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Acid-Catalyzed Condensation of Model Oligo(dimethylsiloxanediol)s

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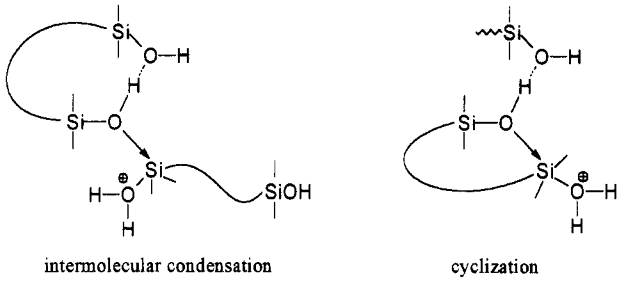
ABSTRACT: The kinetics of condensation of octamethyltetrasiloxane-1,7-diol, tetradecamethylheptasiloxane-1,13-diol, and the mixture of oligo(dimethylsiloxanediol)s $H(OSiMe_2)_nOH$ (n = 4-19) catalyzed by trifluoromethanesulfonic (triflic) acid were studied in dichloromethane solution. Rates of cyclization and linear growth of various siloxanediols were compared. The conversion rate decreases with the length of siloxane chain up at least 9 SiO units in the molecule. Complex kinetic dependencies indicate that the mechanism of silanol condensation catalyzed by triflic acid in dichloromethane is complicated by the equilibria involving acid, silanol, and water. The scope of operation of the mechanism involving basic assistance by a silanol group (intra-inter catalysis) in the condensation of silanols is discussed.

Introduction

Condensation involving silanol groups is one of the most important reactions in the synthesis of siloxane polymers.[1-3] Its role in the cationic ring-opening polymerization of cyclosiloxanes is also discussed.[4-6] In particular, the intramolecular condensation (end-to-end closure) of bifunctional growing chains is responsible, at least partially, for the extensive formation of cyclics during this process. Cyclization is also the most important side reaction in polycondensation of oligosiloxanediols leading to polysiloxanes. Thus, it is important to establish the kinetic features of the mechanism of ring closure and to look for the conditions in which the yield of cyclics could be minimized.

Competition of cyclization and linear growth in condensation of decamethylpentasiloxane-1,9-diol was studied a few years ago in dioxane and dichloromethane.[7,8] Contrary to the classical kinetics observed in basic solvents such as methanol or dioxane (i.e., first-order cyclization and second-order linear condensation), cyclization in dichloromethane was found to follow second-order kinetics. Moreover, the overall condensation of decamethylpentasiloxanediol was over 30 times faster than the condensation of the analog having only one silanol group, undecamethylpentasiloxanol. Both features indicate that a special mechanism operates when oligosiloxanediols are subject to condensation in acid-base inert solvents such as dichloromethane. To explain these observations, a mechanism of the condensation has been proposed which involves basic assistance of a third silanol group in the condensation act. The classical mechanism of acid-catalyzed silanol condensation involves protonation of a silanol group, making the adjacent silicon atom more electrophilic, followed by nucleophilic attack of another silanol group.[9] The assistance of a base involving formation of a hydrogen bond with the silanol group acting as a nucleophile enhances its nucleophilic character in the substitution reaction. Since the strongest base in an inert medium is the silanol function, the participation of a third silanol group from another molecule (in cyclization) or from the other end of the reacting chain (in intramolecular condensation) has been postulated. This mechanism was referred to as intra-inter catalysis (Scheme 1).[8]

Scheme 1



intermolecular condensation cyclization

The presented mechanism of the condensation of oligosiloxanediols in inert solvent implies that the proportion of cyclics and linear polymer should be independent of the initial monomer concentration. Indeed, the yield of $(Me_2SiO)_5$ in the condensation of $H(OSiMe_2)_5OH$ catalyzed by TfOH in dichloromethane changes only from 30 to 20 mol % in a concentration range of $H(OSiMe_2)_5OH$ 0.05-0.2 mol/L.[7] The cyclic/linear product ratio depends on the acid used as the catalyst and, for example, for CH_3SO_3H was found to be ca. 1:1.[8]

The efficiency of this type of catalysis should depend on the distance between silanol end groups in the chain and on the conformational probability of their encounter. Indeed, recent results suggest that the yield of cyclics is much lower when the mixture of longer siloxanediols is subject to condensation.[10] The condensation of the mixture containing oligomers $H(OSiMe_2)_nOH$ (n = 8-24), $[SiOH]_0$ = 0.4 mol/L, catalyzed by CF_3SO_3H in dichloromethane gave less than 5% of cyclics.[10]

In the same study, the kinetics of condensation of $H(OSiMe_2)_2OH$ catalyzed by TfOH in CH_2Cl_2 was investigated.[10] The reaction performed at $[H(OSiMe_2)_2OH]_0$ = 0.45 mol/L and $[TfOH]_0 = 10^{-3}$ mol/L was initially very fast but rapidly slowed down after ca. 2 min. This behavior was attributed to heterogenization of the system with formation of an inverse emulsion after a limit of solubility of water in CH_2Cl_2 had been reached. Most of the acid was then trapped in the aqueous phase and its concentration in the organic phase dropped rapidly. Further reaction followed second order with the apparent rate constant proportional to $[TfOH]_0$.[10]

The rate of the condensation of $H(OSiMe_2)_2OH$ in a heterogeneous system was shown to increase roughly proportionally with the stirring speed.[10] This points to the contribution of the condensation reaction proceeding

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near the interface where the concentration of silanol groups may be relatively high due to strong hydrogen bondings to water. Bischoff has presented two arguments for the condensation taking place mainly in the organic phase.[10]

(1) The condensation of $H(OSiMe_2)_2OH$ catalyzed by TfOH in water is slower and leads mainly to disproportionation products ($H(OSiMe_2)_3OH$, $H(OSiMe_2)_5OH$, etc.) instead of the expected $H(OSiMe_2)_{2n}OH$ species, whereas in dichloromethane those products are formed in negligible amount.

(2) The second-order apparent rate constant of silanol conversion in the heterogeneous system is increasing proportionally to the initial TfOH concentration in CH_2Cl_2 up to about 10^{-3} mol/L. Further increase of the acid concentration causes virtually no change of the rate constant (although in the first period, when the system was homogeneous, the conversion is faster). This observation may be explained assuming that the reaction is catalyzed by the hydrated acid remaining in the organic phase which reaches the saturation concentration in these reaction conditions.[10]

Tetramethyldisiloxanediol constitutes a rather special case because it is unable to cyclize. It is also more reactive than longer diols (e.g., the second-order rate constant is approximately twice higher than that of $H(OSiMe_2)_4OH$). Thus, it seems interesting to compare the kinetics of condensation of various oligosiloxanediols. It is also important to know how the cyclization ability varies with the chain length of oligosiloxanediols and to verify the scope of applicability of intra–inter catalysis.

This objective was approached by kinetic investigations of the condensation of two model oligosiloxanediols ($H(OSiMe_2)_4OH$ (**I**) and $H(OSiMe_2)_7OH$ (**II**)) and of the mixtures of oligosiloxanediols $H(OSiMe_2)_nOH$, $n = 4$–19 (**III**), and $n = 5$–19 (**IV**) in dichloromethane in the presence of triflic acid.

Results and Discussion

1. Kinetics of Condensation of Model Oligosiloxanediols. Kinetic studies were performed in dichloromethane at 30 °C. The reaction was followed by gas–liquid chromatography and gel permeation chromatography. The use of capillary GC allowed precise calculation of the concentrations of the condensation products up to 21 D units (the symbol D represents a $SiMe_2O$ unit) in the molecule.

$$\begin{tikzcd} HD_nOH \arrow[r, "TfOH"] \arrow[d] & HD_{2n}OH \arrow[r] \arrow[d] & HD_{3n}OH \arrow[r] \arrow[d] & {} \\ D_n & D_{2n} & D_{3n} & \end{tikzcd} \quad (1)$$

The dominating reaction in the process catalyzed by triflic acid in CH_2Cl_2 is condensation; side reactions such as disproportionation (redistribution of dimethylsiloxane units) and chain scrambling are negligible.[11] The experiments at variable initial concentration of the monomer and of the catalyst were performed to establish the kinetic laws of cyclization and intermolecular condensation as well as to find the relation between the concentration of both species and the yield of cyclics and polymer.

As the condensation catalyzed by triflic acid is very fast, low concentration of the catalyst (usually less than 5×10^{-4} mol/L) had to be used to measure initial rates.

The experiments performed at variable concentration of the substrate showed a very unusual dependence of the initial rate on the silanol concentration (Figure 1). The initial rate of silanol consumption increases with $[HD_4OH]_0$, reaching a maximum at about 0.1 mol/L, and then drops with further increase of silanol concentration. The initial rate constants of cyclization and linear product formation calculated according to a second-order kinetic law are summarized in Table 1. Such dependence reflects a dramatic change of the apparent catalytic activity of triflic acid as a function of $[SiOH]_0$. An analogous change of initial rate was also observed in the condensation of HD_7OH and HD_nOH (**III** and **IV**). This behavior differs from that observed for the condensation of HD_5OH catalyzed by weaker acids, CH_3SO_3H and CF_3COOH. In the latter cases, the rate of the reaction increased proportionally to $[HD_5OH]_0$ within the range 0.02–0.2 mol/L and the apparent order in the substrate was found to be about 1.5.[8]

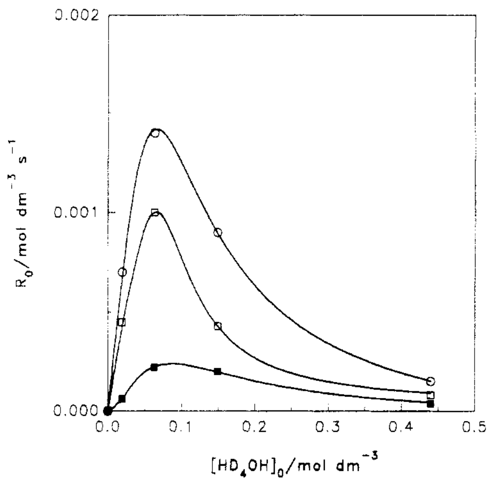


Figure 1. Initial rates of condensation R_0 of HD_4OH as a function of $[HD_4OH]_0$ in CH_2Cl_2 at 30 °C ($[TfOH]_0 = 1.1 \times 10^{-4}$ mol/L): (○) rate of conversion of HD_4OH; (□) rate of formation of D_4; (■) rate of formation of HD_8OH.

The yield of D_4 in the condensation of HD_4OH is nearly constant (52–60%) in the range of $[HD_4OH]_0 = 0.1$–0.9 mol/L (Figure 2). This dependence shows a close analogy to that observed for the HD_5OH system and is in favor of the concept of inter–intra catalysis.[7,8] At lower initial concentrations of the substrate (below 0.1 mol/L), the bimolecular mechanism of cyclization becomes less important and the classical first-order cyclization dominates, which is reflected by the elevation of the yield of D_4 (Figure 2).

In contrast, the yield of D_7 decreases with increasing initial concentration of HD_7OH in the same range of concentrations (Figure 2), which suggests that the basic assistance of another silanol group becomes less significant in this case.

The yield of cyclics does not depend on the concentration of the acid. The experiments made in the presence of water proved that it did not significantly depend on the initial water content, either (Table 2).

Condensation of HD_7OH shows an apparent order in the acid of 0.8 for cyclization and 0.6–0.7 for linear condensation (Figure 3). However, this dependence is subject to an experimental error of about 20%. Working at a catalyst concentration as low as 6×10^{-5} mol/L involves some error in preparation of the catalyst solution. On the other hand, at high TfOH concentration (10^{-3} mol/L) the initial rate of formation of the linear dimer calculated graphically from the plot may be underestimated because of the fast consecutive condensation. Taking this into account, both inter- and intramolecular condensations are likely to show the same, presumably first, order with respect to the catalyst, as observed for weaker acids.[8]

The condensation of the mixtures of oligosiloxanediols **III** and **IV** showed that the initial rate of the reaction

Table 1. Second-Order Initial Rate Constants of HD_4OH Consumption, Cyclization, and Intermolecular Condensation at Various Concentrations of the Substrate in CH_2Cl_2 at 30 °C ($[TfOH]_0 = 1.1 \times 10^{-4}$ mol/L)

$[HD_4OH]_0$ (mol/L)	yield of D_4 (mol %)[a]	$R_0(HD_4OH)$ (mol/L·s)	$k(HD_4OH)$ (L/mol·s)[b]	$R_0(D_4)$ (mol/L·s)	k_c (L/mol·s)[b]	$R_0(HD_8OH)$ (mol/L·s)	k_1 (L/mol·s)[b]
0.019	80	7×10^{-4}	0.48	4.8×10^{-4}	0.65	8×10^{-5}	0.05
0.061	66	1.4×10^{-3}	0.092	1.0×10^{-3}	0.13	2.2×10^{-4}	0.015
0.15	58	9×10^{-4}	0.010	4.3×10^{-4}	9.6×10^{-3}	2.0×10^{-4}	2.2×10^{-3}
0.44	55	1.5×10^{-4}	1.9×10^{-4}	8×10^{-5}	2.0×10^{-4}	3.6×10^{-5}	4.4×10^{-5}

[a] The yield of D_4 was calculated relative to $[HD_4OH]_0$ using the concentration value of D_4 measured at 100% conversion of HD_4OH, just after its disappearance when secondary reactions such as back-biting were negligible. [b] Rate constants were calculated according to the following equations: total consumption of HD_4OH, $k(HD_4OH) = -R_0(HD_4OH)/4[HD_4OH]_0^2$; cyclization, $k_c = R_0(D_4)/2[HD_4OH]_0^2$; formation of HD_8OH, $k_1 = R_0(HD_8OH)/4[HD_4OH]_0^2$. In these equations $R_0(X) = (d[X]/dt)_{t=0}$ and $-R_0(HD_4OH) = R_0(D_4) + 2R_0(HD_8OH)$.

Table 2. Comparison of the Second-Order Initial Rate Constants of the Consumption and Cyclization of Oligo(dimethylsiloxanediol)s in the Condensation of HD_nOH in CH_2Cl_2 at 30 °C ($[TfOH]_0 = 1.0 \times 10^{-3}$ mol/L; (a) Mixture III, $[SiOH]_0 = 0.9$ mol/L; (b) Mixture IV, $[SiOH]_0 = 0.28$ mol/L)[a]

n	$[HD_nOH]_0$ (mol/L) (a)	k (L/mol·s) (a)	k_c (L/mol·s) (a)	yield of $[D_n]$ (mol %)	$[HD_nOH]_0$ (mol/L) (b)	k (L/mol·s) (b)	k_c (L/mol·s) (b)	yield of $[D_n]$ (mol %)
4	0.046	0.04	0.04	50	0			
5	0.052	0.022	0.01	26	0.002	2.5	3.4	40
6	0.056	0.014	0.0036	11	0.0097	2.1	1	25
7	0.056	0.0075	0.003	16	0.0117	1.8	1.7	58
8	0.051	(0.006)	0.0017	18	0.0109	1.4	2.0	68
9	0.046			9	0.0088	0.8	0.8	52

[a] The yields of D_n were calculated relative to $[HD_nOH]_0$ as in Table 1. Rate constants were calculated according to the following equations: total consumption of HD_nOH, $k(HD_nOH) = -R_0(HD_nOH)/2[HD_nOH]_0[SiOH]_0$; cyclization, $k_c = R_0(D_n)/[HD_nOH]_0[SiOH]_0$. In these equations $R_0(X) = (d[X]/dt)_{t=0}$.

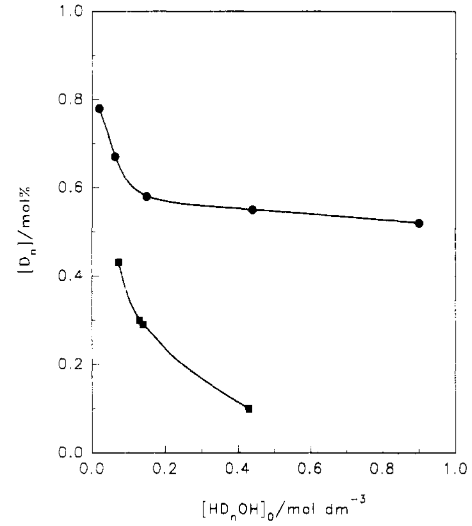


Figure 2. Yield of D_n as a function of $[HD_nOH]_0$ measured at total conversion of HD_nOH: (●) $n = 4$, $[TfOH]_0 = 1.1 \times 10^{-4}$ mol/L; (■) $n = 7$, $[TfOH]_0 = 2.2 \times 10^{-4}$ mol/L.

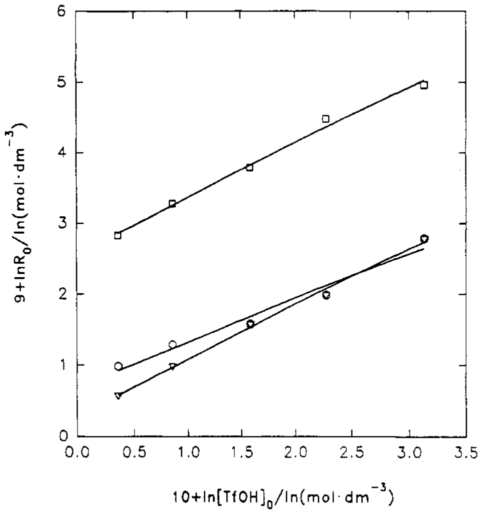


Figure 3. Dependence of initial rate of condensation R_0 of HD_7OH as a function of catalyst concentration in CH_2Cl_2 at 30 °C ($[HD_7OH]_0 = 0.14$ mol/L): (□) rate of conversion of HD_7OH; (▽) rate of formation of D_7; (○) rate of formation of $HD_{14}OH$.

decreased with the chain length up to at least $n = 9$. Using the mixture III (HD_nOH, $n = 4$–19), it was possible to compare the reactivities of oligomers $n = 4$–7 directly from initial conversion rates whereas the kinetic data for the mixture **IV** ($n \geq 5$) allowed comparison of the reactivities of oligosiloxanediols of $n = 5$–9 (Figure 4). (The kinetics of the conversion of longer diols is complicated as they are formed from lower diols and for this reason is difficult to analyze.) Thus, for example, the initial rate of conversion of HD_9OH was nearly 3 times lower than that of HD_6OH while both were present in the solution at similar initial concentrations. The initial rate constants of cyclization and total HD_nOH consumption, $n = 4$–9, calculated according to second-order kinetic law are compared in Table 2. The total yield of cyclic products decreases strongly as the concentration of silanol groups increases. Thus, for the mixtures **III** and **IV** at $[SiOH]_0 = 0.28$ mol/L the total yield of cyclic products was about 50 wt % while at $[SiOH]_0 = 0.9$ mol/L it was below 20 wt % (Figure 5).

The condensation of HD_4OH shows a nonlinear dependence of $1/[SiOH]$ on time. At high SiOH concentration (≥0.8 mol/L), the plot $1/[OH] - 1/[OH]_0$ versus time exhibits a sharp breakpoint (Figure 6), indicating that the rate constant drops rapidly at that moment. The kinetics of SiOH conversion seems to follow second internal order after the breakpoint up to a relatively high SiOH conversion (depending on the $[SiOH]_0$). It was not possible to follow the total silanol concentration in the HD_7OH system up to conversions sufficient to observe such a dependence because the oligomers above DP = 3 (21 D units) were not observable by GC.

This phenomenon has already been observed in the condensation of HD_2OH catalyzed by triflic acid and was attributed to heterogenization of the system due to limited solubility of water in dichloromethane.[10] Indeed, a correlation between the breakpoint and the appearance of an emulsion was observed in the systems discussed here. In the experiments performed at initial HD_4OH concentra-

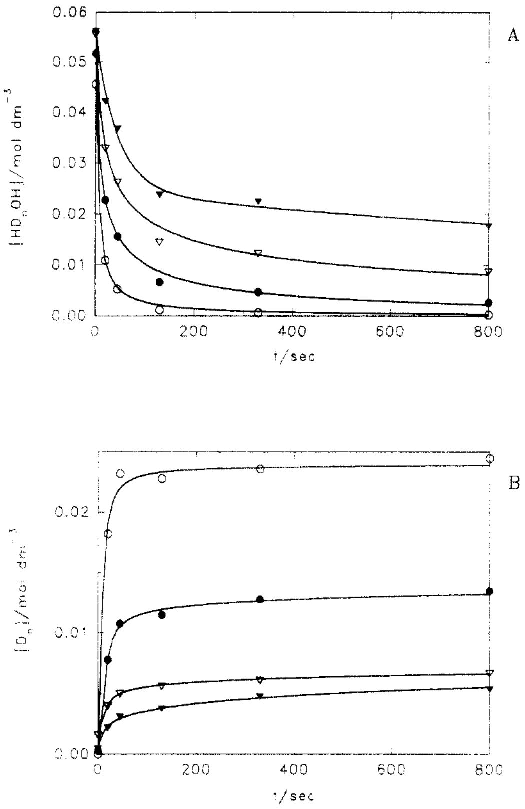


Figure 4. Conversion of oligosiloxanediols HD_nOH, n = 4–7, and formation of the corresponding cyclosiloxanes in condensation of the mixture of oligo(dimethylsiloxanediol)s (**III**) in CH_2Cl_2 at 30 °C ($[SiOH]_0 = 0.9$ mol/L; $[TfOH]_0 = 1.0 \times 10^{-3}$ mol/L): (A) conversion of HD_nOH; (B) formation of D_n; (cop) n = 4; (●) n = 5; (▽) n = 6; (▼) n = 7.

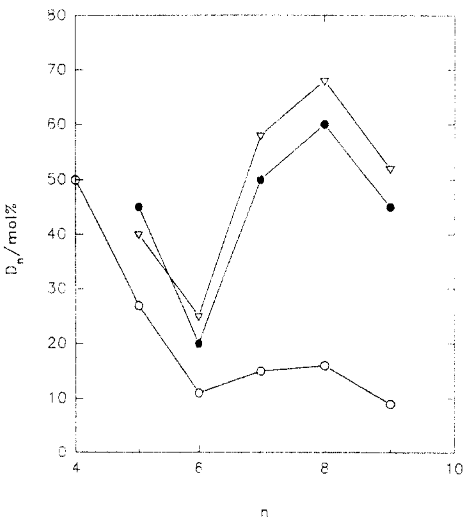


Figure 5. Yield of cyclic siloxanes (in mole percent relative to initial concentration of the corresponding diol) measured at 100% conversion of the original diol in condensation of the mixtures of oligosiloxanediols HD_nOH **III** and **IV** catalyzed by TfOH in CH_2Cl_2 at 30 °C; ($[TfOH]_0 = 1.0 \times 10^{-3}$ mol/L): (○) mixture **III**, $[SiOH]_0 = 0.9$ mol/L; (▽) mixture **IV**, $[SiOH]_0 = 0.28$ mol/L; (●) mixture **IV**, $[SiOH]_0 = 0.28$ mol/L, $[H_2O]_0 = 0.1$ mol/L.

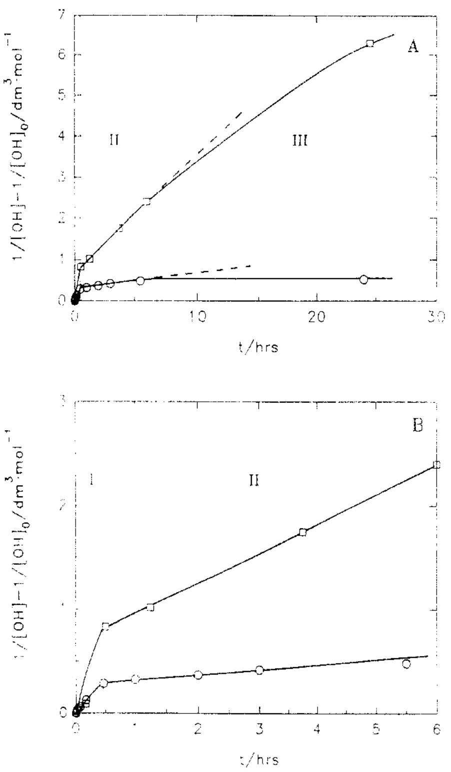


Figure 6. Conversion of silanol groups (second-order plot) with time in condensation of HD_4OH in CH_2Cl_2 at 30 °C. (□) $[HD_4OH]_0 = 0.44$ mol/L, $[TfOH]_0 = 1.1 \times 10^{-4}$ mol/L; (○) $[HD_4OH]_0 = 0.9$ mol/L, $[TfOH]_0 = 1.7 \times 10^{-4}$ mol/L; (A) whole reaction run; (B) expanded time range 0–6 h.

tions of 0.43 mol/L ([TfOH] = 1.1×10^{-4} mol/L) and 0.9 mol/L ([TfOH] = 1.7×10^{-4} mol/L), the decrease of the rate constant appeared after about 30 min, which corresponded to 40% SiOH conversion in the former case and to 30% silanol conversion in the latter case. The amounts of water produced before emulsion was formed were 0.2 and 0.3 mol/L, respectively. The solubility of water in CH_2Cl_2 at 30 °C was found to be 0.17 mol/L.[10] However, it can vary since the water solubility most likely depends on [SiOH], [TfOH], and the length of the siloxane chains.

Three periods of the reaction can be distinguished in the curve of silanol conversion when $[SiOH]_0 > 0.8$ mol/L (Figure 6). At the beginning, fast reaction proceeds in presumably homogeneous solution; then the system becomes heterogeneous and the conversion slows down considerably; at conversion higher than 60–70% of SiOH (which corresponds to 75–85% of HD_4OH conversion), the reaction slows down even more. In the condensation of HD_4OH at low TfOH concentration ([TfOH] < 5×10^{-4} mol/L), only the oligomeric fraction (MW = 3000–5000) was formed after 2 days. When 10^{-3} mol/L of the acid was used ($[HD_4OH]_0 = 0.44$ mol/L), a polymer fraction (MW = 40000, 30%) was formed after 16 h. In contrast, the condensation of HD_7OH or of the mixture of longer diols after the same time gave polymer with MW > 50000 even at acid concentration as low as 10^{-4} mol/L.

When the initial concentration of SiOH groups was below 0.3 mol/L, the system remained homogeneous up to a high degree of conversion. The plots $1/[OH] - 1/[OH]_0 = k_{OH}t$ for these kinetic runs show no sharp breakpoint although they are not perfectly linear, indicating a slow decrease of k_{OH} with the reaction progress (Figures 7 and 8).

This picture might be explained by the increasing participation of less reactive longer oligomers in total silanol conversion. This factor should have greater importance in the first stage of the reaction as the differences of reactivities are probably the greatest for short oligomers. The other factor which may also be partially responsible for the observed behavior is concerned with the esterification of silanol groups by the acid in the first period of the reaction and with the competition of the heterocondensation pathway (this problem is discussed below).

2. Mechanism of Catalysis of Silanol Condensation by Triflic Acid. The unusual dependence of the initial

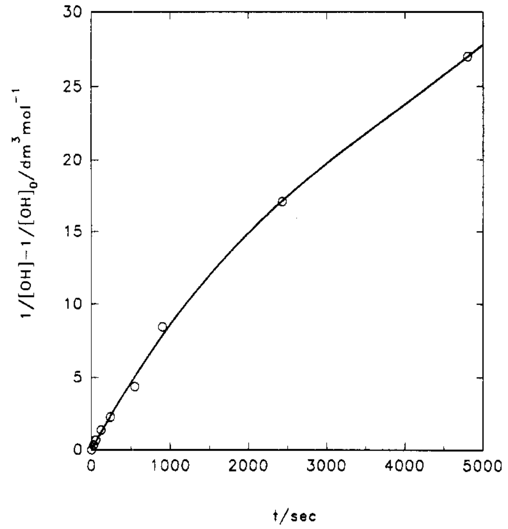


Figure 7. Conversion of silanol groups (second-order plot) with time in condensation of HD_4OH in CH_2Cl_2 at 30 °C. $[HD_4OH]_0 = 0.15$ mol/L; $[TfOH]_0 = 1.1 \times 10^{-4}$ mol/L.

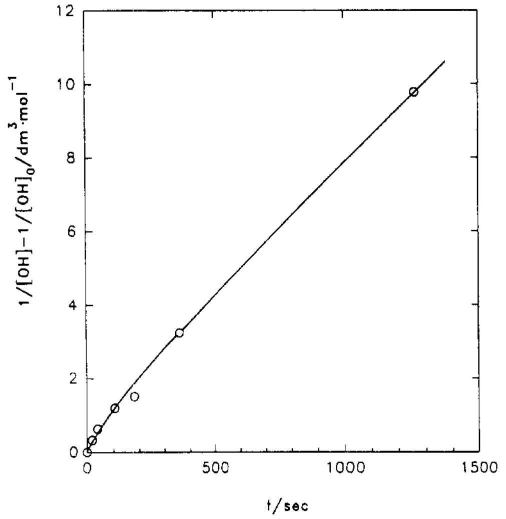


Figure 8. Conversion of silanol groups (second-order plot) with time in condensation of HD_7OH in CH_2Cl_2 at 30 °C. $[HD_7OH]_0 = 0.135$ mol/L; $[TfOH]_0 = 6 \times 10^{-5}$ mol/L.

rate of condensation on the concentration of silanol groups indicates that the mechanism of catalysis of the reaction by triflic acid in dichloromethane is more complex than the classical one proposed to operate in basic solvents such as dioxane[9] and even more complex than the mechanism of catalysis by weaker acids in dichloromethane.[8]

Triflic acid is involved in several equilibria in the system which affect its true concentration and activity. It reacts with silanol groups, forming triflate esters.[5,6,8,10]

$$\sim SiOH + HSO_3CF_3 \rightleftharpoons \sim SiOSO_2CF_3 + H_2O \qquad (2)$$

This reaction is probably much faster than the condensation, and the equilibrium position is reached in the early stage of the process.[10,11] As the condensation proceeds with the formation of water, the acid is being recovered due to the ester hydrolysis.

Esterification may influence the total rate of condensation in two ways: first, it reduces the concentration of free catalyst (especially at the beginning of the process); second, the ester formed can react with silanol groups according to the heterocondensation pathway.

$$\sim SiOSO_2CF_3 + HOSi\sim \overset{TfOH(?)}{\rightleftharpoons} \sim SiOSi\sim + HOSO_2CF_3 \qquad (3)$$

The rate of this process is unknown. The initial rates of both hetero- and homocondensation catalyzed by trifluoroacetic acid estimated in cross-experiments were found to be of the same order of magnitude.[8] For triflic acid, similar kinetic measurements could not be made because the reactions of esterification–hydrolysis and condensation were too fast.[10] However, the condensation of Et_3SiOH with $tBuMe_2SiOTf$ quenched with BSA after about 1 s was reported to give 21% of homocondensation ($Et_3SiOSiEt_3$), 10% of cross-condensation ($Et_3SiOSiMe_2tBu$) products, and only 2% of $tBuMe_2SiOSiMe_2tBu$ resulting from end group exchange.[10] Without knowing the rate of end group exchange, one can only conclude that at the beginning of the reaction the rates of homo- and heterocondensation are similar or that the homocondensation in this particular system is somewhat faster. Although bulky Et_3Si and $tBuMe_2Si$ groups strongly affect the relative rates of both reactions, it seems reasonable to assume that in the permethylated systems the rates of both reactions are not very different.

The acid consumption due to the esterification might be responsible for the observed decrease of the initial condensation rate with increasing initial SiOH concentration. However, contrary to what was observed, the reaction should accelerate as water produced during condensation causes ester hydrolysis and the concentration of the acid increases. Thus, there must be other reasons for the observed decrease of the condensation rate with time.

Triflic acid is known to form strong complexes with water of various stoichiometry.[10,12,13]

$$TfOH + H_2O \rightleftharpoons TfOH{\cdot}H_2O \underset{?}{\overset{nH_2O}{\rightleftharpoons}} TfOH{\cdot}(H_2O)_{n+1} \qquad (4)$$

The esterification equilibrium (2) should be considered together with the complexation equilibria (4) since the interaction of acid with water affects the position of equilibrium (2). It was found that silyl triflates do not hydrolyze to a significant extent in the presence of an equimolar amount of the $TfOH/H_2O$ (1:1) mixture in CH_2Cl_2.[10] As the condensation proceeds, the ester groups are progressively hydrolyzed and the liberated acid is rapidly hydrated. The activity of TfOH–water complexes in catalysis of silanol condensation is unknown. They are much less active than free acid toward the siloxane bond splitting and their activity decreases with growing $H_2O/TfOH$ proportion.[10,12,13]

The condensation system is even more complicated as silanols are able to form strong hydrogen bonds themselves and with water. They exist in highly associated hydrogen-bonded structures in the solid state[14] as well as in concentrated solutions in inert solvents.[8] Since the model siloxanediols used in this study were synthesized by hydrolysis of chlorosiloxanes, they contain some water which was difficult to remove due to the interaction with silanol. The water content in HD_4OH and HD_7OH has been estimated independently to be below 1 mol %. This estimation was performed by silylation of the siloxanediol sample with bis(trimethylsilyl)acetamide and calculation of the hexamethyldisiloxane content from the gas chromatogram. Thus, the water content in the solution of 0.15 mol/L of HD_nOH may be at the level of 10^{-3} mol/L, which would be higher than the concentration of TfOH used in most experiments. In such silanol–water aggregates, the acidic proton may be strongly solvated with

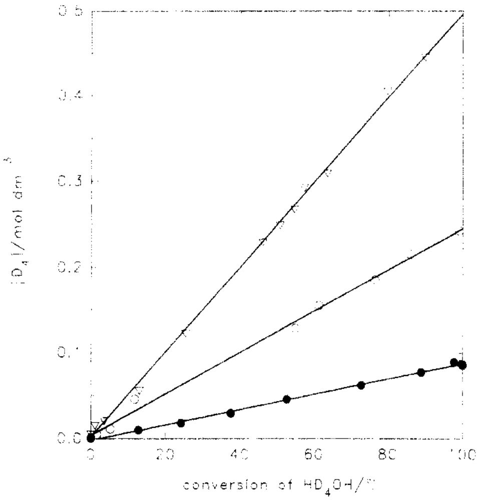


Figure 9. Formation of D_4 as a function of HD_4OH conversion: $[HD_4OH]_0 = 0.15$ mol/L, $[TfOH]_0 = 1.1 \times 10^{-4}$ mol/L; (○) $[HD_4OH]_0 = 0.44$ mol/L, $[TfOH]_0 = 1.1 \times 10^{-4}$ mol/L; (▽) $[HD_4OH]_0 = 0.9$ mol/L, $[TfOH]_0 = 1.7 \times 10^{-4}$ mol/L.

a positive charge highly delocalized, which would strongly change the thermodynamic potential of the acid. The interaction of triflic acid with silanol–water aggregates alone or in cooperation with esterification of silanol groups is probably responsible for the reduction of the initial condensation rate at high concentrations of silanol.

The association system is dynamically changing during the reaction course, which is reflected in complex kinetic dependencies. This makes the more thorough analysis of the condensation mechanism extremely difficult.

3. Scope of Operation of Intra–Inter Catalysis. The kinetic results of the condensation of HD_4OH are analogous to those previously reported for the HD_5OH system, which confirms that intra–inter catalysis operates in this case. The yield of D_4 remains nearly constant over a wide range of $[HD_4OH]_0$ (Figure 2). Additional support of this concept is provided by the linear dependence of D_4 formation as a function of substrate conversion (Figure 9). Such proportionality is expected for second-order cyclization reaction (eqs 5–9).

$$-\frac{d[HD_nOH]}{dt} = k_c[HD_nOH][OH] + 2k_1[HD_nOH][OH] \tag{5}$$

$$\frac{d[D_n]}{dt} = k_c[HD_nOH][OH] \tag{6}$$

Dividing eq 5 by eq 6, we obtain

$$-\frac{d[HD_nOH]}{d[D_n]} = 1 + 2k_1/k_c \tag{7}$$

Hence

$$[D_n] = k_c/(k_c + 2k_1)([HD_nOH]_0 - [HD_nOH]) \tag{8}$$

and

$$[D_n]_\infty = k_c/(k_c + 2k_1)[HD_nOH]_0 \tag{9}$$

where k_1 means the average linear condensation constant, k_c means the cyclization constant, and 2 is a statistical factor.

In contrast, assuming first-order cyclization, we obtain the following equations:

$$-\frac{d[HD_nOH]}{dt} = k_c[HD_nOH] + 2k_1[HD_nOH][OH] \tag{10}$$

$$\frac{d[D_n]}{dt} = k_c[HD_nOH] \tag{11}$$

$$-\frac{d[HD_nOH]}{d[D_n]} = 1 + \frac{2k_1}{k_c}[OH] \tag{12}$$

This leads to an expression which, in general, cannot be solved analytically. Nevertheless, according to eq 12, an increasing proportion of $[D_n]$ with SiOH conversion should be observed.

In the case of HD_7OH, the proportion of D_7 to linear products varies with concentration, which indicates that the basic assistance of a silanol group from another molecule becomes less significant. The dependence of $[D_7]$ on HD_7OH conversion is not perfectly linear (Figure 10). The condensation of the mixture of diols shows that the deviation of the dependence $[D_n]$–$[HD_nOH]$ from linearity is larger for greater n (Figure 11). The yield of cyclics, defined as $[D_n]/[HD_nOH]_0$ measured at full conversion of the original diol (just after its disappearance to avoid the influence of slower equilibration processes on $[D_n]$), shows a local minimum at $n = 6$ and a local maximum at $n = 8$ (Figure 5). The cyclosiloxanes D_n, $n = 7$–9, are formed with kinetic enhancement (Figure 5).

The experiments using the mixtures of oligosiloxanediols **III** and **IV** allowed comparison of the rates of cyclization and intermolecular condensation for a number of oligomers. The reactivity of diols decreases with chain length up to at least $n = 9$ siloxane units in a molecule. The total rate constant calculated from the initial rate of consumption of HD_4OH according to the formula

$$k = \frac{-(d[HD_4OH]/dt)_{t=0}}{2[HD_4OH]_0[SiOH]_0}$$

is 2.5 times higher than the corresponding rate constant of HD_6OH conversion, which in turn is approximately 2 times higher than that of HD_9OH (Table 2). Although these rate constants are only formal parameters of the complex reaction and are calculated from experiments carried out at different initial SiOH concentrations, the decrease of the reactivity of the diol with chain elongation is evident.

The kinetic data may be interpreted assuming basic assistance in condensation is provided concurrently by silanol and siloxane oxygen.[8] Although the basicity of the siloxane oxygen is much lower than that of the silanol group,[15,16] the mechanism involving siloxane oxygen assistance may become important in the case of longer oligosiloxanediols when the intramolecular silanol end group assistance is less effective because of the long mean distance of the chain ends or in the case of monofunctional oligosiloxanols. The assistance by the siloxane chain was postulated to explain the kinetics of MeD_5OH condensation.[8] The rate constant of the condensation of HD_5OH was found to be 33 times greater than that of MeD_5OH and nearly 500 times greater than that of MeD_2OH.[8] Basic assistance of a silanol group in the condensation of monofunctional siloxanols must involve a third molecule of the substrate. Third order in the substrate should be observed in such a case. The elevated external order (2.5) was indeed observed for MeD_2OH but not for MeD_5OH, in the case of which the apparent order of condensation was 1.7 and was only slightly higher than that for HD_5OH.

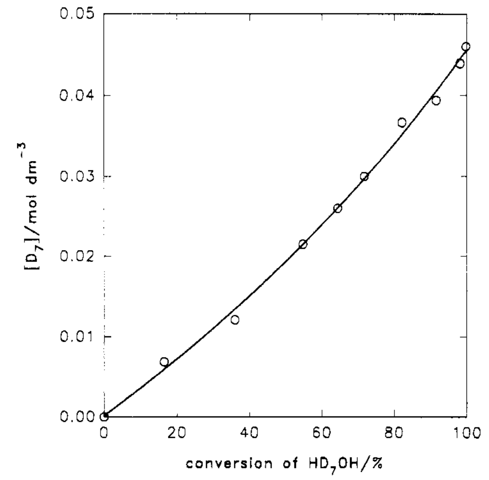


Figure 10. Formation of D_7 as a function of HD_7OH conversion. $[HD_7OH]_0 = 0.43$ mol/L; $[TfOH]_0 = 4.4 \times 10^{-4}$ mol/L.

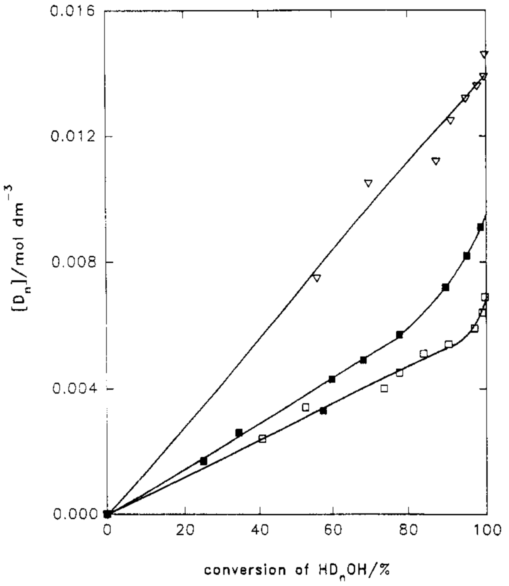


Figure 11. Formation of D_n as a function of HD_nOH conversion in condensation of the mixture of oligo(dimethylsiloxanediol)s HD_nOH, $n = 4$–19 (**III**) ($[SiOH]_0 = 0.9$ mol/L; $[TfOH]_0 = 1.1 \times 10^{-3}$ mol/L); (▽) $n = 5$; (□) $n = 6$; (■) $n = 7$.

This points to the other possible mechanism of activation of MeD_5OH involving intramolecular hydrogen bonding with the siloxane oxygen.[8] The reactivity order $HD_5OH > MeD_5OH > MeD_2OH$ indicates that although hydrogen bonding between two silanol groups is stronger than hydrogen bonding between siloxane and silanol groups, the concentration of the cyclic form of MeD_5OH involving the siloxane–silanol hydrogen bond is much higher than the concentration of $MeD_2OH\cdots HOD_2Me$ complex at the level of SiOH concentrations applied in the discussed work.[8] Considering the equilibria of complex formation

$$[(Si)_2O\cdots HOSi]_0 = K_c[MeD_5OH]_0[SiOSi]_{eff}$$

where $[SiOSi]_{eff}$ means the effective concentration of SiOSi bonds in the vicinity of silanol group and

$$[MeD_2OH\cdots HOD_2Me]_0 = K_c'[MeD_2OH]_0^2; \qquad K_c' > K_c$$

one can conclude that $[SiOSi]_{eff}$ in the MeD_5OH system must be much higher than $[MeD_2OH]_0$ under these conditions. Based on these kinetic data, the rate constant of the reaction proceeding without basic assistance may be considered negligible.

The investigation of $SiOH\cdots HOSi$ and $(Si)_2O\cdots HOSi$ hydrogen complexes formed in HD_5OH solution in CH_2Cl_2 showed that their formation constants are relatively significant and that both $[SiOH]_{eff}$ and $[SiOSi]_{eff}$ are rather high.[8]

Considering the transition states of cyclization and intermolecular condensation in the original intra–inter catalysis mechanism (Scheme 1), both cyclization and intermolecular condensation would require two silanol end groups of a chain to be found within the distance of interaction with each other. In general, the conformational probability of the encounter of both chain ends decreases proportionally to the chain length. (To be more precise, it is reflected in the equilibrium concentrations of cyclic siloxanes.[17]) This should result in reduction of the reactivity of longer oligosiloxanediols with the chain length, as observed, while the cyclic/linear product ratio should remain the same in a series of diols. In an ideal case, this ratio should be 50:50 as observed for HD_4OH.

This is not true if intramolecularly siloxane-assisted silanol species participate in the condensation. The cyclization involving these species is a unimolecular reaction. Actually, the kinetics of cyclization is a superposition of first- and second-order reactions with respect to HD_nOH, the former representing siloxane oxygen assistance in cyclization and the latter representing the assistance of a silanol group from another molecule:

$$\left(-\frac{d[HD_nOH]}{dt}\right)_{cycl} = \frac{d[D_n]}{dt} = k_c'[HD_nOH][SiOSi]_{eff} + k_c''[HD_nOH][SiOH] \qquad (13)$$

where k_c' and k_c'' are the rate constants of the cyclization involving siloxane and silanol assistance, respectively; $[SiOSi]_{eff}$ is the effective concentration of siloxane bonds. Since $[SiOSi]_{eff}$ may be considered constant for a particular oligosiloxanediol, the first component of eq 13 represents first-order cyclization with respect to the diol with the apparent rate constant $k_c = k_c'[SiOSi]_{eff}$.

Analogously, the conversion of HD_nOH to linear products is a sum of two second-order reactions with respect to [SiOH]:

$$\left(-\frac{d[HD_nOH]}{dt}\right)_{lin} = k_l'[HD_nOH][SiOH][SiOSi]_{eff} + k_l''[HD_nOH][SiOH][SiOH]_{eff} \qquad (14)$$

k_l' and k_l'' are the rate constants of the linear condensation with basic assistance of siloxane and silanol groups, respectively, [SiOH] is the total concentration of silanol groups, and $[SiOH]_{eff}$ is the effective concentration of silanol groups.

The role of the second component in eq 13 decreases with [SiOH]. Thus, when total [SiOH] is low, the first-order component of eq 13 tends to dominate. Assuming $[SiOH]_{eff}$ = const for a particular n (chain length of the diol), both components of eq 14 are of second order in SiOH with apparent rate constants $k_l^{i} = k_l'[SiOSi]_{eff}$ and $k_l^{ii} = k_l''[SiOH]_{eff}$.

On the other hand, the rate constants of the reactions involving end-to-end interaction, k_c, k_c'', and k_l^{ii}, decrease with n since they depend on the probability of the chain ends encountering each other. Dividing eq 14 by eq 13, we obtain the ratio of the rates of linear condensation to cyclization

$$-\frac{d[HD_nOH]}{d[D_n]} = \frac{(k_1^{\mathrm{i}} + k_1^{\mathrm{ii}})[HD_nOH][SiOH]}{(k_c + k_c''[SiOH])[HD_nOH]} = \frac{(k_1^{\mathrm{i}} + k_1^{\mathrm{ii}})[SiOH]}{k_c + k_c''[SiOH]} \tag{15}$$

From eq 15 the proportion of D_n should decrease when n increases because the three constants dependent on $[SiOH]_{eff}$, k_c, k_c'', and k_1^{ii}, decrease while k_1^{i} does not. (k_1^{i} is even likely to increase with n as $[SiOSi]_{eff}$ increases.) The proportion of D_n should also decrease with the increase of $[SiOH]_0$ because the numerator in eq 15 increases faster than the denominator. At high [SiOH], when $k_c \ll k_c''[SiOH]$, we obtain as a limit the linear proportion of cyclic/linear products, consistent with eq 7.

Although generally the decrease of the yield of D_n with n has been observed, the cyclics D_7, D_8, and D_9 are formed with kinetic enhancement (Figure 5). This can be explained assuming that intramolecular siloxane oxygen assistance facilitates cyclization, reducing the distance between chain ends according to Scheme 2. According to this scheme, the most favorable conformation should exist for HD_8OH where two nine-membered rings are formed in the transition state. Indeed, D_8 is formed in the largest amount (Figure 5).

HD_6OH probably constitutes the limiting case in which the cyclization involving intramolecular siloxane assistance is less likely because of conformational strain (the transition state would have a bicyclic structure of two seven-membered rings). Thus, the cyclization involving assistance of the second molecule of silanol is the dominating reaction and its rate is determined by k_c''. The siloxane-assisted transition state can participate, however, in intermolecular condensation. This results in enhanced reactivity of this diol toward linear growth, i.e., in a low yield of the cyclization product.

The analysis presented here is simplified. The intermolecular hydrogen bonds between siloxane and silanol groups and the participation of water in the condensation are not considered. The intermolecular siloxane–silanol complexes are probably of minor importance in the range of concentrations in which most of the experiments were performed. Water produced during condensation, being the strongest base in the system, certainly takes part in complexation equilibria, but closer analysis of its possible participation in intra–inter catalysis is very difficult.

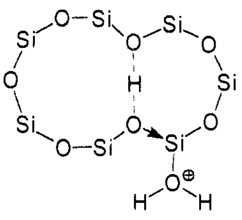
4. Polymer Formation. The catalyst concentration or addition of water does not seem to affect the yield of cyclics and linear polymer and the molecular weight in the condensation of oligosiloxanediols. The yield of polymer and cyclics obviously depends on the initial concentration of SiOH. For example, for $[HD_7OH] = 0.15$ mol/L, and $[TfOH] = 2.2 \times 10^{-4}$ mol/L, 50% of polymer was obtained after 24 h, MW = 30000, while the polycondensation of $[HD_7OH]_0 = 0.9$ mol/L and $[TfOH] = 2.2 \times 10^{-4}$ mol/L after 24 h gave 80% of polymer, MW = 75000. The results of condensation of the mixtures of diols **III** and **IV** were similar. For example, condensation of the mixture of oligosiloxanediols **IV** in the presence of 10^{-3} mol/L of TfOH gave 50% of polymer (MW = 30000) at $[SiOH]_0 = 0.3$ mol/L and 80% of polymer (MW = 30000) at $[SiOH]_0 = 0.9$ mol/L after 24 h.

After a prolonged time, the distribution of products changed due to equilibration processes.

Experimental Section

Solvent. Dichloromethane was purified by the method described in ref 18, finally dried over two sodium films under vacuum, distilled in vacuum to an ampule equipped with a PTFE stopcock, and stored under N_2.

Scheme 2



$HO(SiO)_7H$

Catalyst. Triflic acid (Fluka) was distilled in vacuum. The solution in dichloromethane was prepared and distributed in vacuum to glass bulbs which were then sealed.

Purification of α,ω-Dichlorooligo(dimethylsiloxane)s. ClD_4Cl and ClD_7Cl were separated from the mixture of ClD_nCl oligomers provided by Rhône-Poulenc by repeated vacuum distillation using a column filled with glass rings. Boiling points: ClD_4Cl, 45 °C/0.5 Torr (purity 98%); ClD_7Cl, 100 °C/10^{-3} Torr (purity 94%; impurities: ClD_6Cl and ClD_7Cl).

Preparation of Octamethyltetrasiloxane-1,7-diol (I) and Tetradecamethylheptasiloxane-1,13-diol (II). Model diols were obtained by hydrolysis of the corresponding α,ω-dichlorosiloxanes in diethyl ether[8] using triethylamine instead of pyridine as a HCl acceptor and a small addition of (dimethylamino)pyridine (DMAP) as catalyst. The ether solution after filtration of ammonium hydrochloride was dried with $CaCl_2$, the solvent was removed, and the product was distilled under vacuum. Boiling points: 60 °C/0.5 Torr and 140–150 °C/10^{-4} Torr, respectively. The purity of the products checked by GC was 98% (HD_4OH) and 92% (HD_7OH). In both cases the impurities were oligosiloxanediols $HD_{n-1}OH$ and $HD_{n+1}OH$. Distilled siloxanediols are stable when stored at 0 °C. No condensation was observed after 3 months.

The mixture of α,ω-oligo(dimethylsiloxanediol)s (III and IV) obtained from Rhône-Poulenc (Fluid 48v50) was purified by dissolving in diethyl ether and washing with water to remove residual alkali. The solution was dried with $CaCl_2$, and then ether and the volatile fraction (cyclosiloxanes D_{3-6} and low molecular weight diols HD_3OH and HD_4OH) were removed under vacuum. Two processes gave two products of slightly different composition: one containing diols HD_nOH, $n = 4$–19 (**III**), the other containing diols $n = 5$–19 (**IV**), the maximum being at $n = 6$–8. The molar compositions of the mixtures determined with GC were as follows:

III: $[HD_4OH]_0 = 0.105$; $[HD_5OH]_0 = 0.111$; $[HD_6OH]_0 = 0.12$; $[HD_7OH]_0 = 0.12$; $[HD_8OH]_0 = 0.109$; $[HD_9OH]_0 = 0.098$; $[HD_{10}OH]_0 = 0.085$; $[HD_{11}OH]_0 = 0.064$; $[HD_{12}OH]_0 = 0.051$; $[HD_{13}OH]_0 = 0.038$; $[HD_{14}OH]_0 = 0.03$; $[HD_{15}OH]_0 = 0.026$; $[HD_{16}OH]_0 = 0.017$; $[HD_{17}OH]_0 = 0.013$; $[HD_{18}OH]_0 = 0.009$; $[HD_{19}OH]_0 = 0.006$; average molecular weight 541.

IV: $[HD_5OH]_0 = 0.031$; $[HD_6OH]_0 = 0.15$; $[HD_7OH]_0 = 0.18$; $[HD_8OH]_0 = 0.17$; $[HD_9OH]_0 = 0.137$; $[HD_{10}OH]_0 = 0.098$; $[HD_{11}OH]_0 = 0.069$; $[HD_{12}OH]_0 = 0.048$; $[HD_{13}OH]_0 = 0.036$; $[HD_{14}OH]_0 = 0.025$; $[HD_{15}OH]_0 = 0.019$; $[HD_{16}OH]_0 = 0.012$; $[HD_{17}OH]_0 = 0.009$; $[HD_{18}OH]_0 = 0.006$; $[HD_{19}OH]_0 = 0.005$; average molecular weight 682.

An example chromatogram of the mixture **IV** is shown in Figure 12.

Kinetic Studies. Condensation reactions were carried out under nitrogen at 30 °C. Siloxanediol, CH_2Cl_2, dodecane (used as an internal standard for GC), and a glass ampule containing a known amount of a solution of triflic acid in CH_2Cl_2 were placed in a reactor equipped with a mechanical stirrer. The reaction was started by breaking the ampule containing the catalyst. Samples were withdrawn with a syringe and quenched with pyridine (3×10^{-3} mol/L solution in CH_2Cl_2, about a 5-fold excess with respect to the catalyst), and SiOH groups were silylated with bis(trimethylsilyl)acetamide (BSA) used in a 10-fold excess to ensure fast and complete silylation. Concentrations of siloxane products were determined by gas chromatography relative to an internal reference, n-dodecane.

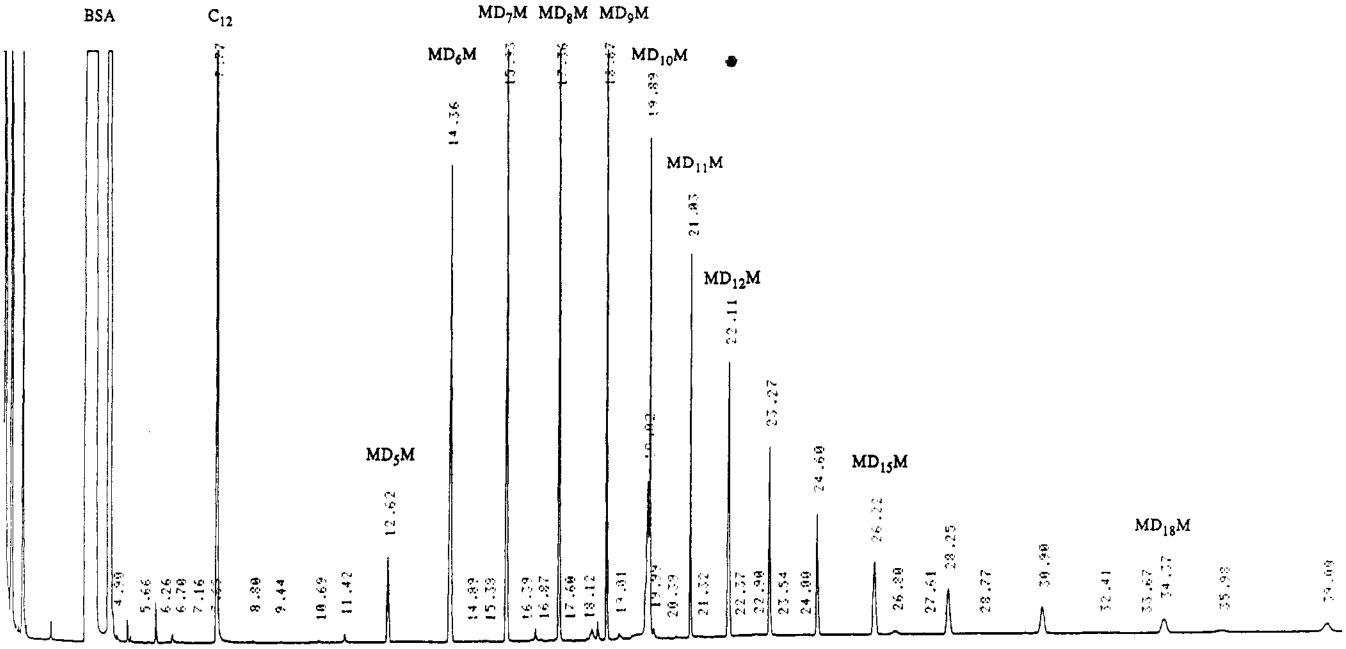


Figure 12. Gas chromatogram of the mixture of oligo(dimethylsiloxanediol)s **IV** silylated with BSA MD_nM, $n = 5$–19, used for kinetic studies. BSA = bis(trimethylsilyl)acetamide; C_{12} = dodecane (reference standard).

Gas-liquid chromatography analyses were performed using a Carlo Erba 6000 chromatograph equipped with capillary columns. Helium was applied as carrier gas. The temperature of the columns was programmed at 12.5 °C/min; detector temperature was 320 °C. Mass response factors determined using model compounds were 2.8 for cyclosiloxanes and 2.55–2.8 for MD_nM, depending on n. To a good approximation, the values 2.55 and 2.8 were used for oligomers of $n = 3$–6 and $n \geq 7$, respectively.

Gel permeation chromatography analyses were performed using a Waters 410 chromatograph equipped with 10^5, 10^4, 10^3, and 500 Å columns. Peak molecular weight and weight fraction of linear polymer (the limit MW > 4000 was arbitrarily chosen) were calculated based on polystyrene standards.

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