Polymerizations of Hexamethylcyclosiloxane Catalyzed by Metal Sulfonate/Acid Chloride Combinations

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ABSTRACT: Hexamethylcyclotrisiloxane (D_3) was polymerized in bulk at 100°C, and the conversion was monitored by ^{1}H-NMR spectroscopy. Various metal triflates, which were inactive as neat salts, were combined with chlorosilanes, chlorostannanes, phenyl phosphonyl chloride, and carboxylic acid chlorides, which were also inactive when added alone. Most 1 : 1 combinations proved to produce active catalysts for the ring-opening polymerization of D_3. When the anions of sodium salts were varied alkylsulfonates and the sulfates were more reactive than the triflate. The samarium triflate/diphenyldichlorosilane combination was found to be the most reactive catalyst on the basis of the triflate ions. Regardless of the catalyst combination, the main reaction products in the early stages of all polymerizations were octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5). The polymerization mechanism is discussed. The reactive catalyst combinations also polymerized D_4 at 100°C. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4114–4120, 2012

Key words: cationic polymerization; polysiloxanes; ring-opening polymerization; silicones

INTRODUCTION

It has been well known for more than 5 decades that cyclosiloxanes can be polymerized by strong protic acids or by strong bases, such as potassium hydroxide or potassium silanolates. Although relatively few studies have been concerned with the polymerizations of hexamethylcyclotrisiloxane (D_3)[1–3] (mainly catalyzed by triflic acid), most publications have dealt with polymerization and equilibration of octamethylcyclotetrasiloxane (D_4). Most cationic polymerizations have been catalyzed by strong protic acids, such as concentrated sulfuric acid and triflic acid,[4–13] and little is known about catalysis by Lewis acids.[14–16] Furthermore, the cationic polymerization mechanism has not completely been elucidated. In contrast, anionic polymerizations[17–20] catalyzed by KOH or potassium silanolates are well understood. Most of these equilibration studies had the purpose of characterizing the frequency distribution of the resulting cyclic oligomers and polymers and characterizing their physical properties.

Quite recently, it was found[21] that acidic metal triflates (with pH < 4.0 as measured in water) are efficient catalysts for the ring-opening polymerization of D_3, where the vast majority of metal triflates are inactive at least at 100°C. In the course of these studies, the 1 : 1 combination of sodium triflate and dichlorodiphenylsilane was found to be a good catalyst for the polymerization of D_3 at 100°C, although neat dichlorosilanes or neat sodium triflate, were inactive. This finding prompted us to study catalyst systems composed of combinations of two inactive species, such as a metal sulfonate and a reactive chlorocompound.

EXPERIMENTAL

Materials

D_3, D_4, yttrium triflate, and 2,6-bis(tertbutyl)-4-methylpyridine (BTMPy) were purchased from Aldrich Co. (Steinheim, Germany) and were used as received. Sodium dodecyl sulfate, dodecylsulfonate, dodecylbenzene sulfonate, and tetraphenylborate were also purchased from Aldrich. The triflates of lithium, barium, magnesium, samarium, and zinc were purchased from Alpha Aesar (Karlsruhe, Germany) and were used as received. Dichlorodiphenylsilane, chlorotriethylsilane, dibutyltin chloride, tribulyltin chloride, phenylphosphonyl dichloride,

TABLE I
Polymerizations of D_3 in Bulk at 100°C with Sodium Triflate and Various Chlorine Compounds as Catalysts[a]

Experiment number	Chlorine compound	Conversion (%) after			
		1 h	6 h	24 h	48 h
1	Chlorotriethylsilane	31.5	87.5	98.0	99.5
2	Dichlorodiphenylsilane	5.5	32.5	99.0	99.0
3	Tributyltin chloride	1.5	2.0	3.0	4.0
4	Dibutyltin dichloride	1.5	2.0	2.0	2.0
5	Phenylphosphonyl dichloride	88.5	99.0	99.0	99.5
6	Benzoyl chloride	2.5	26.0	75.8	98.5
7	Stearoyl chloride	59.0	98.0	99.0	99.5
8	Benzyl chloride	2.5	3.0	4.0	4.0
9	Nitrobenzyl chloride	2.5	3.5	4.0	4.5

[a] Molar feed ratio of D_1 to catalyst = 1000/1.

benzoyl chloride, stearyl chloride, 4-nitrobenzyl chloride, and benzyl chloride were all purchased from Aldrich. Toluene was distilled over P_4O_{10}. All of the chlorocompounds were diluted with dry toluene so that $0.5M$ solutions were obtained.

Polymerizations

Polymerizations of D_3 (number 1. Table I)

D_3 (14.8 g or 200 mmol of repeating units (D_1)) was weighed into a 50-mL Erlenmeyer flask in an atmosphere of dry nitrogen, and preweighed sodium triflate (0.2 mmol) was added at once. The closed reaction vessel was immersed in an oil bath preheated to 100°C. Five minutes after the complete melting of D_3, a magnetic stirring bar and a toluene solution of chlorotriethylsilane (0.4 mL) were added. After 1, 6, 24, and 48 h, small samples were removed from the reaction mixture for ^{1}H-NMR measurements.

All of the experiments listed in Tables I–IV were conducted analogously.

Polymerization of D_4 (number 4, Table V)

D_4 (14.8 g or 200 mmol of D_1) and samarium triflate (0.2 mmol) were weighed into a 50-mL Erlenmeyer

TABLE III
Polymerizations of D_3 in Bulk at 100°C with Dichlorodiphenylsilane and Various Metal Triflates as Catalysts[a]

Experiment number	Triflate of	pH[b]	Conversion (%) after			
			1 h	6 h	24 h	48 h
1	Lithium		10.5	64.5	98.0	99.0
2	Sodium	10.15[22]	5.5	32.5	99.0	99.0
3	Magnesium	4.15[22]	3.0	10.0	99.0	99.0
4	Barium		24.0	29.5	53.5	77.5
5	Zinc	5.75[22]	97.0	98.5	99.0	99.0
6	Yttrium	6.72[21]	14.5	55.0	89.0	98.5
7	Samarium	6.95[23]	99.0	99.0	99.0	99.0

[a] Molar feed ratio of D_1 to catalyst = 1000/1.
[b] Measured in water at 20–22°C with 0.05 mol/L. References given.

flask, and a magnetic stirring bar was added. The closed reaction vessel was immersed in an oil bath preheated to 100°C. After 10 min, a $0.5M$ solution of dichlorodiphenylsilane in toluene (0.4 mL) was injected. After 1, 6, 24, and 48 h, samples of the reaction mixture were taken for ^{1}H-NMR and gel permeation chromatography measurements.

Analogous experiments were conducted with other catalyst combinations (see Table V).

Polymerization of D_3 with the addition of BTMPy (number 1, Table VI)

D_3 (14.8 g or 200 mmol of D_1), sodium dodecylsulfonate (0.2 mmol), and BTMPy (0.4 mmol) were weighed into a 50-mL Erlenmeyer flask in an atmosphere of dry nitrogen. The closed reaction vessel was immersed in an oil bath preheated to 100°C. Five minutes after the complete melting of D_3, 0.4 mL of a $0.5M$ solution of dichlorodiphenylsilane in toluene was injected. After 1, 6, 24, and 48 h, small samples were removed from the reaction mixture for ^{1}H-NMR measurements.

The other experiments of Table VI were conducted analogously.

TABLE II
Polymerizations of D_3 in the Bulk at 100°C with Magnesium Triflate and Various Chlorine Compounds as Catalysts[a]

Experiment number	Chlorine compound	Conversion (%) after			
		1 h	6 h	24 h	48 h
1	Chlorotriethylsilane	3.0	97.0	99.0	99.0
2	Dichlorodiphenylsilane	3.0	10.0	98.0	99.0
3	Dibutyltin dichloride	2.0	3.0	3.5	4.0
4	Phenylphosphonyl dichloride	97.0	99.0	99.0	99.0
5	Benzoyl chloride	1.5	2.5	4.0	7.5
6	Stearoyl chloride	2.5	9.0	10.5	10.5

[a] Molar feed ratio of D_1 to catalyst = 1000/1.

TABLE IV
Polymerizations of D_3 in Bulk at 100°C with Various Sodium Salts and Dichlorodiphenylsilanes as Catalysts[a]

Experiment number	Anion of the sodium salt	Conversion (%) after			
		1 h	6 h	24 h	48 h
1	Triflate	5.5	32.5	99.0	99.0
2	4-Dodecylbenzene sulfonate	40.0	88.5	95.5	99.5
3	Dodecyl sulfonate	46.0	66.5	99.0	99.0
4	Dodecyl sulfate	54.5	98.5	99.0	99.0
5	Tetraphenylborate	0.0	1.5	2.5	3.0
6	Trifluroacetate	3.0	3.5	4.0	5.0
7	Benzoate	0.0	5.0	12.0	13.0

[a] Molar feed ratio of D_1 to catalyst = 1000/1.

TABLE V
Polymerizations of D_4 in the Bulk at 100°C with Various Catalysts Combinations[a]

Experiment number	Catalyst combination	Conversion (%) after			
		1 h	6 h	24 h	48 h
1	Sodium triflate plus dichlorodiphenylsilane	0	0	0	0
2	Sodium triflate plus phenylphosphonyl dichloride	27.0	78.0	92.0	99.0
3	Magnesium triflate plus benzoyl chloride	0	0	0	0
4	Samarium triflate plus dichlorodiphenylsilane	38.0	52.0	87.0	96.0

[a] Molar feed ratio of D_1 to catalyst = 1000/1.

Measurements

The 400-MHz ^{1}H-NMR and 100.2-MHz ^{13}C-NMR spectra were recorded with a Bruker ''Avance 400'' Fourier transform NMR spectrometer (Rheinstetten, Germany) in 5-mm-diameter sample tubes. Deuterated chloroform containing tetramethylsilane (TMS) served as the solvent.

The pH values of the metal salts were measured at 20–22°C at a concentration of 0.05 mol/L with a HANNA (Kehl am Rhein, Germany) pH meter, as reported previously.[22–24]

RESULTS AND DISCUSSION

Polymerizations of D_3

For most polymerizations conducted in this work, D_3 was used as the monomer for two reasons. First, both the ^{1}H-NMR and ^{13}C-NMR signals are well separated from the signals of D_4 and those of higher oligomers or polymers (Table VI), and thus, its conversion could easily and accurately be monitored by ^{1}H-NMR spectroscopy. Second, D_3 is more reactive than all of the other cyclosiloxanes, and thus, it is well suited for testing the activity of new potential catalysts. The structure of the catalysts examined in this work was varied in three directions. In the case of the metal salts, both cations and anions were varied separately. Furthermore, the structure of the chlorocompounds was varied, so that the Cl atoms were connected to four different elements (Si, Sn, P, and C).
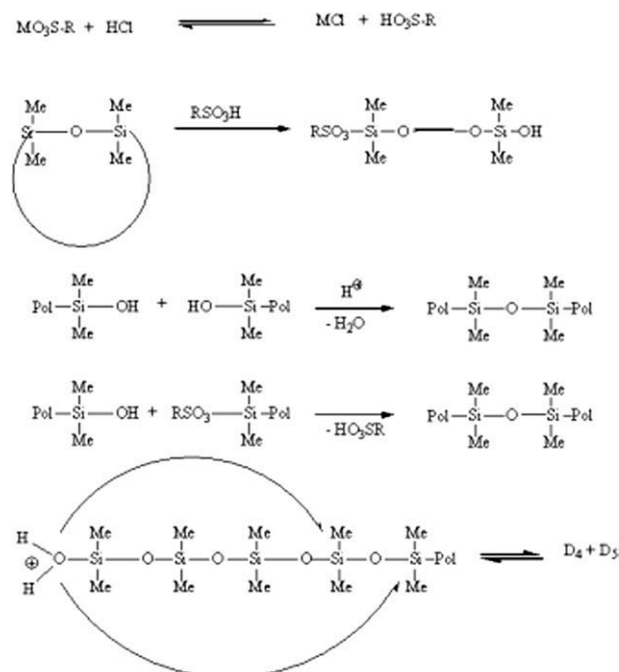
The first series of polycondensations was conducted in such a way that the same metal salt, sodium triflate, was used in all of the experiments, and the chlorocompound was varied (Table I). Sodium triflate exhibits a low acidity (pH = 10.15) when measured in water at 20–22°C[22] and was proven to be not reactive enough to catalyze the polymerization of D_3 in bulk at 100°C.[21] The conversion of D_3 was determined after 1, 6, 24, and 48 h. These reaction conditions matched those used in a previous study on the basis of triflic acid and various metal salts as catalysts. More detailed kinetic studies were not performed because sodium triflate was insoluble in D_3 and because the polymerizations were certainly diffusion-controlled when the reaction mixtures turned viscous. However, the time–conversion measurements performed in this work allowed for a classification of the catalyst combinations into systems of low, moderate, or high reactivity, and a more precise subdivision was not intended. The results compiled in Table I show that five out of nine catalyst combinations were active, whereas four combinations were inactive, namely, the tin chlorides (numbers 3 and 4, Table I) and the benzyl chlorides (numbers 8 and 9, Table I).

If we assumed that the mechanism consisted of the liberation of triflic acid by traces of HCl in the chlorocompounds (Scheme 1), it was understandable that the benzylchlorides were inactive because they were insensitive to neutral water below 25°C. Tributyltin chloride is also insensitive to cold neutral water, but dibutyltin

TABLE VI
^{1}H-NMR and ^{13}C-NMR Chemical Shifts of the Cyclosiloxanes and Polydimethylsiloxane in CDCl$_3$/TMS

Siloxane	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)
D_3	0.17	0.91
D_4	0.09	0.77
D_5	0.08	0.88
D_6	0.13	−6.13
Polydimethylsiloxane	0.07	1.05

Scheme 1 Speculative mechanism of a proton-catalyzed ring cleavage followed by bimolecular condensation steps and by rapid back-biting (M = metal; Pol = polymer chain).

dichloride is several orders of magnitude more sensitive to hydrolysis. Hence, the results obtained with tin chlorides were difficult to understand on the basis of the mechanism outlined in Scheme 1.

An analogous series of polymerizations was performed with magnesium triflate (Table II). Despite its acidity (pH = 4.15),[22] this salt was inactive toward D_3 when used alone.[21] As demonstrated in Table II, the chlorosilane and the phosphonyl chloride also activated this salt, whereas dibutyltin dichloride was again inactive. Therefore, these results confirm those obtained with sodium triflate. However, both carboxylic acid chlorides showed only a low reactivity in contrast to the combination with sodium triflate.

In a third series of polymerizations of D_3, dichlorodiphenylsilane was used in all of the experiments as a cocatalyst, and the metal triflate was varied (Table III). Dichlorodiphenylsilane in combination with sodium or magnesium triflate may be classified as a catalyst system of moderate reactivity. The polymerizations listed in Table III gave two interesting results. First, all of the metal triflates yielded active catalyst, so high conversions were achieved after 48 h. Second, the activity of these catalyst systems varied largely with the cation. After 1 h of polymerization, magnesium triflate proved to be the least reactive metal salt, whereas samarium triflate yielded the most active catalyst system. Complete conversion within 1 h was a remarkable success (number 7, Table III). These results do clearly not display any correlation with the acidity of the metal triflates. Perhaps they reflect different reactivities toward the chlorosilane on the basis of different stabilities of the crystal lattice of metal triflates versus metal chloride.

The fourth series of polymerizations had the purpose of exploring the role of the anion of the metal salts. For this purpose, various salts of sodium were combined with dichlorodiphenylsilane (Table IV). Surprisingly, the sodium dodecyl sulfate and both sulfonates were more reactive than the triflate. In contrast, tetraphenylborate, trifluoroacetate, and benzoate anions proved to be rather inactive. The latter results can be rationalized when the polymerization mechanism is based on the catalytic effect of highly acidic protic acids. The sulfonic acids are several orders of magnitude more acidic than trifluoroacetic acid, benzoic acid, or tetraphenylboric acid. The high reactivity of the sulfonates and dodecylsulfate may have resulted from a less stable crystal lattice, having a lower density of electric charges, so that the reaction with HCl or nonpolar chlorosilanes was facilitated. In summary, the results of Table IV fit in with the mechanism formulated in Scheme 1.

Polymerizations of D_4

To confirm that the catalysts mixtures detected in this work not only reacted with the strained and re-active D_3 ring but also polymerized and equilibrated less reactive oligosiloxanes, a few experiments with D_4 were conducted. The results summarized in Table V prove that the combinations classified as sluggish for D_3 (experiments 1 and 3, Table V) were inactive with the less reactive monomer D_4. However, some of these new catalyst systems may, in principle, polymerize and equilibrate D_4. The catalyst combination used for experiments 2 and 4, which were efficient in the case of D_3, were also active in the case of D_4. However, these polymerizations of D_4 were slower; this was in agreement with its lower reactivity. Indeed, 99% conversion of D_4 was only observed after 48 h, whereas (samarium triflate + dichlorodiphenylsilane) yielded a complete polymerization of D_3 after only 1 h (Table IV). At this point, it should be mentioned that 99% conversion does not mean 99% consumption of D_4 but an almost complete approach to the equilibrium concentration. It should also be mentioned that the margin of error of these conversion measurements was relatively larger (±5% relative to the measured value). Regardless of the margin of error, the data in Table V evidence that catalysts that were reactive toward D_3 also reacted with D_4, whereas the less reactive catalyst combinations were totally inactive (experiments 1 and 3, Table V).

MECHANISTIC DISCUSSION

In a previous study,[21] acid- and base-catalyzed polymerizations of D_3, D_4, and decamethylcyclopentasiloxane (D_5) were compared in bulk at 100°C. It was found that the kinetic courses were quite different. When potassium *tert*-butoxide was used as a catalyst, the chain-growth steps were as fast or faster than the formation of D_4, D_5, and dodecamethylcyclohexasiloxane (D_6) by back-biting. Complete equilibration was achieved within 98 h. In contrast, triflic acid generated the cyclic oligomers as the main reaction products in the early stages of the polymerization. Their rapid formation was then followed by a slower polymerization and equilibration process. On the basis of the literature data,[1–3] the mechanism outlined in Scheme 1 was formulated. The polymerization seemed to be based on condensation steps, which are slower than the back-biting reaction.

The evaluation of the ^{1}H-NMR spectra recorded in this work evidenced that the experiments followed the same pattern as the acid-catalyzed polymerizations of D_3 described previously.[21] Figures 1 and 2 illustrate exemplarily for a sodium triflate catalyzed polymerization of D_3 (number 1, Table I) that the initial formations of D_4 and D_5 were followed by slower equilibration, which was complete after 48 h.
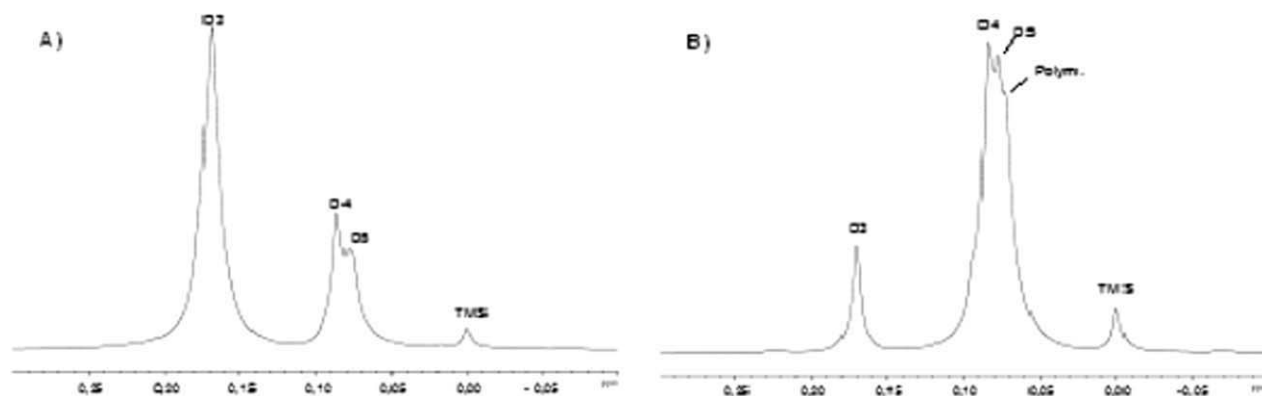
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Figure 1 Evolution of the ^{1}H-NMR spectra during the polymerization of D_3 catalyzed by sodium triflate + chlorotriethyl-silane (number 1, Table I) after (A) 1 and (B) 6 h.
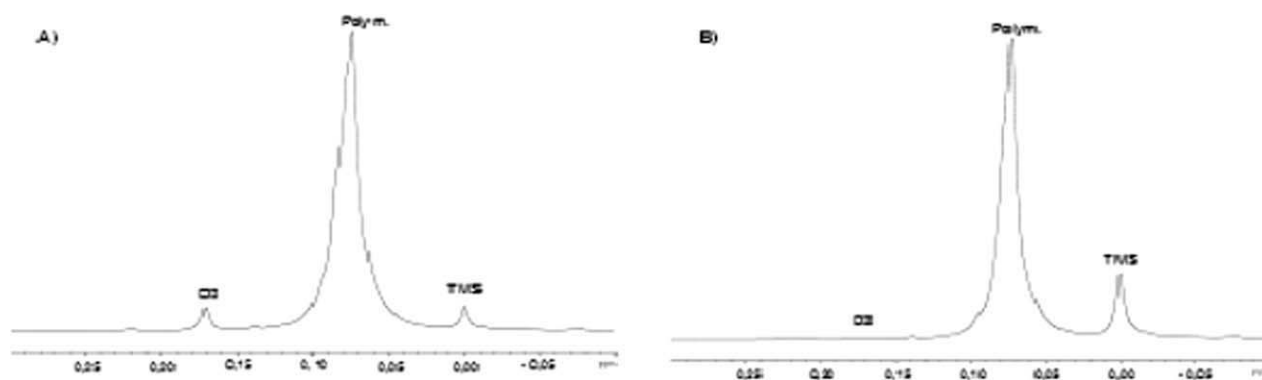

Figure 2 Evolution of the ^{1}H-NMR spectra during the polymerization of D_3 catalyzed by sodium triflate + chlorotriethyl-silane (number 1, Table I) after (A) 24 and (B) 48 h.

The same trend was observable for other sodium sulfonates and sulfates, as demonstrated for dodecyl sulfate (number 4, Table IV) in Figure 3. In agreement with this kinetic pattern, the samarium triflate catalyzed polymerization of D_4 initially mainly yielded D_5, which gradually vanished together with D_4 until full equilibration was reached (Fig. 4). D_6 (and tetradecamethylcyclohexasiloxane-D_7) were barely detecta-

ble because their concentration was low because of energetically unfavorable conformations.[21]

A surprising result of all of the experiments with reactive catalysts was the complete or almost complete equilibration within 48 h. With neat triflic acid, full equilibration was never achieved at 100°C, even after 196 h, although triflic acid was the most acidic sulfonic acid. More precisely, the initiation of this
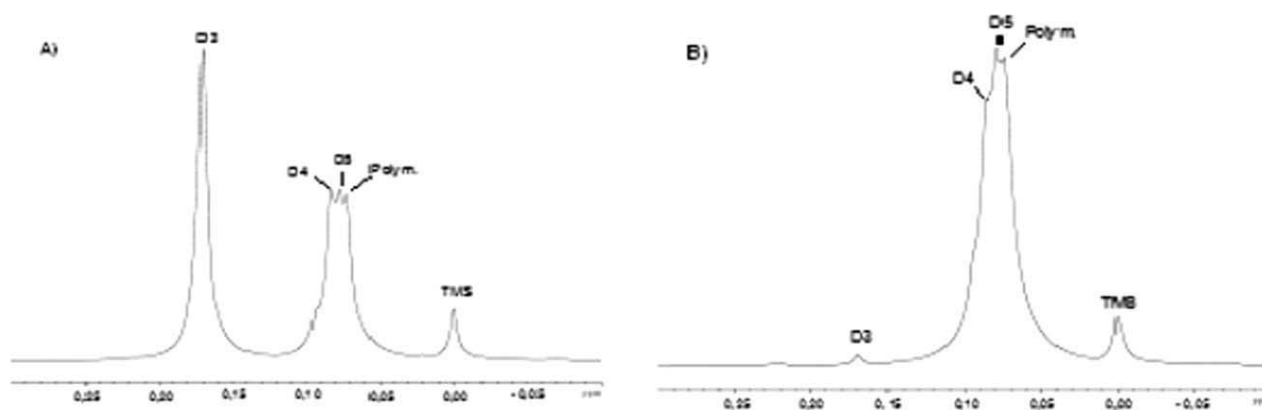

Figure 3 Evolution of the ^{1}H-NMR spectra during the of polymerization of D_3 catalyzed by sodium dodecyl sulfate + dichlorodiphenylsilane (number 4, Table IV) after (A) 1 and (B) 6 h.
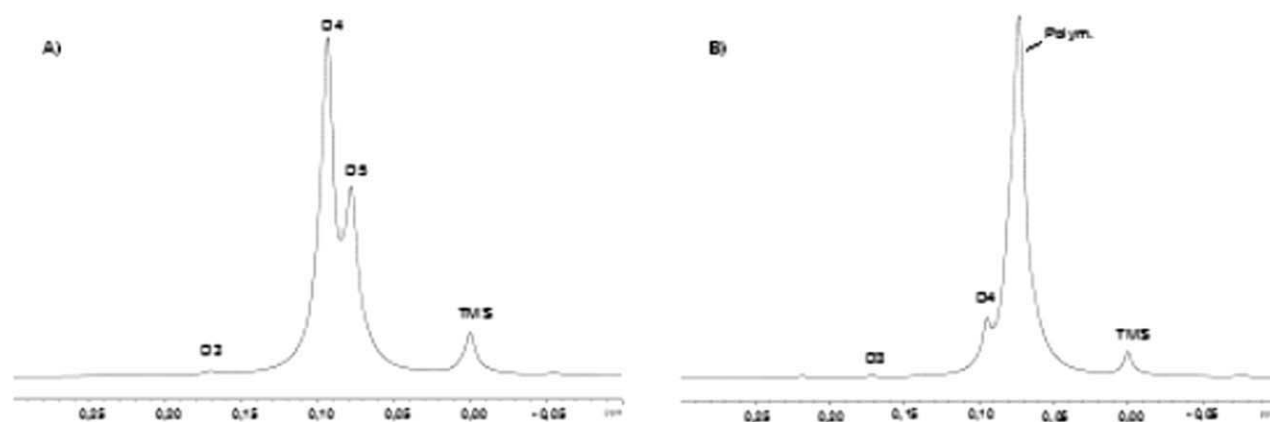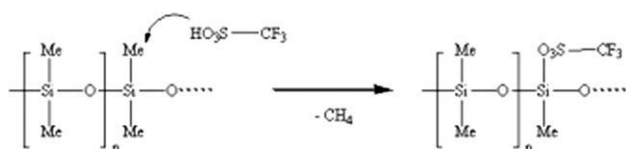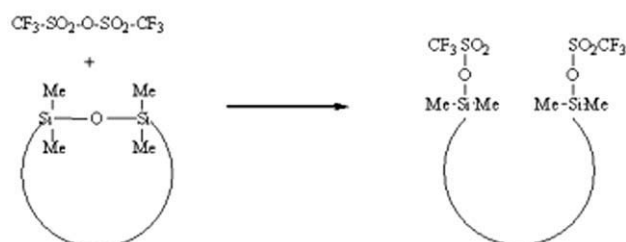
Figure 4 Evolution of the ^{1}H-NMR spectra during the of polymerization of D$_4$ catalyzed by samarium triflate + dichloro-diphenylsilane (number 4, Table V) after (A) 1 and (B) 48 h.

ring-opening polymerization with triflic acid is influenced by the water amount: an addition of 10^{-2} M water increased the rate by three orders of magnitude,[10] whereas a further increase in the water concentration strongly decreased the reaction rate.[25] Because complete equilibration was reached within 48 h with neat bismuth triflate and hafnium triflate, it was postulated in our previous publication[21] that triflic acid was gradually deactivated by Si—C cleavage according to Scheme 2. If this deactivation was indeed operating, it means that either the liberation of triflic acid according to Scheme 1 proceeded continuously over the whole course of the polymeriza-
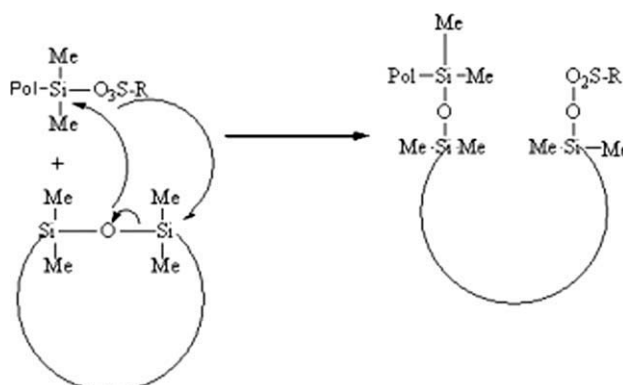
tion or another reaction mechanism was also operating.

An alternative or complementary reaction mechanism is formulated in Scheme 3. The formation of mixed anhydrides or silyl sulfonates may be occurring in the first step. At 100°C, the mixed anhydrides will disproportionate into symmetrical anhydrides, and the sulfonyl anhydrides may cleave the siloxane bonds. The silyl sulfonates may, in turn, initiate and continue the ring-opening[10] and equilibration processes (Scheme 4). Such a mechanism has been discussed in the literature, but clear-cut evidence in favor or against it is still missing. If the Si—C bond cleavage formulated in Scheme 2 is indeed responsible for the deactivation of triflic acid, it indicates that silyl triflates are not reactive enough to catalyze the equilibration of dimethylsiloxanes at 100°C. In other words, a consistent reaction mechanism explaining all aspects of the results obtained in this work cannot be offered at this time, and a detailed study of all mechanistic aspects was beyond the scope of this study.

Scheme 2 Deactivation of triflic acid by Si—C cleavage.

Scheme 3 Formation of mixed anhydrides their disproportionation and the cleavage of cyclosiloxanes by triflic anhydride (M = metal).

Scheme 4 Ring cleavage and chain growth via the direct reaction of silylsulfonate groups with cyclosiloxanes (Pol = polymer chain).

CONCLUSIONS

The experiments of this work evidenced that the combination of a metal sulfonate and a reactive chlorocompound may yield a reactive catalyst for the ring-opening polymerizations of both D_3 and D_4, even when both components are inactive under the given reaction conditions. Furthermore, the best catalysts of this work allowed complete equilibration, in contrast to neat triflic acid. It may be of interest for preparative purposes that stable commercial and inexpensive metal salts, such as sodium dodecyl sulfate or dodecyl sulfonate, may be activated by a trace of a gaseous or liquid chlorocompound, which is itself stable on storage, commercial, and inexpensive. Details of the reaction mechanism are not fully understood yet and need further investigation. The results of this work suggest that good catalysts for the equilibration of siloxanes may be obtained by the activation of solid surfaces containing sulfate or sulfonate ions.

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