Controlled Cationic Polymerization of Hexamethylcyclotrisiloxane[†]

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ABSTRACT: Cationic polymerization of hexamethylcyclotrisiloxane (D_3) initiated by HCl and antimony pentachloride ($SbCl_5$) may give a high polymer (HP) with controlled molecular weight in high yield, and only small amounts of cyclic compounds. Theoretical M_n's were formerly obtained with D_3 using as initiator either triflic acid or a combination of a silyltriflate activated by triflic acid. However, considerable amounts of cyclic compounds were also formed, e.g. 50 wt % D_6/HP and up to 20% macrocycles. D_6 was mainly formed by a reaction involving transitory oxonium ions and macrocycles by cyclization of silanol esters. Using two other initiating systems, the formation of D_6 and macrocycles was significantly decreased and was sometimes suppressed. The polymerization was rapid with $SbCl_5$ and HCl at −10 °C, producing about 90% high polymer of $M_n \geq 10^5$, 10−12% small cycles (only 3% D_6) and no macrocycles. The M_n's agreed with an initiation by HCl and a propagation involving the silanol end groups, which explains the absence of macrocycles and the low amount of D_6. However, the polymer degraded somewhat after the completion of the polymerization. A comparison was done with the initiation described by G. Olah et al., in which a silyl cation (e.g., $(CH_3)_3Si^+$) was formed by reaction of R_3SiH and Ph_3C^+, $B(C_6F_5)_4^-$. At 20 °C, $M_n > M_{n_{th}}$, but degradation occurred afterward, while at −20 °C, $M_n \sim M_{n_{th}}$, and degradation was very slow. However, cyclics formation was, in both cases, larger than with HCl and $SbCl_5$ (25−33%), although very little D_6 formed, which seems to exclude propagation involving mainly silyloxonium ions.

1. Introduction

There has been extensive investigation of D_3 and D_4 cationic polymerizations initiated by protonic acids, especially trifluoromethanesulfonic acid (triflic acid).[1−9] The molecular weights were controlled with D_3.[5,9] This control, as well as the kinetics, could be explained by a polymerization (without significant transfer) occurring on the two silyltriflate end groups. M_n grew linearly from the origin with D_3 conversion and high polymer yield. The esters themselves were nonreactive, but propagation took place in the presence of residual acid. For example, in CH_2Cl_2 at 20 °C with $D_3 \sim 1$ mol·L^{-1} and $CF_3SO_3H \sim 10^{-3}$ mol·L^{-1}, the concentration of macromolecules is 0.4$[CF_3SO_3H]_0$, that of silyltriflates 0.8$[CF_3SO_3H]_0$, and that of unreacted acid 0.2$[CF_3SO_3H]_0$.[7−9] This acid is hydrated with about 1.5 equiv of H_2O.

The main drawback of these polymerizations is the lack of control of cyclics formation. Simultaneously with fast formation of linear high polymer (HP), D_3 polymerization produces an equivalent amount of D_6 and significant amounts of D_9 and macrocycles: e.g., D_6/HP (in wt %) varies with $[D_3]_0$ between 0.4 and 1.3, D_9/HP between 0.1 and 0.2, and macrocycles/HP from 0.2 to 0.7.[8,9] From the variation of relative amounts of D_6, D_9, and macrocycles with $[D_3]_0$ and $[TfOH]_0$, we concluded that cyclics form by two different mechanisms operating simultaneously: cyclization of silanol esters $HD_{3x}OTf$ and a special type of backbiting reaction.[8,9,11] For example, D_6 forms mainly by a reaction involving a transitory tertiary oxonium ion polyD−D_3^+, giving polyD−D_6^+ and then D_6, macrocycles form by cyclization of $HD_{3x}OTf$, and D_9 forms by both mechanisms. This was confirmed using conditions that suppress SiOH groups: macrocycles do not form in the presence of a large excess of the silyltriflate $PhCH_2(CH_3)_2SiOTf$, which also quantitatively incorporated $PhCH_2(CH_3)_2Si$ end groups in the high polymer, with a $DP_n = [D_3]cons_{HP}/[ester]$.[10]

We first attempted to better control the polymerization by using complexes of antimony pentachloride with acyl chlorides such as acetyl chloride or 1-naphthoyl chloride as initiators.[11] Molecular weights were controlled at −10 °C in CH_2Cl_2 (with a first order consumption of D_3), although large amounts of D_6, D_9, and macrocycles formed even in the presence of about 6% 2,6-di-*tert*-butyl-4-methylpyridine (DBMP). In fact D_6/HP (up to 2) could be larger than with CF_3SO_3H initiation.

Our general interpretation was that there are two populations of macromolecules. One population would bear two potentially active sites (or one active site and one nonreacting end group), which produces linear high polymer, and another population, with one active site and a reacting end group at the other end (e.g., CH_3CO_2Si) undergoing end-to-end ring-closure to produce macrocycles and smaller cycles. However, no definite conclusion could be reached about the nature of the growing species and unreactive end groups.

D_3 was also polymerized in the presence of $SbCl_5$ alone (purified by distillation from Cu and then as CH_2Cl_2 solution kept over P_2O_5 films).[11] The rate was only 2−4 times lower than with the same amount of CH_3COCl plus $SbCl_5$. However, the reaction was slowed considerably in the presence of only 5% 2,6 di-*tert*-butyl-4-methylpyridine (DBMP) and no high polymer was formed. This showed that the initial $SbCl_5$ solution contained small amounts of HCl that participated in the reaction unless trapped by DBMP.

In our previous publication,[11] we attempted to reduce or suppress the formation of cyclics in polymerizations initiated by $SbCl_5$ associated with dimethyl dichloro-

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silane, assuming that initiation occurs by activation of SiCl groups (eqs 1−3).

$$(CH_3)_2SiCl_2 + SbCl_5 \rightarrow Cl(CH_3)_2Si^+, SbCl_6^- \quad (1)$$

$$Cl(CH_3)_2Si^+, SbCl_6^- + D_3 \rightarrow Cl(CH_3)_2SiD_3^+, SbCl_6^- \quad (2)$$

$$Cl(CH_3)_2SiD_3^+, SbCl_6^- + (x-1)D_3 \rightarrow Cl(CH_3)_2SiD_{3x}^+, SbCl_6^- \quad (3)$$

The $ClSi(CH_3)_2OSi$ end groups would be deactivated toward electrophilic attack (relative to $CH_3CO_2-Si(CH_3)_2OSi$), thereby preventing cyclization by end-to-end ring closure. With $[SbCl_5] = 2.9 \times 10^{-3}$ mol·L^{-1} and $(CH_3)_2SiCl_2 = 7.26 \times 10^{-4}$ mol·L^{-1}, no macrocycles were formed up to 77% conversion (in 55 min), giving 85% high polymer ($M_n = 10^5$) and a small amount of small cycles (with $[D_5] > [D_6] > [D_4]$). However, after 2.6 h, the amount of high polymer decreased and a lower molecular weight fraction formed together with D_5 and D_6, showing that the polymer degrades after monomer is consumed. Since no hindered pyridine (DBMP) had been added, we did not exclude initiation involving HCl, which might give silanol end groups susceptible to end-to-end ring closure, although they could have been suppressed through condensation of −SiOH-ended macromolecules (eq 4). This publication will try to understand

$$2 \sim SiOH \xrightarrow{SbCl_5,\ HCl} \sim SiOSi \sim + H_2O \quad (4)$$

the possible roles of HCl and of Me_2SiCl_2 in the control of D_3 cationic polymerization co-initiated by $SbCl_5$.

2. Experimental Section

Materials. Methylene chloride (SDS, Pestipur; stabilized with amylene) was refluxed with oleum for 24 h, neutralized and washed with water. A distilled fraction (pure according to gas chromatography) was dried under vacuum on a P_2O_5 film and several sodium films. CD_2Cl_2 (Eurisotop) was only dried over sodium.

2,6-Di-*tert*-butyl-4-methylpyridine (DBMP, Fluka) was sublimated several times under vacuum and dissolved in CH_2Cl_2, and the resulting solution was dried for 5 days on predried silica gel.

D_3 (Rhône Poulenc) was first sublimated under vacuum (purity higher than 99.9%), dried at 80 °C on CaH_2 (1 h) and twice on sodium films (30 min each time), and then after a new sublimation dissolved in CH_2Cl_2.

Trityl Tetrakis[pentafluorophenyl]borate (Ph_3C^+, $B(C_6F_5)_4^-$) was prepared by a modified literature method[12] by mixing $KB(C_6F_5)_4$ (Rhône Poulenc, 4.1 mM) and Ph_3CCl (5.3 mM) in dry hexane (150 mL) and refluxing for 12 h. After filtration, the crude product was dissolved in dichloromethane and filtrated in order to remove KCl formed. The yellow salt was recrystallized in hexane/dichloromethane (10:1).

Dimethyldichlorosilane (Me_2SiCl_2, Aldrich, 99%) and benzyldimethylsilane ($BzMe_2SiH$, Hüls) were redistilled and conditioned under vacuum in sealed calibrated tubes with break-seals, and kept in the dark. Trimethylsilane (Me_3SiH, ABCR) was used as received and conditioned as previously.

Pentamethyldisiloxan-1-ol ($(CH_3)_3SiO(CH_3)_2SiOH$). After synthesis of 1-chloropentamethyldisiloxane from octamethylcyclosiloxane (D_4, Rhône Poulenc), the silanol was obtained as previously described[13] by hydrolysis of the chloride in the presence of an excess of pyridine. After distillation under vacuum (70 °C, 40 mm Hg), a NMR control showed the main fraction of silanol contained as impurity only 20% pyridine. This may explain its stability for several days, and it was used without other purification.

Antimony pentachloride (Baker (99%) or Aldrich (99.9%), samples A, B, and C) was refluxed over copper turnings and distilled under vacuum into break-seal tubes. Samples were prepared as CH_2Cl_2 solutions and either dried over a P_2O_5 film only (samples A, B, and C) or successively over P_2O_5 and a sodium film for 5 min at −30 °C (sample B, Na) in order to suppress or control the amounts of H_2O or HCl present. This "control" was erratic. Although we assumed sample B (passed over sodium) would have the lowest HCl or H_2O concentration, polymerization of D_3 produced mainly D_{3x} cycles and only small amounts of high polymer. Sample A (A, P_2O_5) produced mainly high polymer, but the addition of 5% DBMP (based on $[SbCl_5]$) strongly reduced the polymerization rate without formation of high polymer.

Sample C (C, P_2O_5), which was used the most, contained a large amount of HCl that we could not remove. The HCl content was determined by using equimolar amounts of $SbCl_5$ and DBMP (dried over silicagel) in a CH_2Cl_2/CD_2Cl_2 solution (1:1). ^{1}H NMR analysis under vacuum showed the presence of equal amounts in moles of the base B ($\delta = 1.35$; 2.32; 6.97 ppm) and of BH^+ ($\delta = 1.58$; 2.74; 7.66 ppm). Premixing sample C with various amounts of DBMP, this initial 50% molar amount of HCl could be reduced.

Sample D (Aldrich, 99.99% purity) was used without drying. After being degassed under high vacuum, $SbCl_5$ was distilled and stored under vacuum in calibrated tubes. This sample contained a 45% molar amount of HCl.

Polymerization Procedures. Polymerizations were carried out in an apparatus previously described in detail.[9] For experiment 16, a bulb of 1 mL containing solutions of $SbCl_5$ (0.16 mL; 0.133 mol·L^{-1}), DBMP (0.053 mL; 0.16 mol·L^{-1}), and $(CH_3)_3SiCl_2$ (0.025 mL; 0.207 mol·L^{-1}) was introduced in the apparatus. After vacuum degassing by flame heating, the apparatus was sealed and 7.5 mL of a D_3 solution (0.70 mol·L^{-1}) was introduced. After cooling at −10 °C, the bulb was broken via a magnetic device in the stirred solution. The first three samples were collected by side tubes sealed to the main vessel and isolated by Rotaflo stopcocks after 2.4, 6.1, and 12.3 min. The samples were immediately deactivated by a pyridine solution in CH_2Cl_2 ($[Pyr] = 5[SbCl_5]$). The following samples were collected at longer times in a similar way via a Young tap equipped with an ultrahigh vacuum joint (UHV).

In the system $R_3SiH-Ph_3C^+$, $(C_6F_5)_4B^-$, the trityl salt was first introduced in the D_3 solution before breaking the bulb of the silane solution. In presence of the trityl salt alone, no D_3 consumption was observed after 30 min.

After filtration, deactivated CH_2Cl_2 solutions were directly injected in SEC. Percentages of high polymer, macrocycles, and cycles were determined from SEC chromatogram and more precisely for the small cycles (D_3-D_{12}) by GC. Polymerization rates are initial rates R_{p_0} in mol·L^{-1}·s^{-1} derived from D_3 consumption.

Techniques. Gas chromatographic analysis was carried out with a Carlo Erba GC 6000 Vega equipped with a capillary column (25 m) and temperature programming between 40 and 320 °C.[10] SEC chromatography (Waters Ass.) was done using 7 columns: 5 microstyragel columns Waters (10^5, 10^4, 10^3, 500, and 100 Å) and 2 PL gel columns Touzart et Matignon (100 and 50 Å). The flow rate of toluene, used as solvent, was 1.2 mL/min. The M_n's were calculated using a polystyrene calibration. ^{1}H NMR spectra were recorded on a Bruker AC200 spectrometer using dried $CDCl_3$ or CD_2Cl_2.

3. Results and Discussion

3.1. Reproducibility of Experimental Results According to $SbCl_5$ Origin.

The first experiments with $SbCl_5$ and Me_2SiCl_2 giving predominantly the high polymer[11] were performed with a sample of $SbCl_5$ (A, P_2O_5) only refluxed over Cu, distilled, and kept some time over a P_2O_5 film.

Experiments with samples B (B, P_2O_5 and B, Na, see Experimental Section) were carried out with or without addition of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) and Me_2SiCl_2. They all gave similar results: little or no high polymer, and predominant formation of cycles with $D_6 > D_9 > D_{12} \geq$ macrocycles $> D_4 + D_5$. With the largest amount of DBMP (18% of $SbCl_5$) polymerization was nearly stopped (5% D_3 conversion in 7 h) showing that HCl was necessary for the reaction. With a decreasing amount of DBMP (15% and 10%), conversion increased and HP increased. Using sample B, P_2O_5 with 10% DBMP gave a conversion of 81% in 54 min. Only 10% high polymer ($M_n = 7.6 \times 10^4$) was formed, with 43% D_6, 11% D_9, 6% D_{12}, and 3.5% macrocycles. There was a direct correlation between the amount of residual HCl and HP formation, but the predominant formation of cycles D_{3x} is not easily explained. They could be formed by cyclization of silanol esters $HD_{3x}Cl$ activated by $SbCl_5$ (eqs 5−8).

$$HCl + SbCl_5 \rightleftharpoons H^+, SbCl_6^- \qquad (5)$$

$$H^+, SbCl_6^- + D_3 \rightarrow H(OSi)_3^+, SbCl_6^- \qquad (6)$$

$$H(OSi)_3^+, SbCl_6^- + xD_3 \rightarrow H(OSi)_2D_{3x}OSi^+, SbCl_6^- \qquad (7)$$

$$H(OSi)_2D_{3x}OSi^+, SbCl_6^- \rightarrow (D_3)_{x+1} + H^+, SbCl_6^- \qquad (8)$$

This might occur when [HCl] is low, giving low concentrations of −SiOH, −SiCl, and H^+ $SbCl_6^-$ and a very small rate of condensation of −SiOH (eq 4). An alternative explanation of the major formation of D_{3x} cycles in experiments with sample B, Na would be the accidental presence of a larger amount of water leading to the formation of oligomeric disilanols that can cyclize.

The following two samples C and D of different origins were not treated with sodium, and were prepared either as sample A (sample C) or by simple distillation under vacuum (sample D). They both contained a high concentration of HCl and gave predominantly the high polymer.

3.2. Polymerization with Controlled Concentration of HCl. After the preliminary experiments showing that not only the polymerization rate but also the relative amount of cyclic and linear products depended on HCl concentration, our aim has been to determine the best conditions to suppress cyclics formation and to control the molecular weight. With a pure $SbCl_5$, the effect of the addition of HCl in increasing concentration could have been studied. Unfortunately, we had to use a $SbCl_5$ sample from a third origin ($SbCl_5$, C) and we found that it contained a large amount of HCl that we could not remove. Since it appeared that a predominant formation of high polymer was obtained only with a relatively large amount of HCl (e.g., about 10% of $SbCl_5$), we have modified its concentration by adding an increasing amount of DBMP to $SbCl_5$ containing a 50% molar amount of HCl (see experimental).

Polymerization Rates. For experiment 12 carried out with the addition of 2.9×10^{-3} mol·L^{-1} of $SbCl_5$ (and 1.45×10^{-3} mol·L^{-1} of HCl), the polymerization rate (calculated from the initial slope) was so fast that it could not be determined (see Figure 1). D_3 conversion was 99.7% in 3.2 min ($R_{p_0} > 40 \times 10^{-4}$ mol·L^{-1}·s^{-1}) with 73% HP, only 6% D_6 (< D_5: 7.9%) and 10% macrocycles.

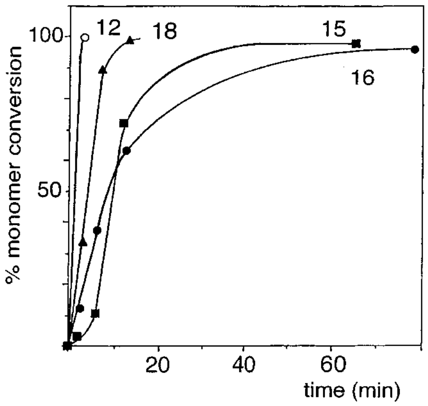


Figure 1. Polymerization of D_3 by HCl−$SbCl_5$ at −10 °C in CH_2Cl_2. $[D_3]_0 = 0.73$ mol·L^{-1}; $[SbCl_5] = 2.9 \times 10^{-3}$ mol·L^{-1}; $[HCl] = 1.45 \times 10^{-3}$ mol·L^{-1}. Experiment 12: no additive; Experiment 18: $[DBMP] = 1.16 \times 10^{-3}$ mol·L^{-1} Experiment 15: $[Me_2SiCl_2] = 0.73 \times 10^{-3}$ mol·L^{-1} Experiment 16: $[DBMP] = 1.16 \times 10^{-3}$ mol·L^{-1} and $[Me_2SiCl_2] = 0.73 \times 10^{-3}$ mol·L^{-1}.

With the same initial D_3, $SbCl_5$, and HCl concentrations (experiment 18) but in the presence of 1.16×10^{-3} mol·L^{-1} of DBMP (which consumed 80% of HCl), the residual HCl concentration is assumed to be 10% of $SbCl_5$ and the polymerization rate decreased strongly (R_{p_0}: 15×10^{-4} mol·L^{-1}·s^{-1}, see Figure 1).

With the same DBMP amount but the supplementary addition of 7.26×10^{-4} mol·L^{-1} of Me_2SiCl_2 (experiment 16) there was a further decrease of R_{p_0} to 7.5×10^{-4} mol·L^{-1}·s^{-1} (see Figure 1). With a large excess of amine over $[HCl]_0$ no polymerization took place (experiments 13 and 14; see Table 1).

The decrease of the polymerization rate between experiments 12 and 18 results from the smaller concentration in HCl. The further decrease in experiment 16 may result from the suppression of the SiOH groups (by reaction with Me_2SiCl_2 in excess) and their replacement by Me_2SiCl end groups. This would imply the occurrence of a propagation on SiOH end groups when they are present (eq 9). In experiment 15, no pyridine

$$\sim\sim SiOH + HD_3^+, SbCl_6^- \rightarrow \sim\sim SiD_3OH + H^+, SbCl_6^- \qquad (9)$$

was present, but 7.26×10^{-4} mol·L^{-1} of Me_2SiCl_2 was added. The shape of the conversion curve was completely different from those of experiments 16 and 18 (with DBMP) for which D_3 consumption was approximately first order in $[D_3]$. The initial rate was much lower, showing an inhibitory effect of Me_2SiCl_2, but was followed after 6 min by an autoacceleration, which led to a rate larger than for experiment 16. A similar autoacceleration had been observed for experiment 2 (initiation by $SbCl_5$, A, P_2O_5) also with addition of only Me_2SiCl_2, which contained presumably less than 10% HCl (based on $[SbCl_5]$). In these two cases, the strong decrease in the initial rate results probably again from the suppression of SiOH end groups by reaction with Me_2SiCl_2. But, since $[HCl] = 2[Me_2SiCl_2]$ in experiment 15, SiOH may be formed again after Me_2SiCl_2 has been consumed, explaining the autoacceleration above 10% yield.

What may seem more difficult to explain is why in experiment 16 in which [HCl] is lower (DBMP added) the initial rate is larger than in experiment 15 (same amount of Me_2SiCl_2; no DBMP added). In that case, the

Table 1. Polymerization of D_3 by HCl−$SbCl_5$ at −10 °C in the Presence of Hindered Pyridine (DBMP) and $(CH_3)_2SiCl_2$[a]

expt	[HCl] × 10^3, mol·L^{-1}	[Me_2SiCl_2] × 10^3, mol·L^{-1}	[DBMP] × 10^3, mol·L^{-1}	time, min	D_3 convn, %	D_4 + D_5, %	D_6, %	D_9, %	MC, %	HP, %	M_n × 10^{-3}	$M_{n_{th}}$(HCl) × 10^{-3}
2		7.26		2	1.9	0.2	0.8	0.08		1.5	14	
				55	77.1	3.8	2.1			65	102	
12	1.45			3.2	99.7	8.5	6	1	10.3	73	170	82
13	0		2.12	23 h	0							
			(73%)[c]									
14	0	0.726	2.12	24 h	0							
			(73%)[c]									
15	1.45	0.726		1.9	3.1	0.5	0.3			2.3	7	2.5
				5.9	10.5	0.9	0.5			9.2	29	10
				11.7	72.1	3.8	2.8			64.6	136	68
18	0.29[b]		1.16	3.1	33.6	1.4	2.3			29.9	170	180
			(40%)[c]	7.0	89.6	3.9	2.7	0.2		81.7	328	448
16	0.29[b]	0.726	1.16	2.4	12.2	0.45	0.8			10.9	LP 2.3 (3.6%)	60
			(40%)[c]								HP 126 (7.3%)	
				6.1	37.3	1.4	0.8			35.2	102	195
				12.3	63.1	2.4	1.7			57.6	195	311

[a] [$SbCl_5$] = 2.9 × 10^{-3} mol·L^{-1} (experiment 2: sample A, P_2O_5 ; experiments 12−18: sample C, P_2O_5); $[HCl]_0$ = 1.45 × 10^{-3} mol·L^{-1}. $[D_3]_0$: Experiment 2 = 1.31 mol·L^{-1}; experiment 18 = 0.79 mol·L^{-1}; other experiments = 0.73 mol·L^{-1}. [b] [HCl] = $[HCl]_0$ − [DBMP]. [c] % of DBMP based on [$SbCl_5$]. HP = high molecular weight linear polymer. LP = low molecular weight linear polymer. DBMP = 2,6-di-*tert*-butyl-4-methylpyridine.

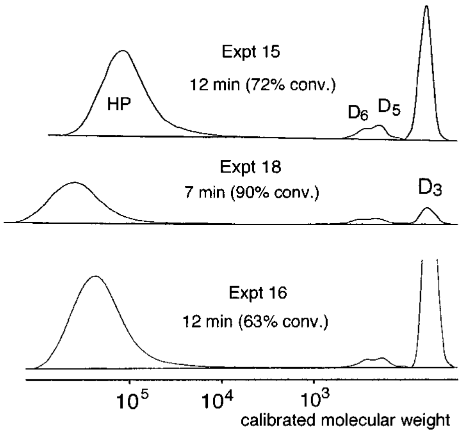


Figure 2. Polymerization of D_3 by HCl−$SbCl_5$ at −10 °C. Absence of macrocycles. SEC chromatograms: $[D_3]_0$ = 0.73 mol·L^{-1}; [$SbCl_5$] = 2.9 × 10^{-3} mol·L^{-1}; [HCl] = 1.45 × 10^{-3} mol·L^{-1} ; Experiment 15: [Me_2SiCl_2] = 0.25 [$SbCl_5$]; Experiment 18: [DBMP] = 0.4 [$SbCl_5$]; Experiment 16: [DBMP] = 0.4 [$SbCl_5$], [Me_2SiCl_2] = 0.25 [$SbCl_5$].

suppression of silanol groups in the presence of Me_2SiCl_2 in excess (0.73 × 10^{-3} mol·L^{-1}) would be expected to be complete after some time, and initiation by $OSiMe_2Cl$ end groups (and eventually on Me_2SiCl_2) seems to be the most likely hypothesis. This might be possible—with a propagation rate lower than with SiOH—in the presence of $HDBMP^+$, $SbCl_6^-$ and excess $SbCl_5$. The $OSiMe_2Cl$ end group would be activated by the salt, as hypothesized for the living polymerization of isobutylvinyl ether at −20 °C in CH_2Cl_2, initiated by $CH_3CH(O\text{-}i\text{-}Bu)Cl/Bu_4NTiCl_5$.[15]

The first isolated polymer sample of experiment 16 was bimodal, which may indicate an initial propagation on two different sites, the most reactive one (yield 7.3%; M_n = 1.26 × 10^5) eventually involving SiOH. See also later the M_n in this experiment.

Formation of Cyclic Compounds. A general feature of these polymerizations with controlled high concentration in HCl is the low amount of cyclics by comparison with experiments initiated by triflic acid or by RCOCl, $SbCl_5$ (see Table 1 and Figure 2).

Only small amounts of D_4, D_5, and D_6 (and D_9) are formed at the beginning. They increase progressively with D_3 conversion, but the total amount is not higher than about 10% of high polymer, except after total monomer consumption. This is the case for experiment 12 (only one sample available at 99.7% yield in 3.2 min), the only experiment in which macrocycles (10%) were observed. This may also result from a degradation reaction at the end of the polymerization as observed after about 1 h in all experiments. This degradation probably involves the strong acid $HSbCl_6$.

In experiment 2 (without additive) which was slower (lower HCl concentration) and in experiments 15, 16, and 18, the absence of macrocycles (see Figure 2) may be attributed to a propagation involving the SiOH groups. There is also a very small formation of small cycles(<10%, with D_5 > D_6 > D_4).

Molecular Weights in Relation to HCl Concentration. With 50% HCl (experiment 12) the experimental M_n ($M_{n_{exp}}$) is about double that of theoretical M_n ($M_{n_{th}}$) based on $DP_{n_{th}}$ = $[D_3]cons_{HP}/[HCl]$. This may result from the condensation of the SiOH end groups (eq 4) toward the end of polymerization, catalyzed by H^+, $SbCl_6^-$.

With only 10% HCl (experiment 18, 40% DBMP) there is a rather fair agreement with $[DP_n]$ = $[D_3]cons_{HP}/[HCl]$, which would imply that the SiOH condensation did not take place. This might result from the lower concentration of SiOH and of H^+, $SbCl_6^-$ when 40% DBMP is added.

When Me_2SiCl_2 is added (experiments 15 and 16), it may control the M_n. This might occur through initiation, particularly in the presence of pyridine if it might act as a donor (eq 10)[14] but appears unlikely, since in experiment 14 in which [DBMP] was higher than $[HCl]_0$, no polymerization occurred in the presence of Me_2SiCl_2 and DBMP in excess.

$$Me_2SiCl_2 + D_3 \xrightarrow{DBMP} ClMe_2SiD_3Cl \qquad (10)$$

The control of the M_n may occur by end-capping of the SiOH end groups (eq 11).

$$HD_{3x}Cl + Me_2SiCl_2 \rightarrow ClSiMe_2D_{3x}Cl + HCl \qquad (11)$$

In experiment 15 (with added [Me_2SiCl_2] = $^1/_2[HCl]_0$), the decrease in the initial rate (Figure 1) results from the inactivation of SiOH groups by Me_2SiCl_2 as long as it is present, giving oligomers with less active end

Table 2. Effect of Silanol Addition ($(CH_3)_3SiO(CH_3)_2SiOH$) on D_3 Polymerization Initiated by HCl−$SbCl_5$ at −10 °C

$[D_3] \times 10^3$, mol·L^{-1}	$[SbCl_5] \times 10^3$, mol·L^{-1}	$[HCl] \times 10^3$, mol·L^{-1}	[silanol] × 10^3, mol·L^{-1}	t, min	D_3 convn, %	HP, %	$M_n \times 10^{-3}$	$M_{n_{th}} \times 10^{-3}$
1.1	3.17	1.42		15	1.5	1.5		
				45	40.3	38.8	88	60
				120	86.5	66.4	113	101
1.02	2.96	1.07	0.895[a]	15.5	20.5	19	36	21.6
				30	52	49	48	54.7
				43	78	62	76	70.2
				60	97	73.4	60	81.4

[a] Addition 11.6 min after HCl−$SbCl_5$ initiation.

groups. However, HCl is re-formed in eq 11, leading to autoacceleration and giving a total number of macromolecules equal to [Me_2SiCl_2].

In experiment 16, in which $SbCl_5$, HCl, Me_2SiCl_2, and DBMP are present, the lower concentration in HCl leads to slower condensation reaction and to a possible growth on SiOH at the beginning in parallel with a propagation on the OSiCl end groups. The high molecular weight fraction in the bimodal distribution observed after 2.4 min (11% HP yield) would result from a fast growth on SiOH (eq 9), and the low molecular weight fraction from the activation of SiCl. The bimodality "disappears" at higher yield because polymer of high molecular weight is progressively formed on the two SiCl end groups after SiOH has disappeared. At higher HP yield (35 and 57%) the DP_n are lower than expected from the initial HCl concentration and blocking of SiOH by Me_2SiCl_2 ($DP_{n_{th}} = [D_3]cons_{HP}/[HCl]$). This may result from further initiation by HCl resulting from the blocking reaction, which would lead to a calculated M_n = 158 000 at 57% HP, if reinitiation occurred quantitatively after the fast blocking. The experimental M_n = 195 000 may result from the presence of coupled macromolecules of the polymer formed initially on SiOH end groups.

Polymerization in the Presence of Silanol. Propagation involving silanol groups (with either monomer or silanol activated by HCl−$SbCl_5$) explains both the control of the M_n by HCl concentration, the very small formation of D_6 and the absence of macrocycles. To justify this hypothesis, an experiment was done with addition of a model silanol ($(CH_3)_3SiO(CH_3)_2SiOH$) as initiator (see Table 2). A new solution of $SbCl_5$ was used (sample D), only purified by distillation and dissolved in dry CH_2Cl_2. The HCl concentration in this sample was 45% of [$SbCl_5$]. Without added silanol, the polymerization of D_3 (1.1 mol·L^{-1}) occurred with an induction period (with $[SbCl_5] = 3.17 \times 10^{-3}$ mol·L^{-1}) and then with a first order in [D_3] (see Figure 3). In a second polymerization, 0.89×10^{-3} mol·L^{-1} of the silanol was added after 11 min and led to an apparent rate constant three times larger than the experiment without silanol (see Figure 3 and Table 2). Since the silanol sample contained 20% of pyridine (see experimental), the remaining free HCl amount is only 0.28×10^{-3} mol·L^{-1}. The M_n of the high polymer is approximately one-half of that in the experiment without silanol addition for a similar HP yield ($DP_{n_{th}} = ([D_3]cons_{HP}/([HCl] + [RSiOH]))$. This results from the presence in this $SbCl_5$ sample of HCl in concentration near to that of the silanol. After 1 or 2 h, degradation occurs giving mainly D_5, with a slow decrease of the M_n.

3.3. Comparison of the Various Controlled Cationic Polymerizations of D_3. In D_3 polymerization initiated with a silyl triflate (activated by 10% triflic acid) propagation involves either an activated ester or an oxonium, and M_n is controlled by the ester concentration. Macrocycles formation is strongly reduced (or absent) because nucleophilic silanol groups are absent, and D_6 formation is assumed to result from the presence of oxonium species (as is also the case with triflic acid alone).

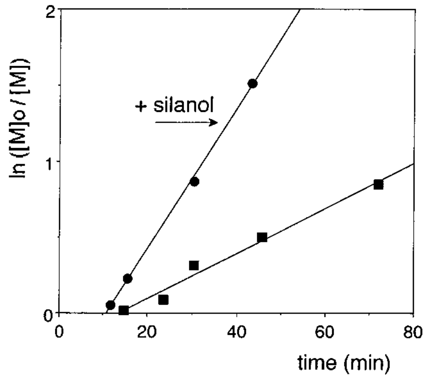


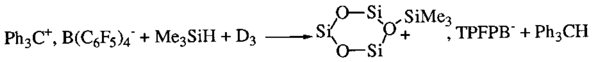
Figure 3. Kinetics of D_3 polymerizations initiated by HCl−$SbCl_5$ at −10 °C. Effect of silanol addition. $[D_3]_0 \sim 1$ mol·L^{-1}; $[(CH_3)_3SiO(CH_3)_2SiOH] = 0.895 \times 10^{-3}$ mol·L^{-1} (■) without silanol or (●) in the presence of silanol (added after 11.3 min).

With HCl−$SbCl_5$, both M_n and cyclics control are observed since propagation involves SiOH end groups. The very strong reduction in D_6 formation is attributed to the absence of oxonium ions.

However, a partial control of the M_n and a reduction of cyclics formation in D_3 polymerization were recently observed when a silane activated by a triphenylmethyl cation salt was used as initiator.[16,17] Propagation was assumed to involve silyloxonium ions, but no information was given about the type of cyclic compounds formed simultaneously with high polymer. We have performed a few experiments in order to compare the results with those of the HCl−$SbCl_5$ system.

3.4. Polymerization Initiated by $R_3SiH-Ph_3C^+$, $B(C_6F_5)_4^-$. Olah et al.[16] have prepared tertiary silyloxoniums at low temperature in CD_2Cl_2 by reaction of a silane (e.g., trimethylsilane) with triphenylmethyl tetrakis(pentafluorophenyl)borate (trityl TPFPB: Ph_3C^+, $B(C_6F_5)_4^-$) in the presence of $(CH_3)_3SiOSi(CH_3)_3$ (M_2), D_3 and D_4 (eqs 12−13).

$$Ph_3C^+, B(C_6F_5)_4^- + Me_3SiH + M_2 \rightarrow [(CH_3)_3Si]_3O^+, (TPFPB)^- + Ph_3CH \quad (12)$$


(13)

These oxonium ions were identified through ^1H and ^{29}Si NMR at −70 °C and are stable at this temperature.[16] At higher temperatures, they disappear progressively even if they still could be seen at −30 °C.[17] From NMR data, it was concluded that polymerization took place

Table 3. Comparison of D_3 Polymerizations Initiated in CH_2Cl_2 with $HCl-SbCl_5$ or $R_3SiH-Ph_3C^+$, TPFPB$^-$

[HCl] × 10^3, mol·L^{-1}	[SbCl$_5$] × 10^3, mol·L^{-1}	*T*, °C	time, min	D_3 convn, %	D_6, %	MC, %	total cyclics, %	HP, %	cyclics/HP, %	$M_n \times 10^{-3}$	$M_{n_{th}}$ x 10^{-3}
1.45	2.9	−10	5.9	10.5	0.5	0	1.3	9.2	12.4	29	10
	(Me_2SiCl_2 = 0.73)		11.7	72.1	2.8	0	7.5	64.6	11.8	136	68
0.29	2.9	−10	3.1	33.6	1.4	0	3.7	29.9	12.3	170	180
	(DBMP = 1.16)		7	89.6	2.7	0	7.9	81.7	9.7	328	448

[R_3SiH] × 10^3, mol·L^{-1}	[Ph_3C^+] × 10^3, mol·L^{-1}	*T*, °C	time, min	D_3 convn, %	D_6, %	MC, %	total cyclics, %	HP, %	cyclics/HP, %	$M_n \times 10^{-3}$	$M_{n_{th}}$ x 10^{-3}
10.9			1.5	44	6.5	0	11	33	33	8.6	9.2
(($CH_3)_3SiH$)	9.1	−20	6.5	57	6.8	0	14	43	32	14.2	12.5
			62	99	7.5	6	27	72	37.5	21	21
4.6			1.7	40	2.5	3.8	10	30	33	56.5	16.2
(Bz(Me)$_2$SiH)	4.7	+20	4.1	82.9	3.7	5.1	17.8	65.8	27	61.8	35.5
			6.5	97.2	3.2	6.2	19.8	77.6	23	57.1	41.7

$[D_3]_o$ for $HCl-SbCl_5$ = 0.79 mol·L^{-1}; for Ph_3C^+ = 1 mol·L^{-1}.

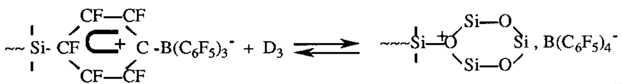
at −50 °C with D_3 but that no polymerization occurred with D_4 even at −20 °C.[17]

Polymerizations with various [monomer]/[initiator] ratios were also carried out in CH_2Cl_2 under argon.[17] After initiation at 0 °C by adding $(CH_3)_3SiH$ (in excess over Ph_3C^+) to a solution of D_3 or D_4 and trityl TPFPB, polymerization was carried out at room temperature for 2−15 h with measurements of yield and molecular weight. Polymer was isolated by precipitation with methanol, with yields of 74−82% (D_3) or 80−85% (D_4). SEC chromatograms showed the presence of small amounts of cyclic oligomers that were not identified (at least 15% with D_3, < 5% with D_4).[16]

Resumption polymerization experiments with both D_3 and D_4,[17] in which an equivalent amount of monomer was added (after 2 h for D_3 and 10 h for D_4), led to the approximate expected increase in molecular weight; and it was concluded that "the propagating silyl oxonium ends are long lived". However, the $DP_{n_{exp}}$ of the linear polymers were lower (by a factor of about 0.5) than those of the $DP_{n_{th}}$ based on [Ph_3C^+] and polymer yield.[17]

Various aspects of these relatively slow reactions are difficult to explain by a propagation involving stable silyloxonium ions present on all macromolecules. A comparison with the rates observed in similar conditions with triflic acid as initiator has shown that with D_3 the polymerization rates are lower and with D_4 only slightly higher than with CF_3SO_3H.[16] Silyloxonium ions may be involved with triflic acid, but their concentration has been shown by conductimetry to be extremely low.[10] For both types of initiation, equilibrium between active species in small amount and dormant species has to be considered.

One possibility considered would be the formation of relatively stable arenium species involving the pentafluorophenyl groups, in equilibrium with tertiary oxonium ions (eq 14). In that case, the situation for



(14)

propagation would be similar to that occurring with CF_3SO_3H as initiator, which could explain the formation of large amounts of D_6 by a special backbiting reaction involving this tertiary oxonium. For this reason, preliminary experiments were performed in CH_2Cl_2 with the initiator of Olah et al., particularly in order to examine the type and amount of cyclic products formed.

Polymerizations were performed by mixing D_3 with Ph_3C^+ TPFPB$^-$ and adding the silane last (see Table 3). At −20 °C, the silane was $(CH_3)_3SiH$ and at 20 °C, $PhCH_2(CH_3)_2SiH$ (BDMS, with a higher boiling point). The rate was much faster than was expected from the reaction times (2−24 h) used by Wang et al.[16,17] With [D_3] ~ 1 mol·L^{-1} and [Ph_3C^+] = 4.6 × 10^{-3} mol·L^{-1}, D_3 conversion was 97% in 6 min at +20 °C. At −20 °C, the initial rate was smaller and conversion was 99% in 62 min.

The high polymer yield decreased afterward at 20 °C (e.g., 77% after 6 min to 52% after 3 h). There was, simultaneously, a decrease of the M_n and the formation of increasing amounts of D_4, D_5, and D_6 tending toward their equilibrium concentration. At 77% polymer yield, cyclics formation is small, respectively [D_4] = 3%, [D_5] = 5%, [D_6] = 3%, and [macrocycles] = 6%. The amount of D_6 is much lower than in polymerization initiated by CF_3SO_3H, and comparable to that formed with $HCl-SbCl_5$ (see Table 3). For polymerization at −20 °C, the polymer degradation was not important after 2 h. The M_n does not change significantly with conversion at +20 °C and is always larger than $M_{n_{th}}$. This might result from the simultaneous occurrence of condensation reactions.

The reaction leading to the destruction of silyloxonium ions above −30 °C has not been identified but certainly involves CH_2Cl_2, as suggested by Olah et al.[16] When the oxonium ions were formed from M_2, there was formation of polysiloxane and $Si(CH_3)_4$ by condensation reactions, and also of $(CH_3)_3SiCl$[16] resulting probably from a reaction of the silicon cation in equilibrium (eqs 15−17).

(15)

$$(CH_3)_3Si^+ + CH_2Cl_2 \rightarrow (CH_3)_3Si{-}Cl + ClCH_2^+ \quad (16)$$

$$ClCH_2^+ + (CH_3)_3SiH \xrightarrow{?} CH_3Cl + (CH_3)_3Si^+ \quad (17)$$

Similar reactions may occur with the growing Si^+ after initiation (eq 18).

$$(CH_3)_3Si^+ + D_3 \rightarrow (CH_3)_3Si[OSi(CH_3)_2]_2O(CH_3)_2Si^+ \quad (18)$$

The total amount of $(CH_3)_3Si^+$ formed, if reaction 17 occurs, would be equal to [$(CH_3)_3SiH$], explaining the

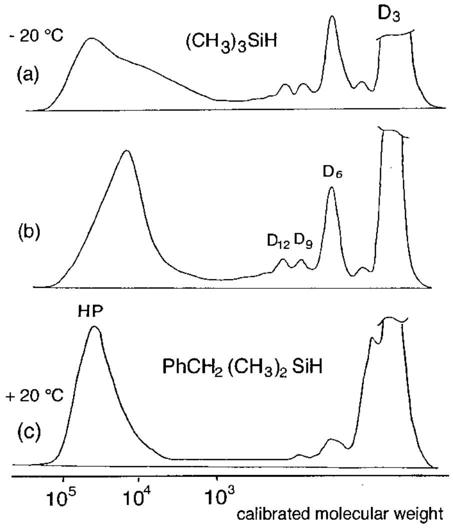


Figure 4. Polymerization of D_3 initiated by $R_3SiH-Ph_3C^+$,-$TPFPB^-$. SEC chromatograms. $[D_3]_0 = 1$ mol·L^{-1}. Conversions: (a) 44%; (b) 57% ($(CH_3)_3SiH$); (c) 40% ($PhCH_2(CH_3)_2SiH$). See Table 3 for initiator concentrations.

low M_n values in ref 17, for which the $(CH_3)_3SiH$ concentration was double that of $[Ph_3C^+]$.

At −20 °C, the M_n increases linearly with conversion and is near $M_{n_{th}}$. The amount of D_6 formed is larger than at 20 °C (7%, with $D_6/HP = 16\%$), which may indicate the presence of a larger but limited concentration of transitory oxonium ions. At both −20 and +20 °C, a relatively large amount of cyclics including macrocycles is formed (25−35% of HP), which may result from end-to-end ring closure or from backbiting (see Figure 4). At −20 °C, D_6, D_9, D_{12}, and D_{15} are formed in significant amounts and may result from the presence of water in low concentration that may react with R_3Si^+ or $R_3SiMnSi^+$ (eq 19).

$$R_3SiMn^+,\ TPFPB^- + H_2O \rightarrow R_3SiMnOH + H^+,\ TPFPB^- \quad (19)$$

H^+, $TPFPB^-$ is also an initiator, giving silanol end groups at both ends, and then leading to the formation of D_{3x} cycles (i.e., D_9, D_{12}, and D_{15}; see Figure 4). D_6, in much larger amount, may also result from a reaction involving oxoniums. The formation of $R_3SiMnOH$ and H^+, $TPFPB^-$ might also explain the bimodality for the polymerization obtained at 44% yield by a simultaneous propagation on two different active sites (see Figure 4a).

At 20 °C, the small cycles formed are mainly D_4, D_5, and D_6, resulting probably from backbiting reactions. Macrocycles and/or linear oligomers are also present, which may be formed by cyclization or condensation of oligomeric disilanols.

4. Conclusion

There are several analogies between polymerization of D_3 in CH_2Cl_2 initiated by $HCl-SbCl_5$ and by $(CH_3)_3SiH-Ph_3C^+$, $B(C_6F_5)_4^-$. At −10 °C in the first case and at −20 °C in the second one, a satisfactory control of the M_n may be obtained, together with a large increase in the linear polymer yield (up to 90% in the first and 75% in the second case). However, with $HCl-SbCl_5$, a degradation of the high polymer occurs (giving mainly D_4 and D_5) after total D_3 consumption, which is attributed to residual $HSbCl_6$. A similar degradation was also observed with the silane initiated polymerizations carried out at 20 °C (which may also involve the strong acid $HB(C_6F_5)_4$) but was very slow at −20 °C.

In both cases, the formation of D_6 is strongly decreased, particularly with $HCl-SbCl_5$. This is attributed to the absence (or to the low concentration) of tertiary silyloxonium ions in these systems. However, the larger amount of D_6 formed with the silane at −20 °C than at +20 °C may result from the presence of some silyloxonium ions at the lower temperature.

The mechanisms of these polymerizations are not yet fully understood. With $HCl-SbCl_5$, the results are best explained by a polymer growth involving the silanol end groups resulting from initiation by HCl present in the system. A small amount of $HSbCl_6$ in equilibrium may activate either SiOH or more likely the monomer. This hypothesis is strongly supported by preliminary experiments with $HCl-SbCl_5$ in which the addition of the model silanol $(CH_3)_3SiO(CH_3)_2SiOH$ has led to a strong increase in the rate (first order in $[D_3]$) and to an approximate DP_n control.

High polymer formation in polymerizations initiated by transitory silyl cations with a low nucleophilic counterion such as $B(C_6F_5)_4^-$ is apparently more complex than had been assumed and is unlikely to involve propagation on ternary silyloxonium ions. At −20 °C, the high polymer formation is very rapid from the beginning and might involve transitory Si^+ species. These species might react with CH_2Cl_2 and with water present in the medium, giving SiCl and SiOH end groups. A propagation involving SiOH and catalyzed by $HB(C_6F_5)_4$, analogous to that considered with $HCl-SbCl_5$, cannot be excluded.

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