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# Polymers from the hydrolysis of tetraethoxysilane\*

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The hydrolysis of tetraethoxysilane was studied under various solvent and temperature conditions. A method was developed by which reaction rates can be measured even in the presence of alcohols other than ethanol. The structures of the resulting polymers were dependent upon the reaction conditions employed, those formed at high temperature being highly condensed materials.

## INTRODUCTION

The acid-catalysed hydrolysis of tetrafunctional silicon compounds has been the subject of numerous investigations<sup>1, 2</sup>. The acid-catalysed exchange of polar groups at silicon is widely documented<sup>2, 3</sup>. Since a tetrafunctional molecule is involved, a wide variety of linear and cyclic structures is possible as products from these reactions<sup>3</sup>. A common practice is to hydrolyse tetraethoxysilane in alcoholic solvents to obtain condensed polysilicates<sup>4, 5</sup>. When an alcohol other than ethanol is employed as the reaction medium, the final polymer structure is further complicated by incorporation of some solvent through the exchange process.

Recently in our laboratories, it became necessary to know with some certainty the structures of condensed polysilicates obtained from the hydrolysis of tetraethoxysilane under several different solvent and temperature conditions. Furthermore, it was necessary to determine the rate of both the hydrolysis and the ester exchange reactions. Thus, it was advantageous to develop a method of investigating the hydrolysis and the resulting polysilicate.

## EXPERIMENTAL

A Victoreen 4000 Series gas chromatograph employing a 2 m × 3 mm Porapak Q column and a thermal conductivity cell was used for all gas chromatographic (g.c.) analyses. Nuclear magnetic resonance spectra (n.m.r.) were obtained using a Varian A-56/60 spectrometer. All n.m.r. spectra were obtained in 20% solutions of carbon tetrachloride using tetramethylsilane as an internal standard. Number-average molecular weights were determined in toluene using a Mechrolab Model 301 Osmometer. Waters Associates polystyrene standards with number-average molecular weights of 1220 and 2020 were used for calibration.

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## G.c. calibration procedure

Mixtures of varying mole ratios of ethanol and solvent alcohol were prepared and 1.00 ml of methyl ethyl ketone was added to each as an internal standard. The mole ratios of alcohols chosen were expected to cover the range encountered during hydrolysis. G.c. analysis was performed on each mixture and a plot of relative peak areas (alcohol/ketone), versus mole of alcohol was constructed for both ethanol and the solvent alcohol in question. Methyl ethyl ketone was chosen as the internal standard since it did not react with the system, had no apparent effect upon the solubility of the silicate, and was sufficiently different in its retention time from the alcohols to allow accurate measurements.

## General hydrolysis procedure

All reactions at 25°C were performed in Pyrex flasks sealed with septum caps. Reactions at 110°C were carried out in heavy walled, sealed Pyrex tubes. A mixture of solvent alcohol (0.125 mol), tetraethoxysilane (0.050 mol), water (0.080 mol) and methyl ethyl ketone (1.00 ml) was blended to give a homogeneous solution. Hydrochloric acid (0.20 ml of 0.10 N) was added and the reaction vessel was sealed. During the low temperature runs, samples for g.c. analyses were periodically withdrawn through the septum cap. Relative peak areas (alcohol/ketone), were converted to moles of alcohol from the calibration curve. In this way, the course of the reactions was easily followed as a function of time.

## Isolation of condensed polysilicates

After hydrolysis, the reaction mixtures were frozen in liquid nitrogen and the flask was connected to a vacuum system. A vacuum of 0.01 mmHg was maintained while the solutions were slowly warmed to room temperature. G.c. analyses before and after this procedure showed identical compositions of the alcohols.

## RESULTS AND DISCUSSION

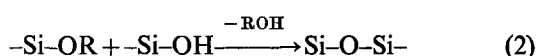
## Hydrolysis and ester exchange

Theoretically, the acid-catalysed hydrolysis of tetraethoxysilane in two or more equivalents of water leads to the formation of silicon dioxide and ethanol as the only products. If, however, the reaction is carried out in an alcoholic solvent with limited amounts of water, partly hydrolysed condensed silicates are produced<sup>4</sup>. In theory, the condensed polysilicates can form either as linear chains or as ring systems.

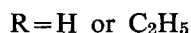
The formation of the condensed polysilicates is the result of a complex sequence of reactions. First, the silicate ester is hydrolysed as shown by:



The polysilicate is then formed through condensation of either silicate hydroxyl groups or hydroxyl and ester groups:



where



The alternating sequence of hydrolysis and condensation steps continues until the ultimate molecular weight is attained and all water is consumed. When an alcohol other than ethanol is employed as the solvent, a third reaction, that of ester exchange, must also be considered. The final structure of the condensed polysilicate must reflect all three reactions.

In general, the production of ethanol can be taken as a measure of the progress of the hydrolysis reaction. However, when an alcohol other than ethanol is employed as the reaction medium, ethanol is formed both by hydrolysis and by ester exchange and these processes must be separated. This was accomplished by simultaneously measuring the amount of ethanol liberated and the amount of solvent alcohol consumed. The amount of solvent alcohol consumed must be equal to the amount of ethanol liberated by the exchange process. Thus, the amount of ethanol generated by hydrolysis is obtained by subtracting that amount liberated by exchange from the total ethanol produced during the reaction. From these data the ratio Si:OC<sub>2</sub>H<sub>5</sub>:solvent in the final polymer structure can be calculated. Here, percentage exchange is based upon the final polymer composition.

The hydrolysis of tetraethoxysilane at 25°C was carried out in alcohols of differing structural types. As shown in Table 1, no trend was established with respect to the hydrolysis reaction. Since very small amounts of water cause large changes in the amount of apparent hydrolysis, the difference in the percentage hydrolysis may reflect residual water in the solvents. Table 1 does, however, show that the distribution of alkyl groups in the condensed polysilicate is highly dependent upon the structure of the solvent alcohol.

Table 1 Hydrolysis and ester exchange of tetraethoxysilane at 25°C

Solvent	Hydrolysis (%)	Exchange (%)
methanol	76	44.7
Cellosolve (ethylene glycol mono ethyl ether)	63	45.9
isopropanol	63	35.2
t-butanol	67	0

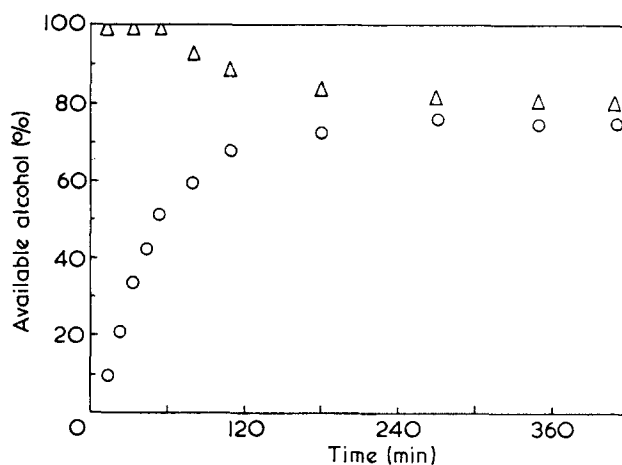


Figure 1 Rate of hydrolysis and ester exchange during the polymerization of tetraethoxysilane in isopropanol at 25°C.  $\Delta$ , Isopropanol;  $\circ$ , ethanol

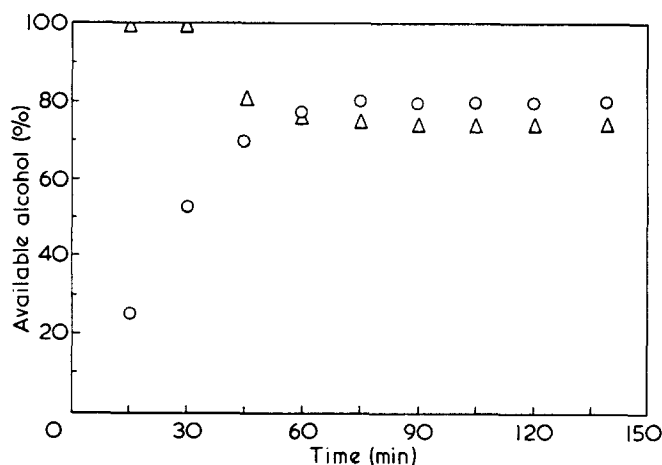


Figure 2 Rate of hydrolysis and ester exchange during the polymerization of tetraethoxysilane in Cellosolve at 25°C.  $\Delta$ , Cellosolve;  $\circ$ , ethanol

With respect to the exchange process primary alcohols are more reactive than secondary alcohols while the tertiary alcohol did not undergo exchange.

Reaction rate data for the production of ethanol at 25°C was obtained in the case of Cellosolve and isopropanol. Examination of Figures 1 and 2 reveals that the rate of hydrolysis (generation of ethanol) is more rapid in Cellosolve than in the secondary alcohol. The initial rate in Cellosolve was  $3.5 \times 10^{-2}$  mol/min as compared to  $2.5 \times 10^{-2}$  for isopropanol. It is interesting to note that the ester exchange reaction occurs only after hydrolysis is complete.

As shown in Table 2, increased reaction temperatures had little influence upon the extent of the ester exchange reaction, but did increase the apparent percentage hydrolysis. The term 'apparent hydrolysis' is used here since the 110°C reaction results in a more highly condensed polymer.

The ester exchange reaction was also examined using ethanol as the solvent. This was accomplished by performing the hydrolysis in  $\beta$ -deuterated ethanol. In this case, the exchange reaction resulted in an equal distribution of the ethanols between polymer and solvent. Thus, the exchange reaction is solely a function of the alcoholic medium employed as solvent.

The distribution of alkoxy groups in the final condensed polysilicate is highly dependent upon the mole fraction of solvent alcohol employed. Polymers with a

Table 2 Effect of temperature upon the tetraethoxysilane hydrolysis and ester exchange

Solvent	Temperature (°C)	Hydrolysis (%)	Exchange (%)
isopropanol	25	63	35.2
isopropanol	110	78	38.7
Cellosolve	25	63	45.9
Cellosolve	110	75.5	44.5

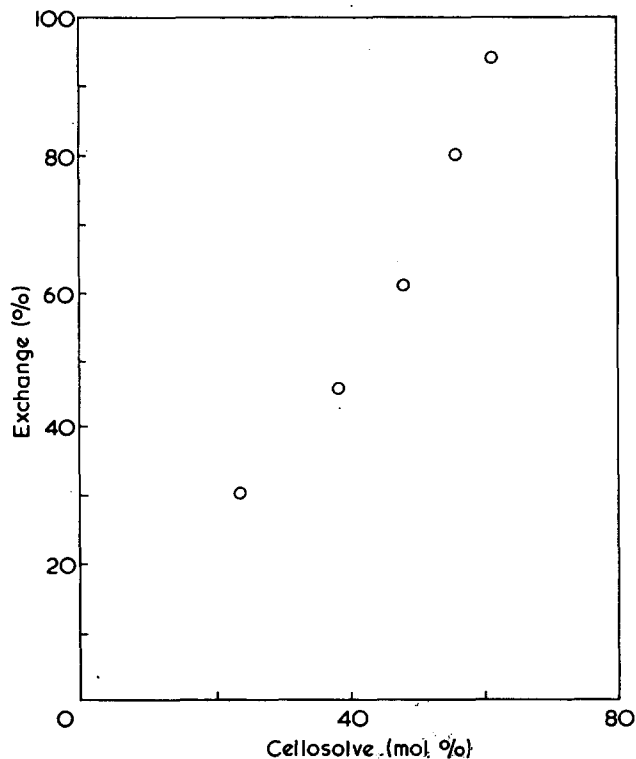


Figure 3 Extent of the exchange reaction as a function of the Cellosolve concentration

Cellosolve content from 0 to 100% can be obtained simply by adjusting the mole ratio of Cellosolve to tetraethoxysilane (Figure 3).

Polymer structure

The g.c. method described previously yields information regarding the relative ratios of silicon to alcohols. In order to have a complete description of the polysilicate, however, the silicon to hydroxy ratio must also be known since it will reflect the extent of condensation. This was done by removing the solvents and hydrochloric acid, and then measuring the n.m.r. spectra of the pure polymers. In all cases, the methyl groups appeared as overlapping multiplets centred at  $\tau=9.17$ . The methylene groups and the secondary proton of isopropanol appeared as overlapping multiplets centred at  $\tau=6.34$ . The hydroxy proton appeared as a broad peak at  $\tau=5.34$ . By comparing the area under the hydroxyl proton peaks to that under the alkyl peak, sufficient information was obtained to generate an empirical formula.

The condensed polysilicate obtained from the 25°C hydrolysis of tetraethoxysilane in isopropanol was found to have the empirical formula

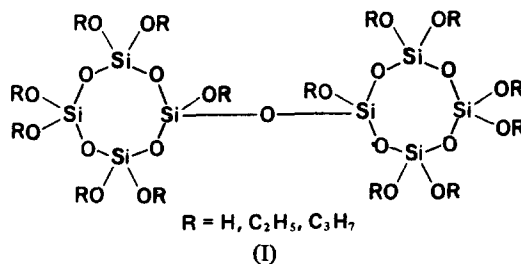


This formula is significant in that it requires a cyclic structure and not linear chains. A completely linear system would have the formula  $\text{Si}_n(\text{OR})_{2n+2}$ , where

OR represents the total of all hydroxy and alkoxy groups. It was not possible to draw a structure for the empirical formula as given. However,



can be drawn as two connected rings each containing four silicon atoms as shown in structure (I). The number-

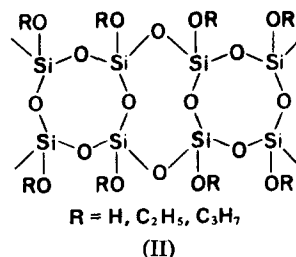


average molecular weight of the polymer was determined to be 1002 which is in good agreement with the calculated molecular weight of 996.

The structure of the hydrolysis product obtained at 110°C in isopropanol is much more complex. The products empirical formula was found to be



Here the silicon to OR ratio is almost 1:1 indicating a highly condensed material. Structure (II) is one possible way to represent such a structure.



The molecular weight of this material was determined to be 2212. However, it is much more than a 'dimer' of (I) since a much higher ratio of silicon to alkoxy is observed. The polysilicate (II) contains approximately 28 silicon atoms and can be derived by condensation of molecules of (I).

Structures identical to (I) and (II) were also obtained and identified from the Cellosolve reactions.

CONCLUSIONS

The combined use of g.c., n.m.r. and molecular weight measurements provides a technique for the determination of the exact structures of condensed polysilicates. Since the structures of the polymer obtained by hydrolysis of alkoxy silanes vary widely with reaction conditions, the method should be of assistance to other investigators working in this area. The method is also useful for obtaining hydrolysis and ester exchange rate data.

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