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.

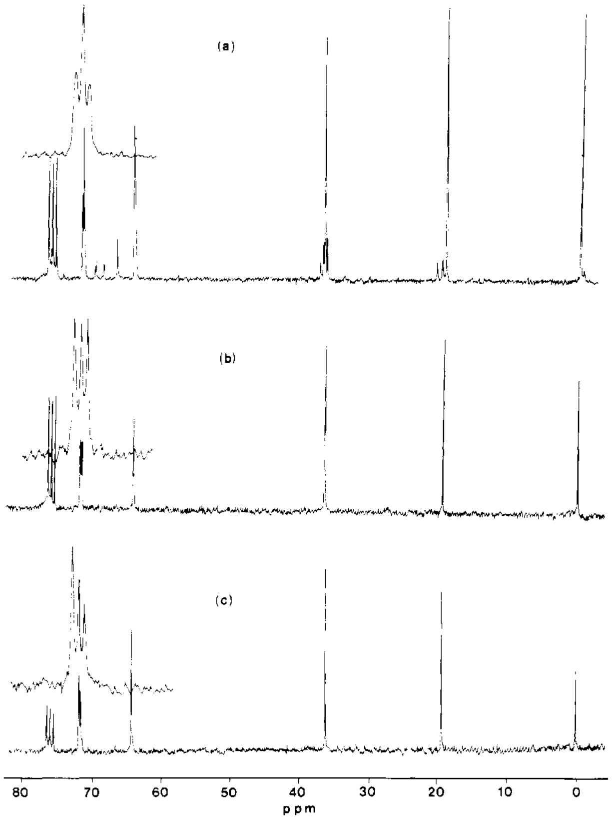

Figure 1. ^{13}C NMR spectra of poly(2-MOCB): (a) prepared with 1:0.5 $(i\text{-Bu})_3Al–H_2O$ at −78 °C; (b) prepared with 1:0.5:0.5 $(i\text{-Bu})_3Al–H_2O$–Acac at 30 °C; (c) prepared with 1:0.5:1 $(i\text{-Bu})_3Al–H_2O$–Acac at 30 °C.

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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Table I
Polymerization of 2-MOCB with Modified $(i\text{-Bu})_3$Al Initiators[a]

added per mole of $(i\text{-Bu})_3$Al	temp, °C	time, h	polymer yield, wt %	$\overline{M}_n$[b] × 10^{-3}	$\overline{M}_w$[b] × 10^{-3}	[η],[c] dL/g
0.5 H_2O[d]	0	45	92	12	38	0.35
0.5 H_2O	−78	120	67	210	475	3.7
0.67 H_2O	60	49	94	4	16	
0.67 H_2O	−30	0.25	45	33	147	
0.67 H_2O[e]	−30	88	72	74	185	2.6
1.0 H_2O	−30	25	86	57	145	
0.5 H_2O, 0.5 Acac	30	266	41	40	770	
0.5 H_2O, 0.5 Acac	0	1107	0.9			
0.5 H_2O, 0.5 Acac	−30	138	0.8			
0.4 H_2O, 0.8 Acac	30	843	60	290	895	6.9
0.5 H_2O, 1.0 Acac	30	721	37	300	970	
1.0 H_2O, 0.5 Acac	30	836	1.9			

[a] Polymerizations carried out in *n*-heptane solution under the following conditions (unless otherwise indicated): concentration of monomer, 3.4 mol L^{-1}; concentration of initiator ($(i\text{-Bu})_3$Al basis), 0.07 mol L^{-1}. [b] Determined by gel permeation chromatography in THF. [c] Intrinsic viscosity was measured in chloroform at 25 °C. [d] Concentration of monomer, 7.5 mol L^{-1}; concentration of initiator, 0.15 mol L^{-1}. [e] Concentration of monomer, 1.0 mol L^{-1}; concentration of initiator, 0.02 mol L^{-1}.

with the previous assignment of the signals.[1] It is noted that the triplet signals at 72.6, 72.7, and 72.8 ppm arising from the methine carbons in the stereochemical triads in the head-to-tail structures appear in intensity ratios very close to 1:2:1, indicating randomness of the configuration and no stereoselection by the applied initiator. The spectra 1b and 1c of the polymers prepared with the coordination initiators clearly indicate the absence of head-to-head, tail-to-tail structures as found also by Oguni and Hyoda for the polymer prepared with their initiator. Interestingly, we find, however, a marked shift in the intensity distribution of the triplet signals, appearing at the same positions as in spectrum 1a from the triad structures, being 1:1:1.2 in the case of 1b and 1:1.2:1.6 in the case of 1c. Therefore, the distribution of the chiral carbons is not random in the polymers prepared with the coordination initiators. Thus these initiators are able to exert an influence on the stereochemistry of the propagation. It is seen that the signal at 72.8 ppm arising from the syndiotactic triad, as already assigned to the lowest field,[2] grows in intensity at the expense of the signals from the heterotactic and isotactic triads. This effect appears to be accentuated by increasing the amount of acetylacetone in the initiator. However, as already pointed out, this amount must be limited.

In the case of the cationic polymerization of 2-MOCB, stereospecificity is not found because both of the oxygen–carbon bonds in the cyclic oxonium ion may open in the propagation step, and it appears that the chain end is not able to exert a controling influence during the propagation of this monomer. Vandenberg found[5,6] with this type of cationic initiator that tactic polymers could be obtained in the case of the disubstituted epoxides *cis*- and *trans*-2,3-epoxybutane, since with these monomers a chain end interaction with the oxonium ion causes the ring opening to take place in a specific manner or an enantiomeric selection takes place during the process. in the case of the coordination polymerization of 2-MOCB the basic condition for obtaining head-to-tail polymers is fulfilled, namely, that the bond breakage in the cyclic propagating intermediate occurs in a specific manner. The coordination complex also has some ability to select between the two enantiomeric forms of the monomer, yielding a less than random proportion of heterotactic structures. The nature of this controlling influence, however, has not been investigated, and it is not known presently if the polymers produced are homogeneous with respect to stereochemical distribution.

Experimental Section

Materials. The monomer 2-MOCB was prepared as previously described.[1] Triisobutylaluminum (Fluka, practical grade) was used as received. *n*-Heptane was distilled and was more than 99.5% pure as determined by gas chromatography. Acetylacetone (Merck, synthesis grade) was distilled prior to use.

Initiator Preparation. The preparations were carried out in a glovebox by adding water to a solution of $(i\text{-Bu})_3$Al in *n*-heptane at 0 °C under magnetic stirring. In the case of the preparation of the coordination initiator, acetylacetone was subsequently added after 30 min (0 °C). The solutions were stirred for 24 h at room temperature prior to use.

Polymerization Experiments. All polymerizations were carried out by using standard high-vacuum techniques. The initiator solutions were added with a syringe to the polymerization ampules. The polymerizations were terminated by addition of ethanol containing concentrated hydrochloric acid. The solutions were subsequently washed with 1 N sodium hydroxide and water.

Characterization of Products. Molecular weights were determined by gel permeation chromatography (Waters Model 200) using THF solvent and polystyrene gel columns with porosities 10^6, 2×10^4, 10^4, and 10^3 Å. The molecular weight values were calculated on the basis of a calibration curve obtained with narrow molecular weight samples of polystyrene from Water Associates. The calculations were based on the principle of extended chain lengths applying a *Q* value (weight per Å) of 15.4. The ^{13}C NMR spectra were obtained in deuteriochloroform at room temperature with tetramethylsilane as internal reference on a Bruker HX270 FT spectrometer operating at 67.89 MHz.

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Decalin Ring Structures in the Products of BF_3-Catalyzed Oligomerization of Cyclopentene

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Cationic polymerizations of alkenes are commercially important processes for the preparation of widely used

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