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Cationic Polymerization of Hexamethylcyclosiloxane (D_3): Kinetics and Mechanism of Cyclics Formation

Toskas G., Moreau M., Sigwalt P.

Summary: In cationic polymerization of hexamethylcyclotrisiloxane (D_3) in methylene chloride, a control of the mol wts could be observed with various initiators such as RCOCl/ $SbCl_5$ or trifluoromethanesulfonic acid (TfOH) and its derivatives. But an important difference with usual living polymerizations is the simultaneous formation of large amounts of cyclic oligomers D_{3x}, their weights increasing linearly from the origin. A second population of much larger DPn has been shown to consist of macrocycles (MC). It was concluded that while MC result from end-to-end ring closure of a fraction of linear macromolecules, the small D_{3x} cycles (essentially D_6) are formed independently by a selective back-biting reaction involving oxonium end-groups. However, it has been proposed again in recent publications in which various initiators were used (including TfOH) that D_{3x} cyclics of all sizes result from end-to-end ring closure reactions between the (electrophilic) active site for propagation and a silanol end group.

In the present paper, the initiator used was the mixed anhydride of trifluoroacetic and trifluoromethanesulfonic acid, which give non-nucleophilic $CF_3CO_2(CH_3)_2Si$ end-groups. The residual acid present in the anhydride was neutralized by varying amounts of 4-methyl,2,6-di-*t*-butylpyridine (MDTBP). The linear increase of the HP molecular weight and the formation of large amounts of D_{3x} oligomers were observed again. The weight ratio of D_6 was larger than for TfOH initiation ($1 < D_6/HP < 1{,}5$) and when a large excess of MDTBP on the acid was used, D_6/HP was even higher but MC formation was completely suppressed. This confirms the difference in the mechanisms giving MC and D_6 and agrees with small D_{3x} cyclics formation involving the silyltriflate end-groups alone (and probably the derived oxonium sites).

Keywords: cationic polymerization; hexamethylcyclotrisiloxane; trifluoromethanesulfonic acid

Introduction

Cationic polymerizations of hexamethylcyclotrisiloxane (D_3) in methylene chloride using various initiators have given high polymers (HP) with controlled molecular weights: $Mn = [M]_{HP}/[I]_o$. But there is generally a simultaneous formation of large amounts of D_{3x} cycles of low mol wts (mainly D_6) and of smaller amounts of macrocycles MC [1,2,3].

In the present paper, it is shown that the amount of MC may be reduced and eventually suppressed by changing the nucleophilicity of the initiator moiety, while the amount of D_6 formed may increase, with $[D_6]/[HP]$ remaining constant during the polymerization. This shows that D_6 and MC are not formed by the same mechanism.

D_4 slow polymerization initiated by CF_3SO_3H has been found to be mainly controlled thermodynamically [4], the products being a linear high polymer of Mn independent from initiator concentration and small cyclics formed by backbiting (with $D_5 > D_6 > D_7 > D_8$). The faster D_3 cationic polymerization is generally

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Laboratoire de Chimie des Polymères, Université Pierre et Marie Curie, UMR 7610 Case 185, 4, place Jussieu 75252 Paris cedex 05 France
E-mail: mimoreau@ccr.jussieu.fr

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kinetically controlled, with Mn of the HP increasing linearly from the origin (Mn_{lin}) for a variety of initiators [1–3], but with formation of very large amounts of D_{3x} cycles.

The observation of Mn_{lin} shows that the concentration of the HP macromolecules remains constant during the polymerization, and the first order observed for monomer consumption can be explained if HP is formed by a chain reaction on a constant concentration of active sites. Their nature is still a matter of discussion, but for example in the case of initiation by triflic acid (TfOH) it was concluded that they could be either triflic esters activated by the acid or tertiary siloxonium ions formed with D_3, or both [2,3]. The end-groups were shown to be essentially silyl triflates (75% of $[TfOH]_o$), 25% of the acid remaining in the form of the hydrates $CF_3SO_3^-H_3O^+$ and CF_3SO_3H, $2H_2O$ [5], water resulting from either the esterification of the silanols formed by ring opening of D_3 or of an homocondensation of these silanols.

Various silyl triflates such as $(CH_3)_3SiOTf$, $Bz(CH_3)_2SiOTf$ or $CF_3SO_3[Si(CH_3)_2O]_n$-SO_2CF_3 [3] do not initiate D_3 polymerization (at 20 °C in CH_2Cl_2) in the presence of a "proton trap" (e.g. with ~10% of added 4-methyl,2,6-di-*t*-butylpyridine (MDTBP)) whereas the addition of a very small amount of TfOH started the polymerization.

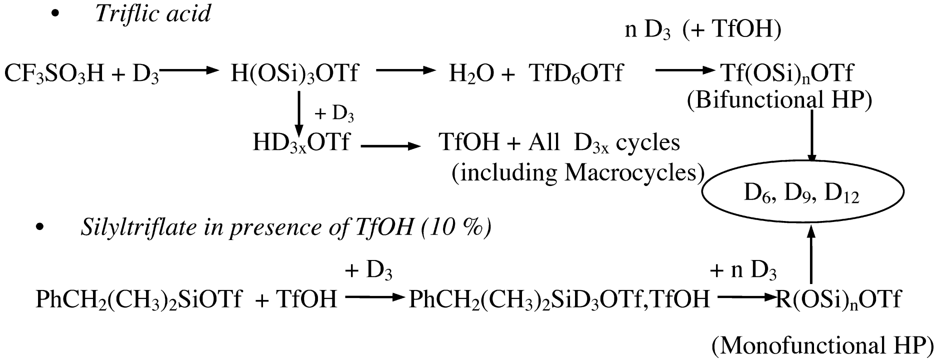
Another important result observed with different initiators (CF_3SO_3H [2], $R_3SiOTf + TfOH$ [3], $NaphCOCl + SbCl_5$ [1]) is the simultaneous formation of a very large amount of small D_{3x} cycles with $D_6 > D_9 > D_{12}$, e.g. D_6/HP in weight from 0,5 to 2 according to the system, and of a significant amount of high mol wt oligomers assumed to be macrocycles MC of mol wts between 2.10^3 and 5.10^4 (e.g. MC/HP in weight from 0,1 to 0,2). The conclusion was based on the absence in these higher oligomers of fragments of tagged initiator present as end-groups in the high polymer (e.g. NaphCO or $Bz(CH_3)_2Si$). For the various initiators mentioned, there was a linear increase with monomer conversion (at least up to 50% conversion) of the weight amount of the high polymer, of macrocycles, D_6, D_9 and D_{12}, with $D_6 \sim HP > MC > D_9 > D_{12}$.

The formation of all D_{3x} cycles was initially explained by the occurrence of end-to-end ring closure reactions ("end-biting") between e.g. triflate and silanol, competitive with the formation of the HP by chain propagation [6], but the resulting continuous formation of acid on cyclization was shown not to be consistent with the constant concentration of macromolecules since initiation would have occurred continuously.

The explanation proposed for the simultaneous and proportional formation of linear high polymer and of macrocycles is the presence of two populations of macromolecules. One, leading to the linear HP, would bear two end-groups active (or potentially active) for propagation (e.g. silyl triflates when TfOH is the initiator) and the other population only one active end-group, the other one (e.g. ~SiOH) being reactive for cyclization (see Scheme 1). This is in agreement with the strong increase of the ratio MC/HP with TfOH concentration observed with TfOH initiation [2]. But since D_6/HP remains constant when [TfOH] increases, this may only be explained if D_6 formation occurs on sites similar or identical to those active for propagation. The proposed mechanism [1,2] is that of a special type of backbiting reaction between a tertiary silyloxonium ion formed with D_3 and a siloxane oxygen of the chain, giving as intermediate for D_6 formation a favored eight-membered cyclic transition state. In D_3 polymerizations initiated by CF_3SO_3H, CH_3COCl-$SbCl_5$ or $NaphCOCl$-$SbCl_5$, the weight amount of the macrocycles MC is independent of their mol wts as shown by SEC (see e.g. Fig. 3 in [2]). This corresponds to a rate constant of cyclization $k_{ci} = k\ i^{-1}$ $(i = DP)$, as was observed experimentally for the cyclization of styrene and poly (ethylene oxide) in good solvents [7]. This leads [2], for a population n_i of mol wt M_i, and since n_i is proportional to k_{ci}, to

$$n_i = k'\ k_{ci} = k'' i^{-1} \quad \text{and to}$$

$$n_i M_i = k'' x M_i / i = \text{Constant}$$



Scheme 1.

It was verified from the UV absorption of the polymer formed by initiation with NaphCOCl-$SbCl_5$, that the NaphCO moiety is present in the HP but absent in the MC [1].

As shown in Scheme 1, macrocycles are formed on a low stationary state concentration of silanol esters, which may also give oligomeric D_{3x} cyclics in small weight amounts, but the major D_6 formation involves tertiary siloxonium ions in equilibrium with silyl triflates end-groups.

For initiation by benzyl dimethylsilyl triflate (and 10% CF_3SO_3H) [3], there was a satisfactory agreement between Mn_{SEC}, Mn_{osm} and Mn_{uv} calculated from the UV absorption of the isolated high polymer, showing that each macromolecule contained approximately one $Ph(CH_3)_2SiO$ end-group. But the peak corresponding to the HP is asymmetrical, with a population of lower mol wt in a similar range (10^3–10^4) as the MC formed with TfOH alone, but with a weight amount increasing with M_i. An UV absorption of the SEC chromatogram shows a strong absorption of the end-groups $Ph(CH_3)_2SiO$ in that population. This indicates the presence of an important (and perhaps major) content of linear polymer of low mol wt, but does not permit to exclude the presence of a fraction of macrocycles, which might have resulted from a reaction of this still relatively nucleophilic siloxane end-group by an active site at the other end.

We have assumed that initiation leading to a less nucleophilic end-group might suppress completely the formation of macrocycles, without a similar suppression of the D_6-D_9 formation, and this has been done by using as initiator the mixed anhydride of triflic acid with trifluoroacetic acid ($CF_3COOSO_2CF_3$).

In the presence of TfOH, it should ionize in CF_3CO^+, TfO^-TfOH. CF_3CO^+ is a strong electrophile, which should react with D_3 giving a silyl ester end group deactivated toward end-biting by the electroattractive CF_3 group.

Experimental Section

Materials

All reagents were purified under vacuum and stored in sealed tubes.

D_3 (m.p. 64 °C) was reacted at 80 °C with CaH_2 and then on sodium films (purity > 99,9%). Dichloromethane was dried on P_2O_5 and sodium films. $CF_3SO_3COCF_3$ (Aldrich) was distilled (b.p. 62–63 °C) and diluted with CH_2Cl_2 under vacuum. 4-Methyl,2,6-di-*tertio*-butylpyridine (MDTBP, Fluka) was sublimated several times, dissolved in CH_2Cl_2 and dried over silicagel.

Polymerization Procedures

Polymerizations were carried out under vacuum in an apparatus previously described [2]. The anhydride solution was mixed in a sealed glass bulb with about 10% of MDTBP. Polymerizations were started by breaking the glass bulb in the stirred monomer solution containing also generally 5% of MDTBP. The presence of the glass bulb did not permit to flame the reaction vessel under vacuum.

The first four samples were collected through 4 different lateral tubes during the first minutes, the following ones being collected at longer intervals. All samples were deactivated under vacuum by pyridine in CH_2Cl_2. They were analyzed by Gas chromatography up to 300 °C (up to D_{15}) and by SEC in toluene [3].

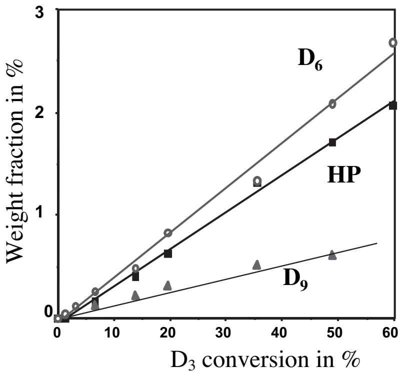


Figure 1.
Polymerization of D_3 initiated by $CF_3COO\ SO_2CF_3$ in CH_2Cl_2 at −10 °C. Formation of D_{3x} cycles and linear high polymer (HP) with D_3 conversion. $[D_3] = 1{,}25$ mol L^{-1}; $[CF_3COOSO_2CF_3] = 3{,}13 \times 10^{-4}$ mol L^{-1}; $[MDTBP] = 4{,}63 \times 10^{-5}$ mol L^{-1}.

Results and Discussion

^1H NMR of the reaction products of the mixed anhydride solution with the hindered base MDTBP showed that it contained 7 mole % of acids (triflic + trifluoroacetic).

Preliminary polymerization experiments, realized at 20 °C, showed the absence of control of the mol wts of the linear polymer (Mn_{lin}) with the original anhydride solution, and only slightly better results when 10% MDTBP was added.

The following experiments were done at −10 °C at different D_3 concentrations, for which Mn control was observed, with $[CF_3COOSO_2CF_3] = 3{,}14 \times 10^{-4}$ mol L^{-1} mixed with ~10% MDTBP in the initiator bulb and 5% MDTBP in the monomer solution.

Polymerizations with a Small Excess of MDTBP on Acid: $[MDTBP]_{tot}/[Acid]_o \sim 2$

Two experiments were realized at −10 °C with 0,78 and 1,25 mol L^{-1} of D_3, and one at −5 °C with 1,58 mol L^{-1} of D_3 (because at this concentration D_3 was partially insoluble at – 10 °C).

In these polymerizations, the weight fractions of the linear polymer (HP), D_6 and D_9 increased linearly with D_3 conversion (see Fig. 1). The weight amount of D_6 is larger than that of the linear HP, and D_6 / HP is constant (~1,2 above 10% conversion) (see Table 1). The weight ratio D_9/D_6 is also constant (~0,25).

Polymerizations were first order in monomer concentration (see Fig. 2) and the Mn of the linear polymer increased linearly with D_3 conversion (see Fig. 3).

These results are similar to those observed with polymerizations initiated by a silyl triflate and triflic acid [2] and are interpreted in the same way: Polymerization occurring on activated silyl triflate end-groups or on siloxonium ions in equilibrium. What is less easily understood is that propagation occurs when hindered base is in excess over the acids, and with an apparent rate constant still relatively high (see Fig. 2 and Table 1).

For various polymerizations with $[D_3]_o$ varying from 0,8 to 1,50 mol L^{-1} the linear increase of the M_{peak} with conversion (see Fig. 4) indicates that the concentration of macromolecules is constant. The polymolecularity index of the HP increases only slightly with conversion (from 1,36 to 1,54).

However, the Mns are systematically larger than the $Mn_{th} = [M]_{cons}/[Anh]$ by a factor of about 2 (1,5 for $[D_3]_o = 0{,}8$ mol L^{-1}; 2 for $[D_3]_o = 1{,}25$ mol L^{-1}; 2,5 for $[D_3]_o = 1{,}58$ mol L^{-1}). For the various $[D_3]_o$, the ratios Mn/Mn_{th} are larger than 2 at low conversions but reach a limit after

Table 1.
Polymerization of D_3 initiated by $CF_3COOSO_2CF_3$ in presence of a small excess of MDTBP over $[Acid]_o$. Percentages in weight of D_{3x} cyclics, large oligomers (LO) and high polymer (HP) with time. $[D_3] = 1{,}25$ M $[Anh] = 3{,}13 \times 10^{-4}$ mol L^{-1}; $[MDTBP] = 4{,}63 \times 10^{-5}$ mol L^{-1}. T = −10 °C; CH_2Cl_2.

Time min	D_3 % Conv	D_6	D_9	D_{12}	LO	HP	D_6/HP	D_9/D_6	$M_{peak} \times 10^{-3}$	$Mn \times 10^{-3}$	Mn/Mn_{th}
3,2	1,2	0,4	0,15	0,06	0,39	<0,1		0,33			
8,5	3,1	1,2	0,36	0,15	1,3	nd		0,30			
16,7	6,6	2,6	0,86	0,22	1,3	1,6	1,6	0,33	79		
33,2	13,8	4,9	1,3	0,27	2,8	4,1	1,2	0,26	125	102	2,80
56	19,6	8,3	2,2	0,36	2,2	6,3	1,31	0,26	186	153	2,73
90	35,5	13,4	3,1	0,52	4,9	13,2	1,01	0,23	312	236	2,01
150	48,9	20,8	5,2	0,86	4,3	17,1	1,21	0,25	427	304	1,98
210	59,7	26,8	6,2	0,90	4,1	20,7	1,31	0,25	664	379	2,07

about one hour, indicating that the formation of silyl triflates (and initiation) is complete after that time.

The final Mn larger than Mn_{th} may be attributed to a smaller effective anhydride concentration active for initiation, which may result from its partial hydrolysis by adventitious water at the beginning of the polymerizations. Since the presence of the initiator bulb did not permit to heat the reaction vessel with a flame, the presence of water on the walls may lead to about 10^{-4} mol L^{-1} in the monomer solution. The increase of Mn/Mn_{th} observed when $[D_3]_o$ is larger may also result from the presence of residual water in D_3.

On mixing the initiator with D_3 solution, several competitive reactions should occur. The faster is probably the hydration of acid by H_2O (Equations 1, 2, 3) followed by hydrolysis of the anhydride by water (Eq. 4) and by the reaction of the anhydride with D_3 giving silyl triflates (Eq. 5)

$$CF_3SO_3H + H_2O \rightarrow CF_3SO_3H,\ H_2O \quad (1)$$

$$CF_3SO_3H, H_2O + H_2O \rightarrow CF_3SO_3H,\ 2H_2O \quad (2)$$

$$CF_3SO_3H + nH_2O \rightarrow CF_3SO_3H,\ nH_2O \quad (3)$$

$$CF_3COOSO_2CF_3 + H_2O \rightarrow CF_3COOH + CF_3SO_3H \quad (4)$$

$$CF_3COOSO_2CF_3 + D_3 \rightarrow CF_3CO(OSi)_3OSO_2CF_3 \quad (5)$$

Hydration of the acid by water gives a variety of hydrates CF_3SO_3H, nH_2O with

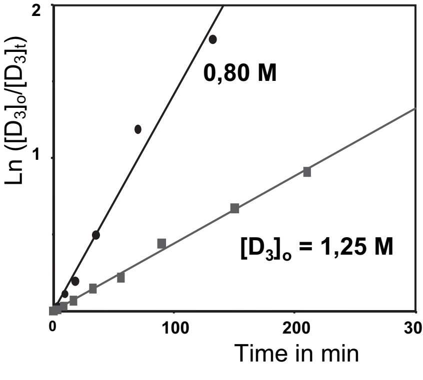


Figure 2.
D_3 polymerization with $CF_3COOSO_2CF_3$. First-order in monomer. $[CF_3COOSO_2CF_3] = 3{,}13 \times 10^{-4}$ mol L^{-1}; $[MDTBP] \sim 4{,}5 \times 10^{-5}$ mol L^{-1}. T = −10 °C

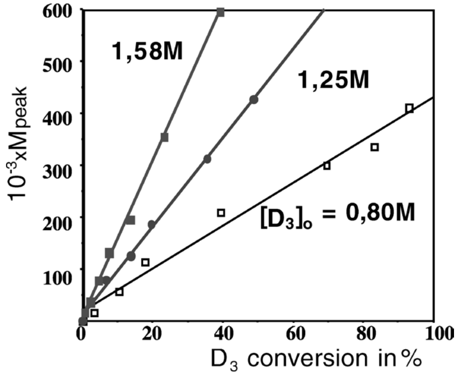


Figure 3.
Variation of molar masses with D_3 conversion. $[D_3] = 1{,}58$ mol L^{-1} (T = −5 °C) and 0,8; 1,25 (T = −10 °C); $[Anh] = 3{,}13 \times 10^{-4}$ mol L^{-1}; $[MDTBP] = 4{,}63 \times 10^{-5}$ mol L^{-1}.

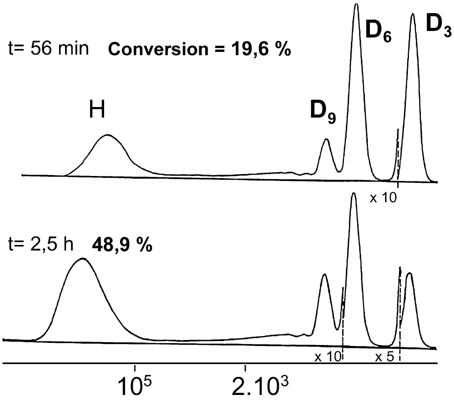


Figure 4.
SEC chromatograms. Variation of D_{3x} cycles and linear high polymer with D_3 conversion. $[MDTBP]/[Acid]_o \sim 2$. $[D_3] = 1{,}25$ mol L^{-1}; $[MDTBP] = 4{,}63 \times 10^{-5}$ mol L^{-1}; $[CF_3COOSO_2CF_3] = 3{,}13 \times 10^{-4}$ mol L^{-1}. T = −10 °C

increasing degrees of hydration n. The lower hydrates (n = 1 or 2) are stable in the presence of silyl triflates and do not react with them [2,5]. The weakly reactive monohydrate probably does not hydrolyse the mixed anhydride, which may however react with the dihydrate giving CF_3SO_3H and CF_3CO_2H:

$$\begin{aligned} & CF_3COOSO_2CF_3 + CF_3SO_3H,\ 2H_2O \\ & \quad \rightarrow CF_3CO_2H + CF_3SO_3H \\ & \qquad + CF_3SO_3H,\ H_2O \end{aligned} \tag{6}$$

The monohydrate initiates slowly D_3 polymerization, but is much less reactive than the free acid [5]. It activates the silyl esters for propagation [3], and also probably the reaction of D_3 with the anhydride.

In the experiments with $3{,}1 \times 10^{-4}$ mol L^{-1} of anhydride, $2{,}1 \times 10^{-5}$ mol L^{-1} of $[acid]_o$ and $[MDTBP]_{total} = 4{,}6 \times 10^{-5}$ mol L^{-1}, the absence of inhibition results from the hydrolysis of the anhydride by water ($\sim 1{,}5 \times 10^{-4}$ mol L^{-1}) giving $0{,}77 \times 10^{-4}$ mol L^{-1} of monohydrate of TfOH, in excess over MDTBP concentration and which may cocatalyse both the formation of silyl triflate (Eq. 5) and the propagation reaction.

In these experiments with a relatively small excess of MDTBP over the initial acid concentration $[Acid]_o$, the SEC shows the presence of oligomers larger than D_{12} (LO) (see e.g. Fig. 4). This does not permit to exclude the possible presence of macrocycles, which might be linked to that of a relatively large amount of triflic acid monohydrate. But we shall see that these large oligomers may be suppressed when proton trap concentration is larger (see Fig. 5).

Polymerization with Large Excess of MDTBP on Acid: $[MDTBP]/[Acid]_o \sim 7$

The observation of a total inhibition in the experiment with 10^{-3} mol L^{-1} of anhydride ($[acid]_o = 7 \times 10^{-5}$ mol L^{-1}) and 5×10^{-4} mol L^{-1} of MDTBP (Table 2) might have resulted, with $[H_2O] \sim 1{,}5 \times 10^{-4}$ mol L^{-1}, of the partial hydrolysis of the anhydride giving CF_3CO_2H and CF_3SO_3H neutralized by the larger MDTBP concentration. But this does not explain that, after 20 min, there is a slow formation of D_6, D_9 and very small amounts of D_{12}, followed after 2 hours by HP formation, with an autoacceleration after 3 hours of D_6, D_9 and HP formation (Table 2), with the absence of oligomers larger than D_{15} and macrocycles (Fig. 5).

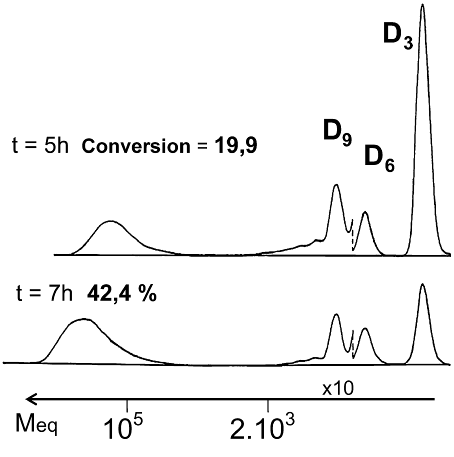


Figure 5.
SEC chromatograms. $[MDTBP]/[Acid]_o \sim 7$. $[D_3] = 1{,}25$ mol L^{-1}; $[MDTBP] = 5{,}1 \times 10^{-4}$ mol L^{-1}; $[CF_3COOSO_2CF_3] = 1 \times 10^{-3}$ mol L^{-1}. T = −10 °C

Table 2.

Polymerization of D_3 initiated by $CF_3COO\ SO_2CF_3$ in presence of a large excess of MDTBP over $[Acid]_o$. Percentages in weight of D_{3x} cycles and high polymer (HP) with time. $[D_3] = 1{,}25$ M $[Anh] = 1{,}0 \times 10^{-3}$ mol L^{-1}; $[MDTBP] = 5{,}1 \times 10^{-4}$ mol L^{-1}. $T = -10\,°C$; CH_2Cl_2.

Time min	D_3 % Conv	D_6	D_9	D_{12}	HP	D_6/HP	Mpeak × 10^{-3}	Mn × 10^{-3}	PDI	Mn/Mn_{th}
37	0,82	0,69	0,13	–	–	–	–	–	–	–
120	2,6	2,4	0,22	–	<0,5	–	55,9	–	–	–
300	19,9	14,2	2,3	0,40	3	4,7	143,9	105	1,49	12,6
420	42,4	25,9	3,9	0,49	12,2	2,1	319,5	158	2,06	4,6
1290	97,7	42,4	5,7	1,04	46	0,92	210	120	2,38	1,0

These results may be explained by the initial reaction of $[TfOH]_o = 7 \times 10^{-5}$ mol L^{-1} and $[H_2O] \sim 1{,}5 \times 10^{4}$ mol L^{-1} giving TfOH, $2H_2O$, less electrophilic than the monohydrate and inactive as cocatalyst for the activation of the various reactions.

However, a very slow hydrolysis of the anhydride (the strongest electrophile present) might occur, involving the dihydrate (Eq. 6) (or water from the walls of the vessel) and producing CF_3SO_3H (in the monohydrate form) and CF_3CO_2H, which may both be cocatalysts for the hydrolysis and the initiation reaction.

The inhibition of polymerization for 20 min followed only by a slow formation of D_{3x} cyclics for 120 min is in agreement with the proposed mechanism of specific backbiting of the growing linear polymer chain. When the rate of polymer growth is very slow, the backbiting reaction may be faster and only D_6 is formed at the beginning, and later also D_9 and D_{12}. The slow increase of acid concentration leads to a relative increase of the rate of HP growth, which may indicate a different role of the acid in this growth and in D_{3x} formation. D_6,D_9 and D_{12} concentrations also increase (but more slowly than that of the HP) reaching values related to the equilibrium concentrations of $\sim SiD_3^+$, $\sim SiD_6^+$and $\sim SiD_9^+$.

This equilibrium is different from the thermodynamic equilibrium, which may be reached in polymerizations of D_4, D_5 or D_6 [4, 12] giving $D_4 > D_5 > D_6 > D_7$...Up to 42% conversion there is no formation of D_4 and D_5. However after 1290 min macrocycles were still absent, but 0,2% of D_4 was formed as well as about 2% of a high polymer of lower mol wt ($Mpeak = 7.10^3$), which indicate some degradation of the linear polymer. The decrease of the M_{peak} might result from a depolymerization in D_{3x} cycles. The limit value of D_6/HP is near to one as observed in the polymerizations without inhibition.

Mechanism of the Formation of D_{3x} Cyclic Products

As discussed in the introduction, we proposed that small D_{3x} cyclics are formed through a selective backbiting reaction of the linear polymer chain by tertiary siloxonium ions $\sim SiD_3^+$ (formed by ionization of silyl ester end groups by triflic acid or its hydrate). A bimolecular reaction between $\sim SiD_3^+$ and D_3, giving $\sim SiD_6^+$, seems quite unlikely since it would necessitate the simultaneous ring opening of the oxonium and of D_3. The simple ring-opening of the strained $\sim SiD_3^+$ with formation of $\sim SiD_3D_3^+$ (propagation step) should be easier and faster. End-biting (end-to-end ring closure) is not possible with bifunctional polymer formed with triflic acid (see Scheme 1) but may occur if a fraction of triflic acid or more likely its monohydrate may be reformed continuously giving linear oligomers with a silanol end group and an ester end-group. This should be the mode of formation of the macrocycles. But the available data are in disagreement with the formation of D_6 and D_9 by a mechanism involving the reaction of a silanol end group with the electrophilic growing end group (silyl triflate or siloxonium ion). This reaction should be favoured by larger triflic acid concentration leading to larger end-group concentrations while the opposite was observed.

1) The D_6/HP weight ratio is smallest ($\sim$0,25) with the largest TfOH concentration, both for initiation by TfOH alone [2] or with a silyl triflate and TfOH [3].
2) The largest value of D_6/HP has been observed with the mixed anhydride, in the presence of hindered base.
3) The formation of macrocycles should result from cyclization of the silanol ester and increased with TfOH concentration, as expected [2]. But macrocycles could be completely suppressed for mixed anhydride initiation and the largest MDTBP concentration for which [TfOH] should be the smallest, while D_6/HP was still $\geq$1.

However, in a paper on cationic polymerization of a cyclotrisiloxane with mixed dimethyl and diphenyl siloxane units D_{3Ph} ($Ph_2SiOMe_2SiOMe_2SiO$) by CF_3SO_3H in hexane at 30 °C [8] it was concluded that linear polymer (HP) chain growth occurs on siloxonium active sites but that the formation of all D_{3x} results from the competitive cyclization by reaction of the oxonium end-group with the other end-group (silanol).

But the amount of D_6 formed for polymerization of D_3 in heptane at 30 °C [6] is similar to that in CH_2Cl_2. Even if the polymerization rates are smaller in heptane than in CH_2Cl_2, they are of the same order of magnitude [9], which is more in favor of similar mechanisms in the two solvents. With such a scheme, triflic acid reformed at each cyclization step should also be able to initiate the formation of new macromolecules.

Unfortunately, no information was given in this paper [8] about the mol wts and yields of linear polymer (and about the possible presence of macrocycles).

A similar competition between propagation giving the linear polymer and cyclization between the siloxonium end group and a silanol end-group has been proposed recently by Grzelka et al for D_3 polymerization in toluene initiated by $Et_3SiH + Ph_3C^+ B(C_6F_5)_4^-$ or by the isolated complex $H^+(H_2O)_3 B(C_6F_5)_4^-$ [10]. As could be expected the rate was much smaller (by a factor of 350) with the hydrate complex.

The formation of D_{3x} cyclics by end-to-end ring closure appears more likely in this case, and was proposed by us for very similar initiating systems: $(CH_3)_3SiH$ or $Bz(CH_3)_2SiH$ and $Ph_3C^+B(C_6F_5)_4^-$ in CH_2Cl_2 at – 20 °C and 20 °C [11]. At 20 °C, $D_5 > D_6 \sim D_4$ indicating their main formation by classical backbiting, and there is no Mn control. D_6 amounts are small ($\sim$3%). At -20 °C, $Mn = Mn_{th}$ and D_6 formation is larger ($\sim$6%). This may result from some contribution of a selective backbiting mechanism since oxonium ions are more stable at -20 °C. Since smaller but significant amounts of D_9, D_{12} and D_{15} are also formed, we proposed that D_{3x} cycles may also be formed by the reaction of $H^+(C_6F_5)_4B^-$ with D_3, giving linear oligomers, which cyclize through the silanol end-group. The mechanism of HP formation would be different, resulting from initiation by $Bz(CH_3)_2Si^+$ and growth on $Bz(CH_3)_2SiD_xOH$, this silanol reacting with D_3 activated by $H^+ (C_6F_5)_4B^-$.

Unfortunately no information is given in ref [10] about the variation of the mol wt of the polymer with yield, but the predominant formation of D_{3x} in this case might result from a similar end-biting reaction independent from linear polymer growth.

The monomer activated mechanism was also proposed for D_3 propagation by the strong protonic acid $H^+SbCl_6^-$ in CH_2Cl_2 at -10 °C giving a HP with controlled Mn, very small amounts of D_6 and no macrocycles [11]. This was explained by propagation on a silanol end-group, the other end-group being the non nucleophilic $ClSi(CH_3)_2O$.

In conclusion, for polymerization of D_3 by CF_3SO_3H in toluene [8] the formation of D_{3x} cyclics by end-biting appears to be quite unlikely. But a mechanism involving end biting of silanol end-groups for the polymerization in hexane with $B(C_6F_5)_4^-H^+$[10] is possible.

Mechanism of Linear Polymer Formation

Linear polymers formed through initiation by triflic mixed anhydride, acid activated silyl triflate or triflic acid alone all bear a potentially active silyltriflate end-group but it is not known if propagation occurs directly on this ionized end-group ($\sim(CH_3)_2Si^+$,TfO^-,TfOH) or on a tertiary siloxonium ion $\sim SiD_3^+$ resulting from its reaction with D_3. In that last case it is not known whether $\sim SiD_3^+$ is only a transitory species or in stable equilibrium with D_3.

The concentration of siloxonium species is certainly much lower than that of the silyl triflate since the increase of conductivity of TfOH in dried CH_2Cl_2 solution, which is very low, only increases marginally on D_3 addition. With $[CF_3SO_3H] = 10^{-3}$ mol L^{-1} at 20 °C, the specific conductivity of 0,95 μS increased up to 1,2 μS, 20 min after addition of D_3 (1 mol L^{-1}) for a conversion of 75% [3]. If SiD_3^+ concentration is resulting from the equilibria

$$\sim \mathrm{SiOTf} + \mathrm{TfOH} \underset{k_i}{\overset{k_{TF}}{\rightleftarrows}} \sim \mathrm{SiOTf,\ TfOH} \qquad (7)$$

$$\sim \mathrm{SiOTf,\ TfOH} + \mathrm{D_3} \overset{k_i}{\rightleftarrows} \sim \mathrm{SiD_3^+,\ TfO^-,\ TfOH} \qquad (8)$$

$$[\sim \mathrm{SiD_3^+, TfO^-,\ TfOH}] = \mathrm{K_{Tf}K_i[SiOTf][TfOH][D_3]} \qquad (9)$$

and if propagation is first order in $[\sim SiD_3^+]$ and in $[D_3]$

$$\mathrm{R_p} = k_\mathrm{p}\mathrm{K_{Tf}K_i[SiOTf][TfOH][D_3]^2} \qquad (10)$$

This is in disagreement with the first order observed for D_3 consumption.

If $\sim SiD_3^+$ is resulting from a quasi-stationary state between initiation

$$\sim \mathrm{SiOTf,\ TfOH} + \mathrm{D_3} \xrightarrow{k_\mathrm{i}} \sim \mathrm{SiD_3^+,\ TfO^-,\ TfOH} \qquad (11)$$

and deactivation assisted by D_3

$$\sim \mathrm{SiD_3^+,\ TfO^-,\ TfOH} + \mathrm{D_3} \xrightarrow{k_\mathrm{deact}} \sim \mathrm{SiD_3OTf} + \mathrm{D_3,\ TfOH} \qquad (12)$$

$$[\mathrm{SiD_3^+,\ TfO^-,\ TfOH}] = \frac{k_\mathrm{i}\mathrm{K_{Tf}}}{k_\mathrm{deact}} [\sim \mathrm{SiOTf}][\mathrm{TfOH}] \qquad (13)$$

and R_p may be 1st order in $[D_3]$ for a second order propagation reaction

$$\mathrm{R_p} = k_\mathrm{p}\frac{k_\mathrm{i}\mathrm{K_{Tf}}}{k_\mathrm{deact}}[\sim \mathrm{SiOTf}][\mathrm{TfOH}][\mathrm{D_3}] \qquad (14)$$

This is compatible with a formation of D_{3x} cycles by the selective backbiting reactions considered earlier.

In their publication on polymerization of the diphenyl substituted cyclotrisiloxane cited above [8], Chojnowski et al propose that propagation for linear polymer formation occurs through a "chain extension with deactivation", in which $\sim SiD_3^+$ is formed transitorily by equation 11 and decomposes spontaneously to the ester (Eq. 15):

$$\sim \mathrm{SiD_3^+,\ TfO^-,\ TfOH} \xrightarrow{k_\mathrm{deact}} \sim \mathrm{SiD_3OTf} + \mathrm{TfOH} \qquad (15)$$

This leads to

$$[\sim \mathrm{SiD_3^+,\ TfO^-,\ TfOH}] = \frac{k_\mathrm{i}\mathrm{KTf}}{k_\mathrm{deact}}[\sim \mathrm{SiOTf}][\mathrm{TfOH}][\mathrm{D_3}] \qquad (16)$$

$$-\mathrm{d[D_3]/dt} = \mathrm{R_{deact}} = \mathrm{R_p} = k_\mathrm{deact}[\mathrm{SiD_3^+,\ TfO^-,\ TfOH}] = k_\mathrm{i}\mathrm{K_{Tf}[SiOTf][TfOH][D_3]} \qquad (17)$$

There is however some objections to such a mode of polymer growth.

1 - The oxonium ions concentration should decrease with conversion (Eq.16) while we have seen that a small increase of the specific conductivity was observed.

2 - This is not compatible with D_6 formation by the selective backbiting reaction.

In order to form (for example in the case of the mixed anhydride) an equal weight of D_3 units in the HP and in D_6, the rate of D_3

consumption should be twice that of HP formation.

$$\sim \mathrm{SiD}_3^+ + 3D_3 \rightarrow \sim \mathrm{Si(D_3)_2OTf} + \mathrm{D}_6 \qquad (18)$$

This necessitates the incorporation of several D_3 molecules on each formed $\sim SiD_3^+$.

Conclusion

Polymerization of D_3 initiated by $CF_3CO\text{-}SO_3CF_3$ presents many similarities with those initiated by TfOH alone or by silyl triflate activated by TfOH. The formation of the linear high polymer (HP) and that of the D_{3x} cyclic oligomers may be explained in the same way as occurring on the activated silyl triflate end groups.

Unexpectedly, the relative weight amount D_6/HP is larger with the anhydride and in the presence of a proton trap (MDTBP), i.e. when acid concentration should be the lowest. This is again in disagreement with a formation of D_6 and other D_{3x} cycles by end-to-end ring closure of silanol esters, which would be formed by reaction of D_3 with TfOH. This conclusion has been confirmed by the suppression of macrocycles (while D_6 is formed in very large amount) when the largest concentration of proton trap was used.

But several important questions remain unanswered. D_{3x} cycles formation is best explained as involving tertiary siloxonium ions, but are they stable species with measurable lifetimes or only transient intermediates?

Are silyl esters reformed at each propagation step or are they only in equilibrium with the siloxonium ions?

It is tempting to imagine a polymer growth involving the strained $\sim SiD_3^+$ ions with a mechanism similar to tetrahydrofuran polymerization, but propagation by D_3 reaction with an activated silyl triflate still cannot be excluded.

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