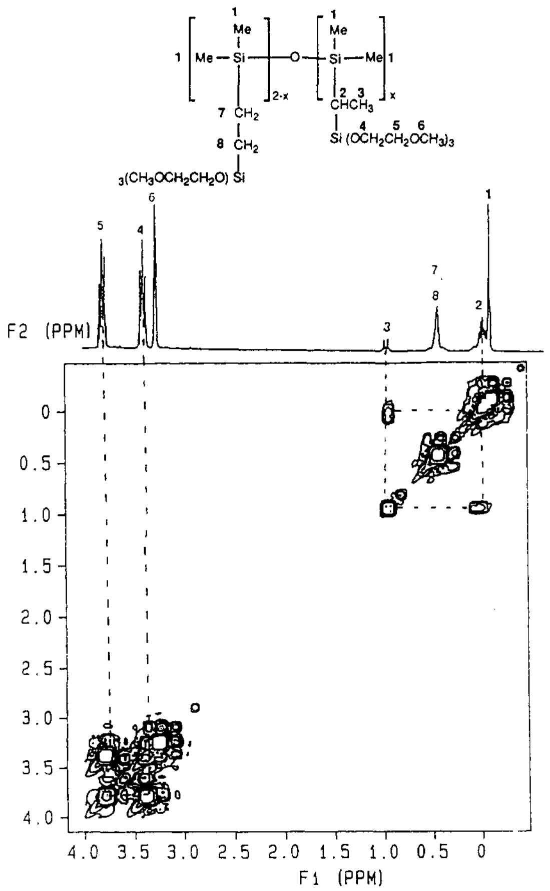


Figure 7. COSY spectrum of siloxane **3c**.

appear as two separate signals (1.7 and 8.3 ppm, respectively) in the ^{13}C NMR spectrum. The ^{1}H NMR assignments for the α adduct can also be confirmed by the HETCOR spectrum (0.2 and 1.3 ppm). The HETCOR experiment allowed identification of the coupling relationships in ($^{1}H-^{13}C$) homonuclear systems and confirmed assignments made from the APT spectrum.

Once the ^{1}H NMR spectrum is assigned correctly, it is possible to determine the extent of Markovnikov (α adduct) and anti-Markovnikov addition (β adduct). If x is defined as the number of $SiCH(CH_3)$ groups, associated with Markovnikov additions, the formula for determining x is given by:

$$\frac{4(m-x)}{3x} = \frac{\int CH_2CH_2 \text{ protons from } ^{1}H \text{ NMR}}{\int CH_3 \text{ protons from } ^{1}H \text{ NMR}} \qquad (3)$$

where m = 23 for siloxane **1**, 33 for siloxane **2**, 4 for tetramethylcyclotetrasiloxane, and 2 for tetramethyldisiloxane. Table 3 gives the values for x and the percent of α adduct formed in all the siloxane coupling agent preparations.

All the siloxane coupling agents were made under very similar experimental conditions. The variations inherent to the starting siloxanes on hydrosilylation with the two unsaturated silanes should provide initial insights into the stereochemical course of hydrosilylation reactions with macromolecules. First, of the two unsaturated silanes, vinyltrimethoxysilane was more reactive than vinyltris(2-methoxyethoxy)silane. Marciniec[30] established a reactivity sequence, based on the yield of β adducts, for the hydrosilylation reactions of vinyltrialkoxysilanes with trialkoxysilanes, such as $HSi(OEt)_3$, in the presence of ruthenium catalysts. Our results affirm this reactivity sequence. Starting with the simplest siloxane, disiloxane **3a**, containing two terminal Si–H groups, the hydrosilylated vinyltrialkoxysilanes would find the smallest steric crowding within this molecule. Not surprisingly then, the sterically more demanding α adduct is formed in highest yield in the hydrosilylation of siloxane **3a** with vinyl-

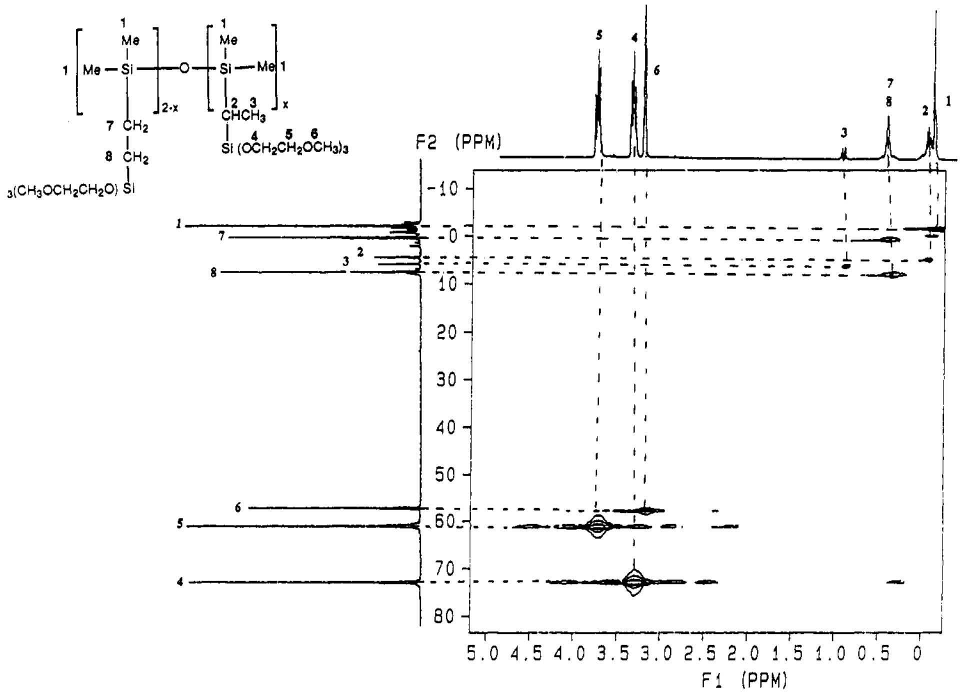


Figure 8. HETCOR spectrum of siloxane **3c**.

Table 3. Ratio of CH_2CH_2 Protons to $CHCH_3$ Protons and the Percent α-Adduct

siloxane no.	$(m - x)/x$	% α-adduct
1b	*d*	*d*
1c	*d*	*d*
2b	24/9	27
2c	24/9	27
3b	1.3/0.7	35
3c	1.6/0.4	20
4b	3.5/0.5	12
4c	3.2/0.8	19

[a] **b** = hydrosilylations with vinyltrimethoxysilane and **c** = hydrosilylations with vinyltris(2-methoxyethoxy)silane. [b] Cal-culated from the proton NMR integral. [c] % α-adduct = $100x/m$. [d] The amount of α-adduct is too small to integrate (i.e., less than 0.5%).

trimethoxysilane. Yields of the α adduct were lower using vinyltris(2-methoxyethoxy)silane, but the reactivity of the latter unsaturated silane was lower throughout all hydrosilylations.

The constrained cyclic geometry of the starting siloxane **4a** imposes steric restraints on the hydrosilylation product geometry, and so the more sterically demanding α adduct is formed in only a low yield. Interestingly, hydrosilylating linear siloxane **2a** with either vinyltrimethoxysilane or vinyltris(2-methoxyethoxy)silane gave identical yields of the α adduct. While siloxane **2a** possesses adjacent pendant Si–H groups (as did siloxane **3a**), it is able to accommodate the extra steric bulk of the α adduct around a silicon atom, due to the inherent flexibility of its linear siloxane backbone. Not surprisingly then, yields of the α adduct were higher for silanes **2a** (cyclic geometry) than siloxane **3a** (linear geometry). Finally, hydrosilylations with siloxane **1a** did not form any detectable α adduct. The Si–H groups on siloxane **1a** are interspersed with dimethylsiloxy units, on a polymer with the highest molecular weight of all the starting siloxane materials. The absence of the α adduct is puzzling, in a siloxane where steric constraints are reduced by the interspersed Me_2SiO groups. Further work continues to evaluate these effects. The stereochemical reproducibility of some siloxane hydrosilylations was checked, by repeating the reaction several times and monitoring the adducts formed. In all cases tried the value for x in Table 3 varied by ±1.

In summary, siloxane coupling agents can be prepared by hydrosilylating vinyltrialkoxysilanes with reactive Si–H groups on appropriate siloxanes, causing relatively few side reactions. Such siloxane coupling agents effectively bind to surfaces.[32] The ability to prepare these siloxanes should help to elucidate the binding mechanisms of aqueous silane solutions to surfaces. Their use in steric stabilization of paint dispersions and in treating fillers for composite manufacture is under evaluation.

Conclusions

Catalytic hydrosilylation of vinyltrimethoxysilane or vinyltris(2-methoxyethoxy)silane onto siloxanes containing Si–H groups can be achieved under appropriate reaction conditions. In most cases, both the α and β hydrosilylation products form. When the Si–H groups are dispersed with dimethylsiloxy units, no detectable α adducts is formed on hydrosilylation. Further work is required to establish whether increasing siloxane molecular weight or decreasing proximity of Si–H groups inhibits the formation of the α adduct. By using ^1H and ^{13}C NMR and FTIR spectroscopy, it was possible to identify the siloxane coupling agents formed during the hydrosilylation reaction. Furthermore, the use of 2D NMR experiments, COSY, and HETCOR permits unequivocal assignment of all spectral resonances, even revealing the occurrence of two concomitant resonances. The ratio of α/β adducts did vary with the siloxane and the silane used and could be determined using an APT NMR experiment. It is likely that some Si–Si bonds formed at the beginning of the reaction, evidenced by the formation of a small amount of hydrogen. Now that siloxane coupling agents can be made, it remains to be seen whether they are as effective in composite applications as their silane counterparts.

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References and Notes

(1) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1982.

(2) Bader, M. G.; Bailey, J. E.; Bell, I. *Materials Science Research (Ceramics in Severe Environments*; Kriegel, W. W., Palmour, H., Eds.; Plenum Press: New York, 1972; Vol. 5.

(3) Atkins, A. G. *J. Mater. Sci.* **1975**, *10*, 819.

(4) Outwater, J. O. *J. Adhes.* **1970**, *2*, 242.

(5) Rosen, M. R.; Goddard, E. D. Proceedings of the 34th Annual Technical Conference, SPI Reinforced Plastics/Composites Institute, Section 19-E, 1979.

(6) Angst, D. L.; Simmons, G. W. *Langmuir* **1991**, *7*, 2236.

(7) Park, J. M.; Subramanian, R. V. *J. Adhes. Sci. Technol.* **1991**, *5*, 459.

(8) Pantano, C. G.; Wittberg, T. N. *Surf. Interface Anal.* **1990**, *15*, 498.

(9) Arkles, B. *Hüls Silicon Compound Register and Review*; Anderson, R., Larso, G. L., Smith, C., Eds.; Hüls America Inc.: New Jersey, 1991; p 59.

(10) Wang, D.; Jones, F. R.; Denison, P. *J. Adhes. Sci. Technol.* **1992**, *6*, 79.

(11) Allen, K. W. *J. Adhes. Sci. Technol.* **1992**, *6*, 23.

(12) Drown, E. K.; Al Moussawi, H.; Drzal, L. T. *J. Adhes. Sci. Technol.* **1991**, *5*, 865.

(13) Bennett, D. R.; Matisons, J. G.; Netting, A. K. O.; Smart, R. St. C.; Swincer, A. G. *Polym. Int.* **1992**, *27*, 147.

(14) Auroy, P.; Auvray, L.; Léger, L. *J. Colloid Interface Sci.* **1992**, *150*, 187.

(15) Cosgrove, T.; Prestidge, C. A.; Vincent, B. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1377.

(16) Noll, W. *The Chemistry and Technology of Silicones*; Academic Press: New York, 1968; pp 442 and 470.

(17) Litvinov, V. M.; Lavrukhin, B. D.; Zhdanov, A. A. *Polym. Sci. USSR, Ser. A* **1985**, *27*, 2474.

(18) Litvinov, V. M.; Lavrukhin, B. D.; Zhdanov, A. A. *Polym. Sci. USSR, Ser. A* **1985**, *27*, 2482.

(19) Dubchak, I. L.; Pertsin, A. I.; Zhdanov, A. A. *Polym. Sci. USSR, Ser. A* **1985**, *27*, 2340.

(20) Viallat, A.; Cohen-Addad, J. P.; Pouchelon, A. *Polymer* **1986**, *27*, 843.

(21) Brown-Wesley, K. *Organometallics* **1987**, *6*, 1590.

(22) Lapp, A.; Xiongwei, H.; Herz, J. *Makromol. Chem.* **1988**, *189*, 1061.

(23) Herz, J.; Belkebir-Mrani, A.; Rempp, P. *Eur. Polym. J.* **1973**, *9*, 1165.

(24) Lestel, L.; Cheradame, H.; Boileau, S. *Polymer* **1990**, *31*, 1154.

(25) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(26) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.

(27) Stein, J.; Lewis, L. N.; Smith, K. A.; Lettko, K. X. *J. Inorg. Organomet. Polym.* **1991**, *3*, 325.

(28) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990**, *9*, 621.

(29) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

(30) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1983**, *253*, 349.

(31) Marciniec, B.; Gulinski, J.; Urbaniak, W. *Polym. J. Chem.* **1982**, *56*, 287.

(32) Britcher, L. G.; Kehoe, D. C.; Matisons, J. G.; Swincer, A. G.; Smart, R. St. C. *Langmuir* **1993**, *9*, 1609.

(33) Crespy, A.; Caze, C.; Loucheux, C. *J. Appl. Polym. Sci.* **1992**, *44*, 2061.

(34) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Germany, 1991; p 218.

(35) The molecular weight of siloxane **1**, as determined by GPC, is inserted into eq 1 where this molecular weight must equal the sum of the molecular weights of the two terminal siloxane groups OSiMe$_3$ and SiMe$_3$ (total = 162), plus the total molecular weight of dimethylsiloxy groups (74n) and the total molecular weight of the (methylhydrogen)siloxy groups (60m). Similarly, from ^{1}H NMR, the ratio of the number of protons associated with SiMe groups to the number of Si–H hydrogens is determined from their respective ^{1}H NMR integrals, thus generating eq 2. Simultaneously solving eqs 1 and 2, it was determined that siloxane **1** had $n = 195$ (Me$_2$SiO groups) and $m = 23$ (Me(H)SiO groups).

(36) Lipp, E. D.; Smith, A. L. *The Analytical Chemistry of Silicones*; Smith, A. L., Ed.; John Wiley and Sons: New York, 1991; Chapter 11.

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