OFFICE OF NAVAL RESEARCH
Contract N/N00014-91-J-1893
R&T Code 4132062

TECHNICAL REPORT NO. 5

Intramolecular vs. Intermolecular Condensation Rates in the Acidic Polymerization of Octaethoxytrisiloxane

by

J. Sanchez and A.V. McCormick
Dept. of Chemical Engineering & Materials Science
University of Minnesota
421 Washington Ave. SE
Minneapolis, MN 55455

July 12, 1993

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. [illegible]

[illegible]

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
7/12/93

3. REPORT TYPE AND DATES COVERED
Technical

4. TITLE AND SUBTITLE
Intramolecular vs. Intermolecular Condensation Rates in the Acidic Polymerization of Octaethoxytrisiloxane

5. FUNDING NUMBERS
N/N00014-91-J-1893

6. AUTHOR(S)
J. Sanchez and A.V. McCormick

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Dept. of Chemical Engineering & Materials Science
University of Minnesota
421 Washington Ave., SE
Minneapolis, MN 55455

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Submitted JNCS

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the U.S. Government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Octaethoxytrisiloxane, $(EtO)_3Si\text{-}O\text{-}Si(OEt)_2\text{-}O\text{-}Si(OEt)_3$, was synthesized and then polymerized in water/alcohol solution in the presence of an acid catalyst. The reaction was monitored with ^{29}Si-NMR. The rate constants of linear and cyclic condensation were estimated by curve-fitting and were compared.
No evidence of depolymerization was found, indicating that condensation is irreversible in our conditions. In addition, it was found that the formation of trimeric cyclic species by ring closure is fast and competes effectively with chain extension condensation. These observations are consistent with previous suggestions, but in addition they provide a quantitative measure of selectivity that is much needed. Quantitative kinetic models for silicon alkoxide sol-gel processes need to account for cyclization at very early stages of the polymerization.

14. SUBJECT TERMS
SiO_2, solgel, NMR, kinetics, trisiloxane, gelization

15. NUMBER OF PAGES
15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

Intramolecular vs. intermolecular condensation rates in the acidic polymerization of octaethoxytrisiloxane

Jorge Sanchez and Alon V. McCormick*

University of Minnesota

Department of Chemical Engineering and Materials Science

421 Washington Ave. SE

Minneapolis, MN 55455

Abstract

Octaethoxytrisiloxane, $(EtO)_3Si\text{-}O\text{-}Si(OEt)_2\text{-}O\text{-}Si(OEt)_3$, was synthesized and then polymerized in water/alcohol solution in the presence of an acid catalyst. The reaction was monitored with ^{29}Si-NMR. The rate constants of linear and cyclic condensation were estimated by curve-fitting and were compared.

No evidence of depolymerization was found, indicating that condensation is irreversible in our conditions. In addition, it was found that the formation of trimeric cyclic species by ring closure is fast and competes effectively with chain extension condensation. These observations are consistent with previous suggestions, but in addition they provide a quantitative measure of selectivity that is much needed. Quantitative kinetic models for silicon alkoxide sol-gel processes need to account for cyclization at very early stages of the polymerization.

---

* to whom correspondence should be addressed

1. Introduction

The polymerization of alkoxides in alcohol/water solutions is a promising route to the synthesis of advanced ceramics [1]. In principle, tailoring the structure and properties of the product can be achieved by controlling the reaction kinetics. However, the large number of possible reaction pathways has been a major obstacle to the development of quantitative models for sol-gel processes. Moreover, most studies of sol-gel reactions have provided only qualitative understanding.

Silicon alkoxides constitute the most studied type of sol-gel systems. The reactions involved in the polymerization of silicon alkoxides are (i) the hydrolysis of alkoxide groups to form silanol groups and (ii) the condensation of the silanol groups to yield siloxane bonds which constitute the backbone of the polymer. Attempts have been made to use ^{29}Si-NMR to measure the kinetics of the polymerization of $Si(OEt)_4$ (TEOS) [2,3], $Si(OMe)_4$ (TMOS) [3] and even $(MeO)_3Si\text{-}O\text{-}Si(OMe)_3$ [4], which is one of the dimeric intermediates formed during the polymerization of TMOS.

It has been shown that in acidic conditions hydrolysis is reversible[5] and fast. Much less is known about condensation. Based on the very low solubility of amorphous silica in acidic alcoholic solutions [6], it is generally assumed that condensation is irreversible in acidic conditions - thereby greatly simplifying kinetics models. This seems to be confirmed by some studies [7].

An area of controversy concerns the importance of intramolecular reactions, also known as ring closure or cyclization. Most polymerization models do not consider cyclization because it is extremely difficult to account for. Besides, intramolecular reactions are often negligible in organic polymerization [8]. However, it has been shown that cyclic intermediates are formed during the polymerization of TEOS and TMOS in acidic conditions [9]. Cyclization seems to be more prevalent in TEOS than in TMOS systems [3]. Indeed, the failure of quantitative kinetic models for sol-gel polymerization has been explained by cyclization effects in these systems [10].

To estimate the relative rate of formation of small rings versus chain extension, we used ^{29}Si-NMR to study the kinetics of polymerization of octaethoxytrisiloxane, $(EtO])_3Si\text{-}O\text{-}Si(OEt)_2\text{-}O\text{-}Si(OEt)_3$, a trimeric oligomer that appears as intermediate in the sol-gel polymerization of TEOS. This molecule is the smallest oligomer that can undergo chain extension *and* ring closure; it thus provides us the opportunity to unambiguously measure the selectivity of intra- versus intermolecular polymerization rates.

2. Experimental Procedures

2.1 Synthesis of octaethoxytrisiloxane

Octaethoxytrisiloxane was synthesized by adapting a procedure described by Dougthy et al. [4]. Octachlorotrisiloxane (97%, Hüls America) was slowly added to a solution of ethylorthoformate (Aldrich) in heptane. The reaction, carried out in an inert atmosphere and monitored by gas chromatography, was carried out at 60°C for two hours. Octaethoxytrisiloxane was isolated and purified by vacuum distillation. Remaining traces of HCl formed during the reaction were removed by degassing with dry nitrogen. A final purification was done with an alumina packed chromatography column. The product was identified by ^{29}Si-NMR as octaethoxytrisiloxane (Figure 1) with a purity greater than 96% from gas chromatography.

2.2 Kinetic Measurements

In a 10 mm NMR tube, 2 ml of octaethoxytrisiloxane were mixed with 2 ml 1 wt.%. $Cr(acac)_3$ (paramagnetic relaxant agent) in absolute ethanol, 300µl deionized H_2O and 23 µl of a calibrated 0.095 N HCl solution. The composition of the resultant solution was thus: 0.97 M octaethoxytrisiloxane/7.94 M EtOH/4.15 M H_2O/5.04 10^{-4} M HCl.

The reaction was monitored at 25°C with ^{29}Si-NMR. Each spectrum was acquired with 32 scans at 99.36 MHz and with a pulse delay of 12 s.

3. Results and Discussion

Figure 2 shows the sequence of ^{29} Si-NMR spectra recorded during the reaction. The NMR spectra show peaks assigned to silanol groups formed by hydrolysis, and peaks attributed to silicon sites in cyclic trisiloxanes [9]. The concentrations of silicon end (Q_1), middle (Q_2) and cyclic units (Q_c) are plotted in Figure 3. The lack of silicon units with three siloxane bonds (branching units Q_3) in the 8-hour period studied shows that branching condensation is very slow for the cycles and chains produced. In particular, the middle unit of the trimeric precursor is much less reactive than its end units.

No depolymerization of the trimer occurs as evidenced by the lack of smaller fragments such as monomeric units (Q_0). This is confirmed by size exclusion chromatography (Figure 4). It appears then that in these conditions, condensation is virtually irreversible and the polymeric intermediates cannot undergo rearrangement; these data are thus akin to a polyfunctional organic polymerization [6].

Since only the end units react during the period studied, the overall extent of polymerization is given by

$$\xi = \frac{[Q_1]_0 - [Q_1]}{[Q_1]_0} \qquad (1)$$

In addition, three cyclic units appear each time two end units disappear when a trimeric cycle is formed. Neglecting the formation of larger cycles, the extent of ring closure is

(2) $$\sigma=\frac{2[Q_c]}{3[Q_1]_0}$$

Finally, the extent of chain extension polymerization is

(3) $$\alpha=\xi-\sigma$$

α and σ are plotted in Figure 5. It can be seen that during the first two hours of the reaction, chain extension is predominant. During this period, the polymers grow rapidly. However, ring closure then becomes the most important reaction, and polymer growth slows. A possible explanation for this behavior is that since the number of chains in the system decreases during polymerization, the probability for a reactive group to react intermolecularly diminishes as it becomes increasingly difficult for an end unit to find an outside reaction partner as the reaction proceeds. This increased competition of cyclization and the very slow rate of branching can explain the remarkably long gel time (on the order of two months at room temperature) of this system, and perhaps the observation of exceedingly high conversion at the gel point [9].

To quantitatively assess the ring-chain competition, the following simple kinetic equation is written

(4) $$\frac{d[Q_1]}{dt}=-2k_\alpha[Q_1]^2-k_\sigma[Q_1]$$

where k_α and k_σ are rate constants for inter- and intramolecular condensation of the end units.

The Si end sites may actually carry from 0 to 3 -OH groups and a great number of reactions involving molecules with various numbers of silanol groups are possible. Since the rate of hydrolysis is much faster than the rate of condensation, to simplify the analytical treatment the rate constants k_α and k_σ are averaged over the extent of hydrolysis on the Si groups. Though we expect these apparent rate constants to depend on the amount of water and the catalyst concentration, the relative values of k_α and k_σ should not be affected and they will be a good measure of the ring-chain competition. The rate constants should also be affected by the initial precursor concentration, as intramolecular reactions are more probable in dilute systems.

The solution of (4) is

$$\frac{1}{[Q_1]} = \frac{1}{[Q_1]_0} + \frac{2k_\alpha}{k_\sigma}(e^{k_\sigma t} - 1) \tag{5}$$

or

$$\frac{1}{1-\xi} = 1 + \frac{2}{\lambda}(e^{k_\sigma t} - 1) \tag{6}$$

where $\lambda = \frac{k_\sigma}{[Q_1]_0 k_\alpha}$ is a dimensionless number describing the tendency to form rings [11].

A curve-fitting of $\frac{1}{1-\xi}$ versus time (shown in Figure 6) gives:

$k_\alpha = 0.027 \ \text{mol}\,l^{-1}h^{-1} \pm 4\%$

$k_\sigma = 0.112 \ h^{-1} \pm 9\%$

where mol refers to moles of silicon end units (Q_1), and

$\lambda = 2.14$

This remarkably high value of λ indicates that octaethoxytrisiloxane has a strong tendency to form small cycles.

4. Conclusion

The study of the sol-gel polymerization of octaethoxytrisiloxane in acidic ethanol/water solution has shown that in our conditions, polymerization is irreversible. In addition, ring closure condensation (cyclization) is relatively fast and actively competes with chain extension condensation. The rapid formation of small rings during silicon alkoxide sol-gel polymerization should considerably affect the gel characteristics, since intramolecular reactions "waste" bonds from the point of view of polymer growth. Moreover, these small cycles branch very slowly and their formation slows down the gelation. It is thus important to consider cyclization effects in any attempt to develop a realistic quantitative model of silica sol-gel polymerization.

This work was supported by a grant from the Office of Naval Research and with a fellowship to J. S. from the Center for Interfacial Engineering at the University of Minnesota. The authors gratefully acknowledge helpful discussions with Prof. C. W. Macosko, Prof. L. E. Scriven, Anshu Gupta and Rich Cairncross at the University of Minnesota.

References

[1] C.J. Brinker and G.W. Scherer, Sol-Gel Science (Academic Press, New York, 1990).

[2] J.C. Pouxviel and J.P. Boilot, J. Non-Cryst. Solids 94 (1987) 374.

[3] B.D. Kay and R.A. Assink, J. Non-Cryst. Solids 99 (1988) 359; 104 (1988)112; 107 (1988) 35.

[4] D.H. Doughty, R.A. Assink and B.D. Kay, Adv. Chem. Ser. 224 (1990) 241.

[5] J. Sanchez and A. V. McCormick, J. Phys. Chem. 96 (1992) 8973.

[6] R. Iler, The Chemistry of Silica (John Wiley & Sons, New York, 1979).

[7] W. G. Klemperer, V. V. Mainz and D. M. Millar, Mat. Res. Soc.Symp. Proc. 73 (1986) 3.

[8] P.J. Flory, Principles of Polymer Chemistry (Cornell University Press, Ithaca, New York, 1953).

[9] L.W. Kelts and N.J. Armstrong, J. Mater. Res. 4 (1989) 423.

[10] J.K. Bailey, M.L. MeCartney and C.W. Macosko, J. Non-Cryst. Solids 125 (1990) 208.

[11] M. Gordon and G. R. Scantlebury, J. Chem. Soc. (B) (1967) 1.

Figure Captions

Figure 1. ^{29}Si-NMR spectrum of synthesized octaethoxysilane.

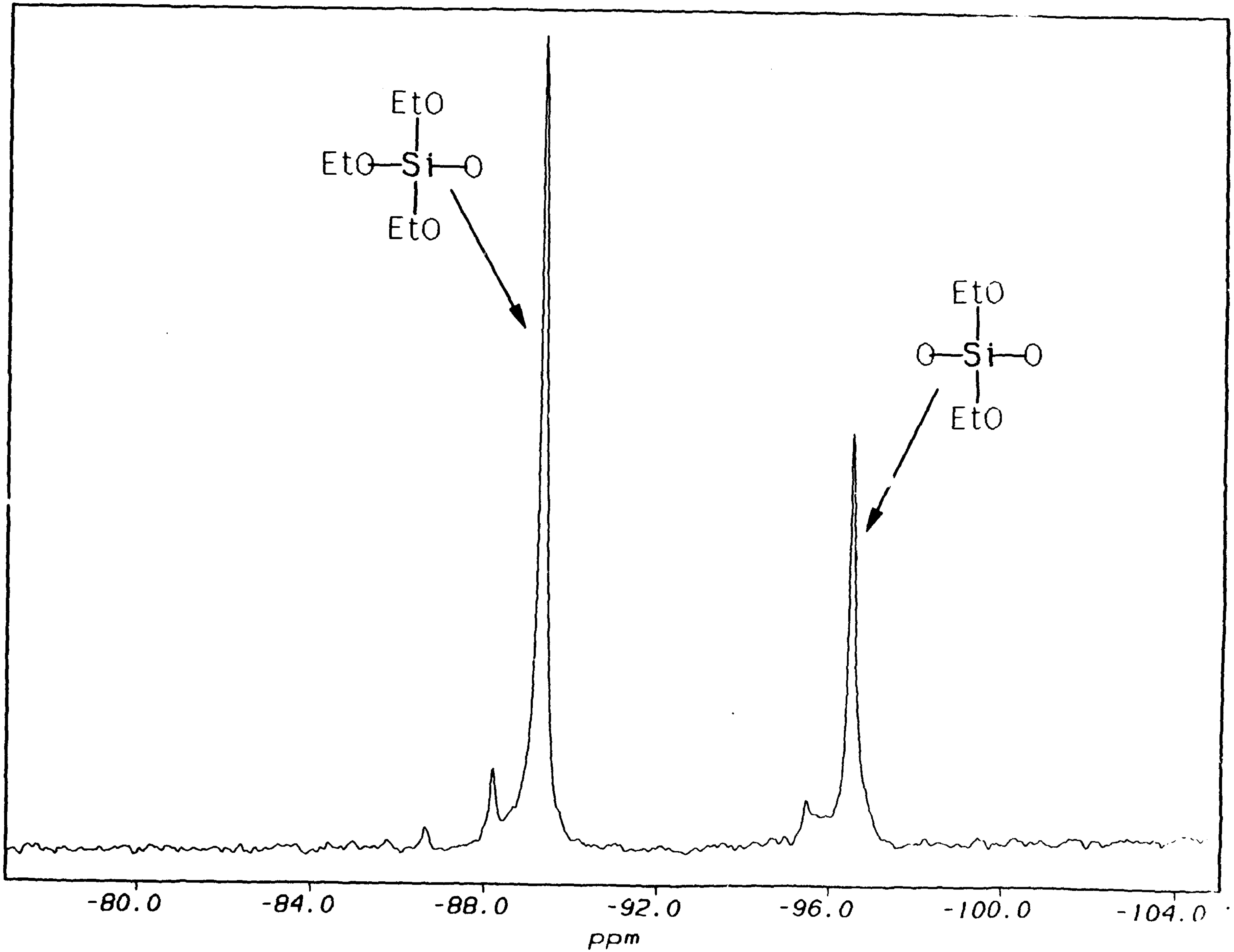
Figure 2. ^{29}Si NMR for the polymerization of octaethoxytrisiloxane. The first spectrum was recorded after 25 minutes of reaction and the following spectra were acquired every 15 minutes, up to eight hours of reaction.

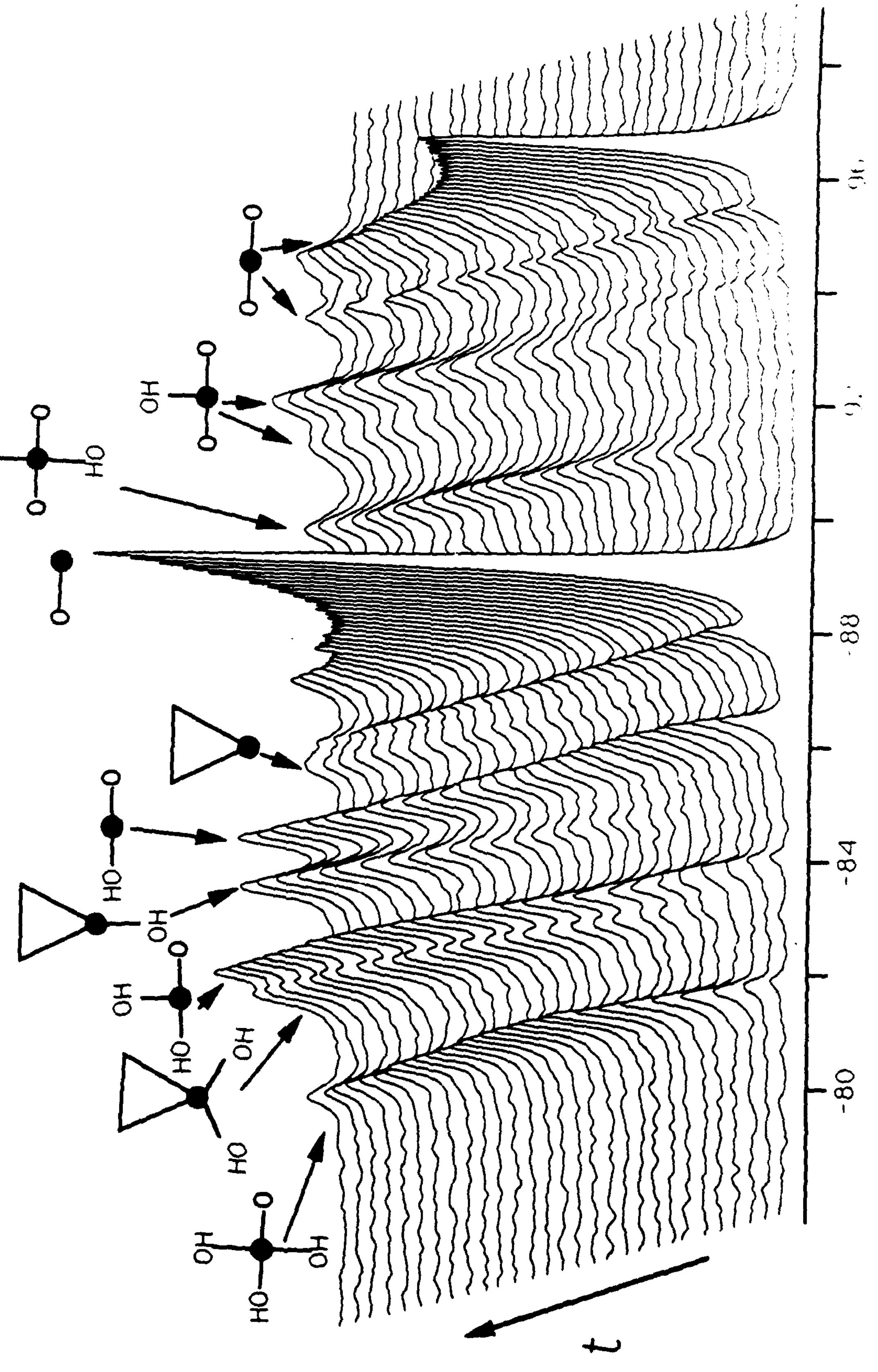
Figure 3. Concentrations of silicon end units (Q_1), middle units (Q_2) and trimeric cyclic units (Q_c).

Figure 4. Size exclusion chromatograph after 6 hours of reaction with proposed peak assignements. The elution solvent was tetrahydrofuran. Note the peak inversion from trimer to hexamer.

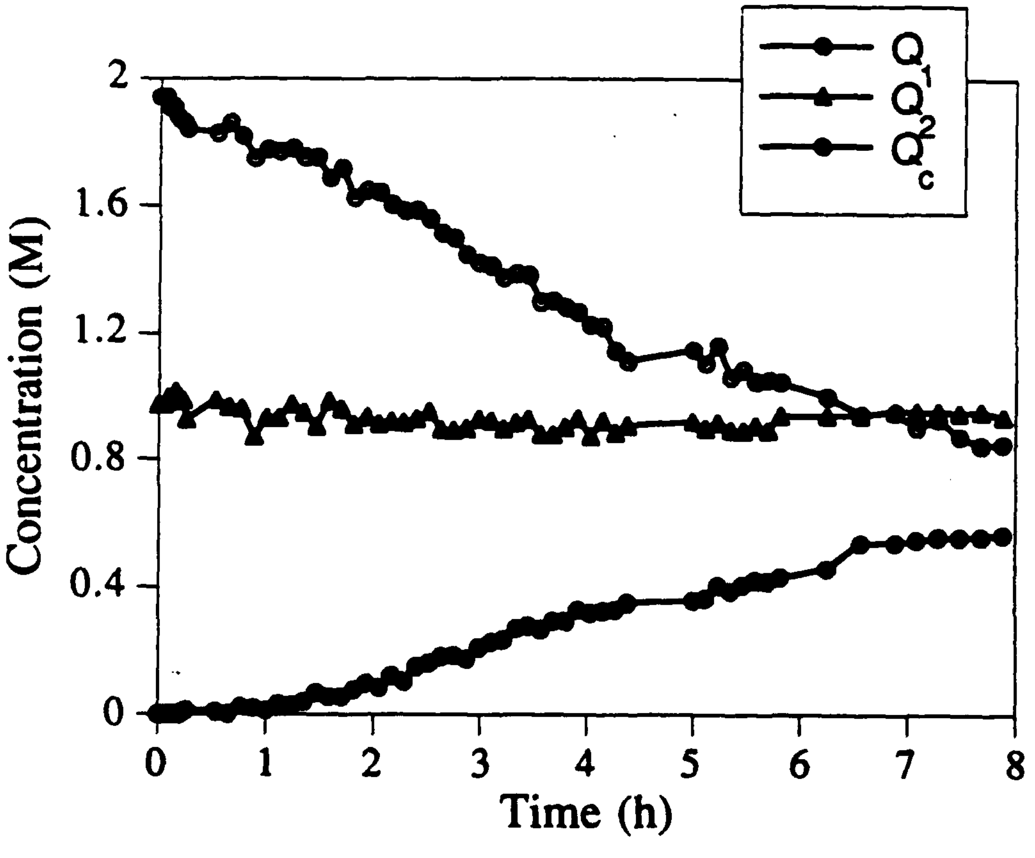
Figure 5. Plot of the extent of cylization (σ) and chain extension condensation (α).

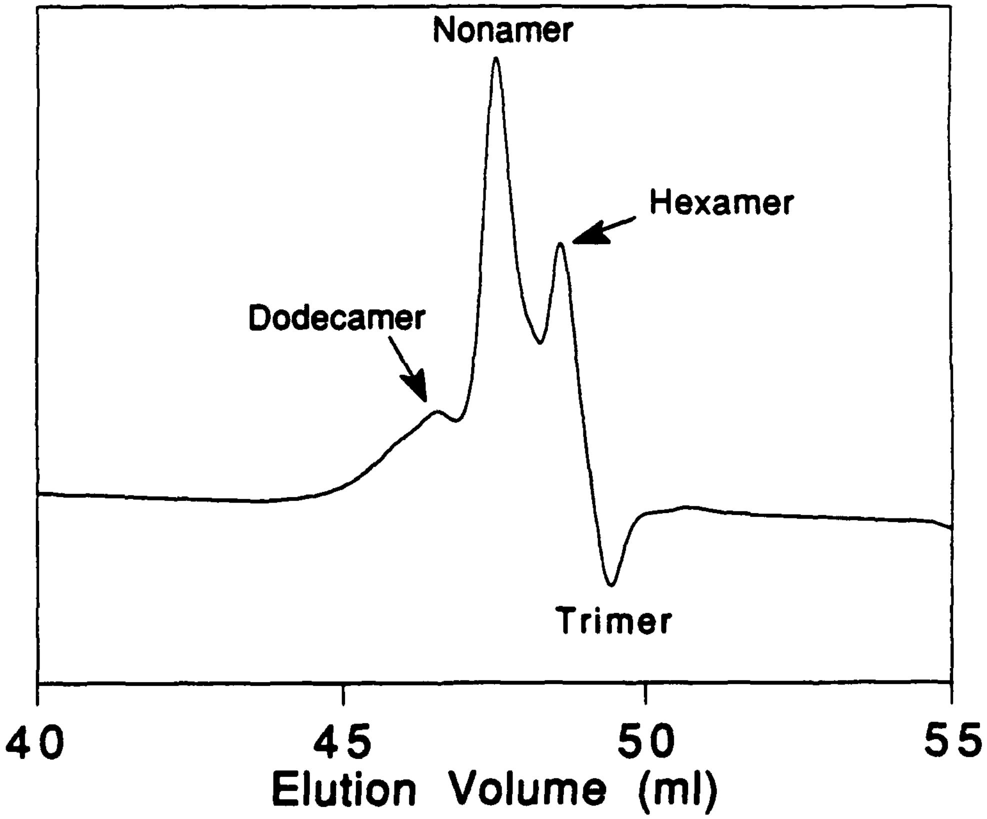
Figure 6. Plot of $\frac{1}{1-\xi}$ and curve-fitting for the determination of the rate constants.

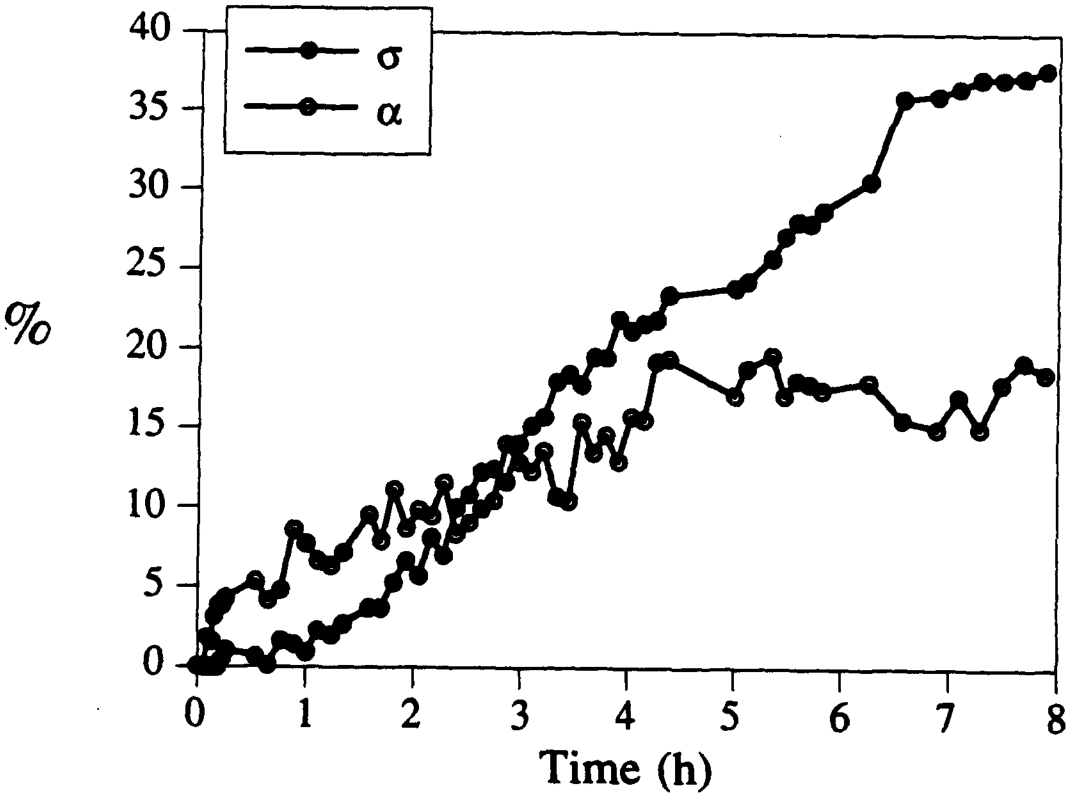

EtO
EtO—Si—O
EtO
EtO
O—Si—O
EtO
-80.0
-84.0
-88.0
-92.0
-96.0
-100.0
-104.0
ppm



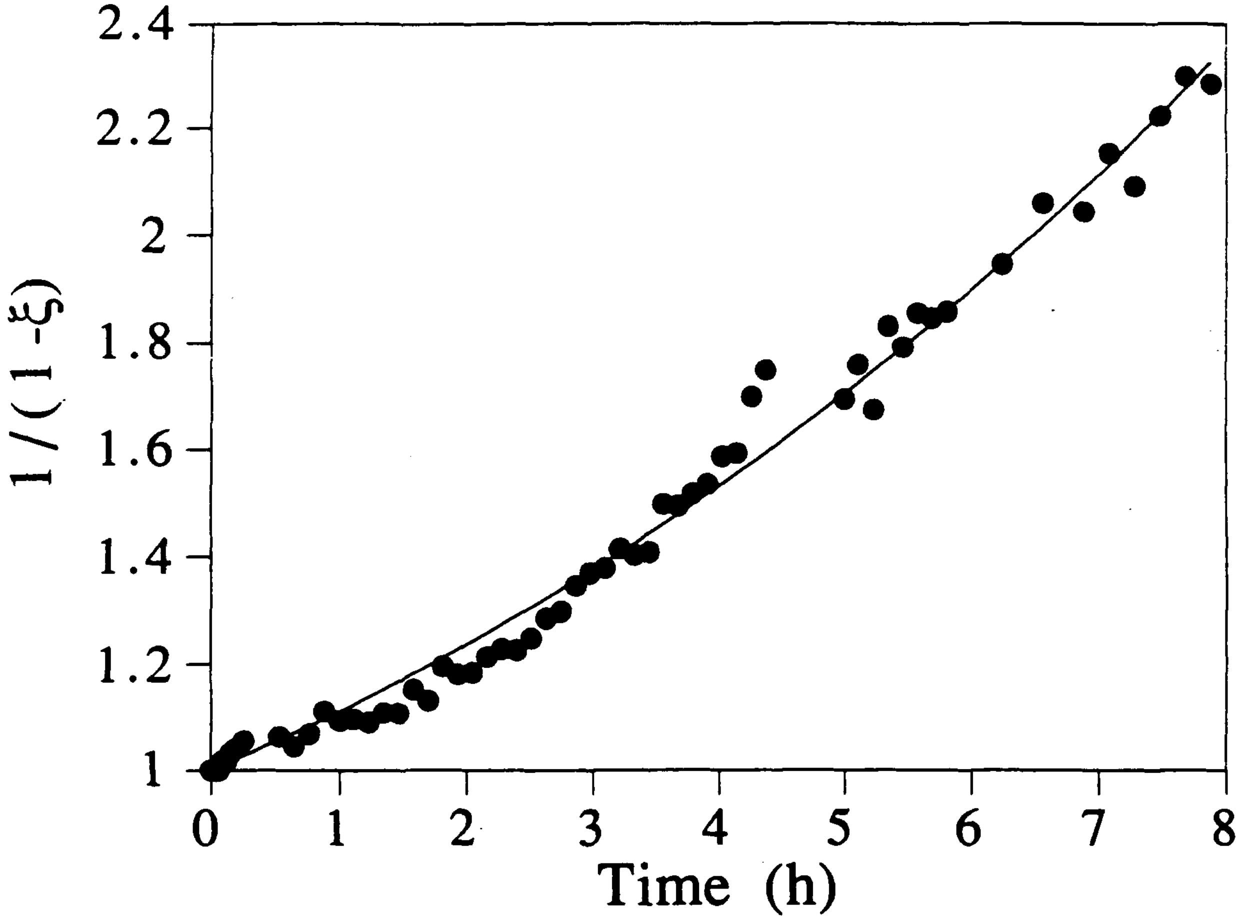
HO
OH
O
-80
-84
-88
ppm
t


Q1
Q2
Qc
Concentration (M)
2
1.6
1.2
0.8
0.4
0
0
1
2
3
4
5
6
7
8
Time (h)


Nonamer
Hexamer
Dodecamer
Trimer
40
45
50
55
Elution Volume (ml)



σ
α
%
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
Time (h)


2.4
2.2
2
1.8
1.6
1.4
1.2
1
1 / (1 - ξ)
0
1
2
3
4
5
6
7
8
Time (h)