Table I

% Me_3SiCl in Me_3SiOMe	result
0.1	no reaction after 30 min
1	∼10% $Me_3SiOSiEt_3$ [a] formed in 30 min
5	solution became hazy in 5 min
10	solution became hazy in 75–90 s
20	solution became hazy in 15 s
25	solution became hazy in 10 s
50	solution became hazy in 5 s

[a] $M^+ = 204$ in chemical ionization mass spectrometer.

To further illustrate the lack of reactivity between a silanol and silyl ether in the absence of a catalyst, we carried out the following experiment. Me_3SiOH, which reacts 600 times as fast as Et_3SiOH in condensation reactions with silyl ethers,[2] was combined with $MeSi(OMe)_3$, which is more reactive than Me_3SiOMe.[3] After 30 min of heating at vigorous reflux, no reaction had occurred as shown by GC analysis.

Experimental Section

General Procedures. The silanes and hexamethyldisilazane were purchased from Silar Laboratories and were purified as described below. Gas chromatographic analysis was carried out with either a Hewlett-Packard 5830A gas chromatograph equipped with a 6 ft × $^1/_4$ in. glass column containing 10% SE-30 on Chromsorb 80/100 W-HP or a Hewlett-Packard 5750 equipped with 4 ft × $^1/_4$ in. stainless steel columns containing either 15% SE-52 on 80/100 W-HP 5750 or 15% SE-30 on 80/100 W-HP 5750. Infrared spectra were recorded as thin films on salt plates on a Perkin-Elmer 598, and NMR spectra were recorded using $CDCl_3$ solutions on a Varian T-60 spectrometer. Mass spectrometry was done with a Varian MAT 311A equipped with a combination chemical ionization–electron impact source.

Synthesis of Et_3SiOH. Et_3SiH (51.8 g, 0.45 mol) was dissolved in diethyl ether (96 g), and a mixture of H_2O (25 g, 1.4 mol), CH_3CN (13.3 g), and a small amount of Pd/C was added. The reaction was stirred at room temperature and monitored by GC. After 2 days, the reaction was complete. The top layer was decanted, filtered through Celite, and dried over $MgSO_4$, and solvent was removed by rotary evaporation. The last traces of CH_3CN were removed from the Et_3SiOH by adding toluene and then distilling the toluene/CH_3CN azeotrope and the excess toluene. The product obtained was 98% Et_3SiOH and 2% $(Et_3Si)_2O$ as established by GC analysis. The IR and NMR spectra were consistent. Anal. Calcd for $C_6H_{16}OSi$: C, 54.48; H, 12.19; Si, 21.24; Cl, 0. Found: C, 54.77; H, 12.00; Si, 20.16; Cl, <0.01.

Synthesis of Me_3SiOH.[4] $(Me_3Si)_2NH$ (17.5 g, 0.108 mol) was dissolved in 50 g of diethyl ether and the solution was added to a 500-mL flask containing 12.5 g of H_2O to which several drops of methyl orange indicator had been added. The mixture was stirred vigorously and cooled in a methanol–ice bath. Aqueous HCl (2 N) was added dropwise just until the indicator remained pink (about 70 mL). A small amount of $NaHCO_3$ was then added until the indicator was orange again. The aqueous and ether layers were separated, the aqueous layer was extracted with 50 mL of ether, and the combined ether fractions were dried over $MgSO_4$. After filtration, the ether was removed under vacuum to yield 18.6 g of Me_3SiOH (95%), which contained ca. 1% $Me_3SiOSiMe_3$ by GC analysis. The IR and NMR spectra were consistent.

Purification of Me_3SiOMe. Me_3SiOMe obtained from Silar Laboratories was distilled from anhydrous K_2CO_3, bp 56–57 °C, to yield pure Me_3SiOMe in which no impurities could be detected by GC. Anal. Calcd for $C_4H_{12}SiO$: C, 46.09; H, 11.61; Si, 26.95; Cl, 0. Found: C, 46.32; H, 11.70; Si, 26.42; Cl, 0.04.

Purification of $MeSi(OMe)_3$. Unpurified $MeSi(OMe)_3$ reacted spontaneously with Me_3SiOH at room temperature. Even after the $MeSi(OMe)_3$ was distilled from K_2CO_3, spontaneous reaction with Me_3SiOH occurred. However, after 20 g of $MeSi(OMe)_3$ was combined with 1 g of CH_3OH and 0.1 g of NaOMe and fractionally distilled through a 5-in. Vigreux column, bp 102–103 °C, to yield $MeSi(OMe)_3$ that was pure by GC analysis, no reaction with Me_3SiOH was observed after 30 min at reflux.

Reaction of Me_3SiOMe with Et_3SiOH. Me_3SiOMe (0.39 g, 3.8 mmol) and Et_3SiOH (0.50 g, 3.8 mmol) were mixed and the solution was analyzed by GC. The solution was sealed in a glass ampule and heated at 60 °C for 1 week. The ampule was opened and GC analysis of the solution showed that no reaction had occurred.

In another set of experiments, various amounts of Me_3SiCl were added to Me_3SiOMe before admixture with an equimolar amount of Et_3SiOH, and the room-temperature reaction was followed by GC or by the time required for a hazy solution to form. Results were as in Table I.

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Reaction between Triethylsilanol and Trimethylmethoxysilane

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A few years ago we reported that products of the reaction between triethylsilanol (Et_3SiOH) and trimethylmethoxysilane (Me_3SiOMe) can be observed by gas chromatography (GC) immediately after mixing at room temperature.[1] We noted that the reaction occurred faster and under milder conditions than anticipated on the basis of earlier studies. White and Olson report that, contrary to our earlier observations, Et_3SiOH and Me_3SiOMe do not react spontaneously at room temperature and their mixtures can be stored for long periods without any products being formed.[2] White and Olson attribute the rapid reaction observed by us to the probable presence of the catalytic impurity trimethylchlorosilane (Me_3SiCl) and further suggest that the level of impurity is 20–25%. They argue that because Me_3SiOMe and Me_3SiCl have nearly identical boiling points, 57–58 °C and 57 °C, respectively, and similar molecular weights, 104.3 and 108.7, respectively, the presence of the Me_3SiCl could have gone undetected in our study.

Fortunately, we still have on hand a sample of the Me_3SiOMe used in our previous study and were able to characterize it further. Now, measured 6 years after the sample was received, the sample shows the presence of Me_3SiCl by mass spectrometry (direct analysis) (MS) but not by GC–MS. The presumption is that the Me_3SiCl is such a reactive compound that it does not survive intact even under relatively mild GC conditions. Duplicate chlorine analyses by Galbraith Laboratories, Inc., gave

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1.86% and 1.97% chlorine. Addition of silver nitrate to the material gave a significant precipitate of AgCl. We conclude that indeed our sample of Me_3SiOMe does contain chlorine as Me_3SiCl. Our elemental analyses indicate that the level of impurity is in the range 5.7–6.0 wt % Me_3SiCl. When our sample is added to Et_3SiOH, cloudiness appears even now within about 1 min, slower than 6 years ago but still rapidly in terms of what White and Olson would predict for the concentration of chlorine that we find. In view of the difficulty of removing and detecting halide impurity in Me_3SiOMe by procedures commonly used to characterize a material before use, we recommend that before distillation and use, investigators routinely purify this material by adding silver nitrate until no more precipitate appears.

Because of the findings reported in this note, the conclusions from our earlier paper need to be modified. Pure Me_3SiOMe and Et_3SiOH do not react spontaneously at room temperature unless a catalyst is present. In the presence of a catalyst they react rapidly and give the products described before: methanol, $Me_3SiOSiEt_3$, $Me_3SiOSiMe_3$, and soon thereafter water. The conclusion that water is not necessary to hydrolyze the silane prior to its condensation with silanol groups remains the same. This conclusion is in agreement with the mechanisms proposed by Hertl,[3,4] who studied the mechanism of the reaction of gaseous silanes with silica, by Koelling and Kolb,[5] who made an infrared study of the reaction between silanes and silica, and by Smith,[6] who studied the reaction of an alkylsilanol with an alkoxysilane.

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Effect of Composition of Modified Trialkylaluminum Initiators in the Polymerization of 2-Methyloxacyclobutane

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Recently, we reported[1] that a high proportion of irregularities of the head-to-head, tail-to-tail type is formed when 2-methyloxacyclobutane (2-MOCB) is polymerized under the influence of the cationic initiators PF_5 and Et_3OPF_6.

Oguni and Hyoda,[2] however, succeeded in controlling the chain propagation to yield high molecular weight polymers with head-to-tail structure devoid of irregularities by using a coordination initiator based on $AlEt_3$ modified with H_2O and acetylacetone in accordance with the preparation by Vandenberg.[3] However, it was concluded that the applied initiator had little stereospecific ability based on polymerization experiments with both racemic and optically active monomers. Also the authors found that without the acetylacetone modifying agent only a polymer with low molecular weight was obtained.

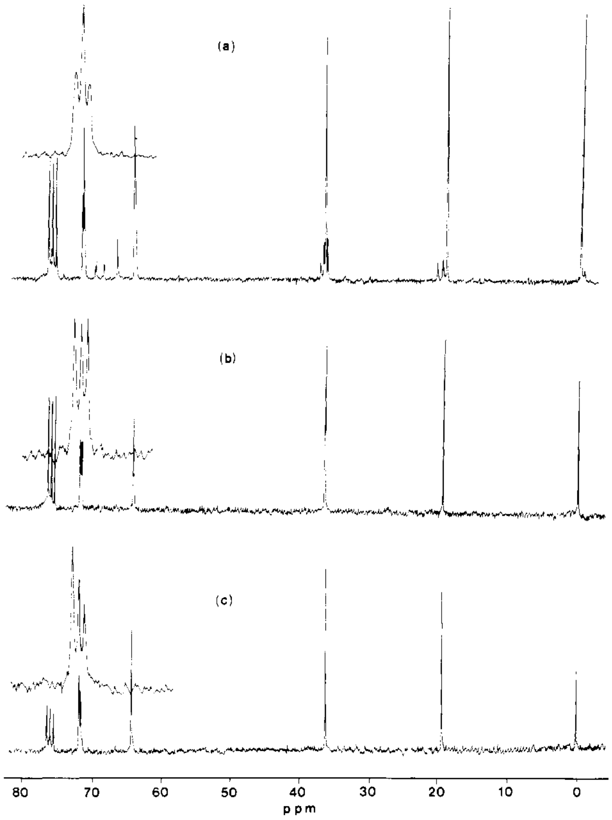

Figure 1. ^{13}C NMR spectra of poly(2-MOCB): (a) prepared with 1:0.5 $(i\text{-Bu})_3Al$–H_2O at −78 °C; (b) prepared with 1:0.5:0.5 $(i\text{-Bu})_3Al$–H_2O–Acac at 30 °C; (c) prepared with 1:0.5:1 $(i\text{-Bu})_3Al$–H_2O–Acac at 30 °C.

Simultaneously, we were investigating the polymerization of 2-MOCB, using $(i\text{-Bu})_3Al$ in the preparations of the initiators. Some representative data are shown in Table I and Figure 1. It is seen that we were able to obtain polymers with very high molecular weights even without the acetylacetone. The trialkylaluminum–water initiators were active toward the monomer at low temperatures and a high yield was obtained even after a short reaction time. The molecular weights are seen to increase sharply with lower polymerization temperature and the behavior is that typical for a cationic initiator. In a recent study of the polymerization of 2-MOCB using Et_3OPF_6 initiator we also obtained polymers with very high molecular weights.[4]

The coordination initiators operate by a different mechanism. A higher polymerization temperature is needed and even under these circumstances the propagation is slower and the yields tend to be lower. On the other hand, very high molecular weights are obtained. In the preparation of the coordination initiator the addition both of water and of acetylacetone should be limited. In separate experiments we found that when the amount of either of these components is increased much above a 1:1 ratio relative to $(i\text{-Bu})_3Al$, the initiator tends to precipitate and the activity drops.

The ^{13}C NMR spectra of some of the polymers are shown in Figure 1. The spectrum 1a of the polymer prepared with the cationic $(i\text{-Bu})_3Al$–water initiator is very similar to that previously published for poly(2-MOCB) prepared with triethyloxonium ion initiator.[1] The head-to-head, tail-to-tail structures are evident in accordance

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