Silicic Acid from Tetraethyl Silicate Hydrolysis. Polymerization and Properties

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Abstract: Silicic acid from tetraethyl silicate hydrolysis in ethanol–water has been studied with regard to composition and polymerization in solution. Trimethylsilation of the silanol groups was used to determine the ratio of ethoxy, hydroxy, and silicon-shared oxygen groups to silicon atoms of the polymers at the time of capping. Changes in these ratios with degree of polymerization and time indicate the apparent functionality (f) per silicon atom to be <2.01 but >2 in polymer solutions that gel. Light-scattering kinetics indicate an f of *ca.* 2.001. The present data fit a hypothesis of early condensation to a "monomer" unit such as $ZSi(OH)_2OSi(OH)_2OSi(OH)_2Z$, and almost linear condensation of these units to form a ribbon of three joined siloxane chains. In this scheme, the periphery of the polymer ribbon is populated with ethoxy and hydroxyl groups, represented by Z. Their distribution and orientation are correlated with gelation kinetics and the excess of f above 2 that is found when the water/tetraethyl silicate (mole ratio) used in the hydrolyses is over 1.67. Properties of the polysilicic acids concentrated by extraction and also by drying at room temperature were briefly studied.

Aqueous silicic acid materials have been used and studied for over a century as alkali silicates and silica gels and, more recently, as collodial dispersions prepared from soluble polymers. In light-scattering and freezing-point studies[1] of the polymerization of water-soluble silicic acids, it was found that the kinetic aspects of the polymerization were most easily explained by an apparent functionality for the monomer involved of slightly over 2 (2.0004–2.05). A very low functionality (2.0001) also has been obtained from ultracentrifugation and viscosity experiments by Audsley and Aveston.[2] Tetraethyl silicate [$(EtO)_4Si$] also has been widely used and studied,[3] but investigations of the composition of the silicic acid in the hydrolysates, its polymerization, and the properties of the polymer are not numerous. Our purpose is to present and interpret some recent results on the preparation and properties of the soluble polysilicic acids from this source.

Experimental Section

Materials. "Tetraethyl orthosilicate" (Ethyl Silicate Pure, Union Carbide Corp.) was used without further purification. Analysis by glpc indicated less than 0.1% ethanol as the major contaminant. Less than 0.1% was nonvolatile at 170°.

Trimethylchlorosilane (Me_3SiCl) (Dow Corning Corp.) was used without purification.

Methods. Hydrolyses of $(EtO)_4Si$ were spontaneous and exothermic after addition of the ingredients at room temperature to a glass bottle, which was capped and shaken, or to a flask equipped with reflux condenser and magnetic stirrer. Reaction times were measured from the time of mixing. The ΔT's observed were 15–50°, depending on the proportions (Table I) and batch size, which ranged from 50 to 600 g (0.24–2.88 moles) of $(EtO)_4Si$.

Capping Reactions with Trimethylchlorosilane.[4] At a given time from the start of the hydrolysis, equal weights of hydrolysate and Me_3SiCl were mixed. An exothermic reaction occurred and two layers formed. The mixtures were stirred overnight at room temperature, and the water-insoluble layer was separated (with aid of extraction (CH_2Cl_2) for the older hydrolysates), washed with water, and dried (Na_2SO_4). Hexamethyldisiloxane from the self-condensation of Me_3SiOH and other materials of low boiling point were removed by evaporation (0.1 mm, 48 hr). The residual capped polysilicic acids could be stored for months without apparent change.

Table I. Hydrolysis Formulations[a]

Input	Parts by weight X series	 Y series
$(EtO)_4Si$	100	100
Diluent, such as EtOH	$92 - X$	$44 - Y$
$H_2O + HCl$	X	Y
	(15% SiO_2)	(20% SiO_2)

[a] Unless otherwise specified, the hydrolysates used 100 g of $(EtO)_4Si$, EtOH diluent, and are designated, *e.g.*, X30 when 30 g of 0.1 *N* HCl was used, and Y44 when 44 g of 0.1 *N* HCl was used.

Analytical Techniques. Nmr spectra were determined at 60 Mc/sec using 20% solutions (CCl_4) of capped polysilicic acids and an external tetramethylsilane reference. Analyses by glpc used standard techniques, and DTA behavior was scanned with a Du Pont 900 differential thermal analyzer.

Number-average molecular weights ($\bar{M}_n$) were determined with a Mechrolab vapor pressure osmometer, Model 302, using standard techniques or by routine ebullioscopic methods. Reference solvents for these methods were prepared by distillation at low temperatures of portions of the hydrolysates. For the capped polysilicic acids, cryoscopy in benzene was used.

Weight-average molecular weights ($\bar{M}_w$) were obtained from angular dissymmetry light-scattering measurements made with the Baum–Billmeyer[5] apparatus and with a well-calibrated but less complex apparatus used for 90° scattering only. The measurements were made on filtered dilutions of the polymerizing stock solution (15% SiO_2). The diluent was 83:17 $EtOH/H_2O$ (w/w), which is close to the estimated composition of the solvent present. A Brice–Speiser differential refractometer was used to make differential refractive index (r) measurements, yielding $dr/dC = 0.057$ cm^3/g of SiO_2 for X45 hydrolysates, which had a density of 0.923 g/cm^3.

Reported pH values should be construed as apparent, since glass electrodes were used without any corrections for solvent effects due to changing $EtOH/H_2O$ ratios.

Gelation was determined at room temperature as the incidence of graininess and pear-shaped bubbles upon inverting bottles partially filled with the hydrolysates. This state was followed by complete nonpourability. It was always preceded by long periods of increasing viscosity.

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(1) M. F. Bechtold, *J. Phys. Chem.*, **59**, 532 (1955).

(2) A. Audsley and J. Aveston, *J. Chem. Soc.*, 2320 (1962).

(3) R. Aelion, A. Loebel, and R. Eirich, *J. Am. Chem. Soc.*, **72**, 5705 (1950).

(4) C. W. Lentz, *Inorg. Chem.*, **3**, 574 (1964).

(5) F. J. Baum and F. W. Billmeyer, Jr., *J. Opt. Soc. Am.*, **51**, 452 (1961).

Hardness was estimated by placing dried chunks or flakes on a plane test surface (mineral crystals and microscope slides), pressing down, and manually rotating them under a firm pad. After broken and adherent fragments were removed by scouring (with No. 0000 steel wool in the case of microscope slides), the test surface was examined for scratches with a magnifying glass.

Theoretical Section

Stoichiometry. The stoichiometry involved in the complete hydrolysis of $(EtO)_4Si$ and the complete condensation of the hydrolysate has been represented in the past by eq 1–3.

$$(EtO)_4Si + 4HOH \longrightarrow 4EtOH + Si(OH)_4 \qquad (1)$$

$$Si(OH)_4 \longrightarrow 2HOH + SiO_2 \qquad (2)$$

$$(EtO)_4Si + 2HOH \longrightarrow 4EtOH + SiO_2 \qquad (3)$$

These equations do not indicate mechanism or the true nature of the product. However, they show that, in the event of complete condensation, 2 moles of H_2O would suffice for the complete hydrolysis of 1 mole of $(EtO)_4Si$. One might assume that the hydrolysis reaction is random so that an amount of water equivalent to partial hydrolysis would yield initially a distribution of $(EtO)_4Si$, $(EtO)_3SiOH$, $(EtO)_2Si(OH)_2$, $(EtO)Si(OH)_3$, and $Si(OH)_4$ that could be calculated statistically. This may occur, but hydrolysates prepared with excess H_2O contain no volatile species (as shown later), indicating that such species are probably involved in rapid redistribution equilibria and are then polymerized so that there remains little or none of the volatile $(EtO)_4Si$ and the presumedly volatile $(EtO)_3$-SiOH. The stoichiometry is better represented for our purposes by eq 4, in which the oxygen atoms in the silicic

$$n(EtO)_4Si + 0.5n(4 - a + b)HOH \longrightarrow n(4 - a)EtOH + [Si(OEt)_a(OH)_bO_{0.5(4-a-b)}]_n \qquad (4)$$

acid product are shared between two Si atoms.

It is apparent that the stoichiometry could be specified if the disappearance of water and appearance of EtOH could be accurately measured without disturbing the equilibria. Although such measurements could be helpful in the hydrolysis stage of the reaction, no suitable analytical tool is available to determine these concentration changes satisfactorily in the condensation stage. Even after precise thermodynamic studies, the significance of measured activities of H_2O and EtOH might be difficult to interpret, since some may be H-bonded to silanol groups or present as hydrated SiO_2.

The capping reaction and the calculation therefrom of the parent silicic acids are assumed to follow eq 5,

$$[Si(OEt)_a(OH)_bO_{0.5(4-a-b)}]_n + nbMe_3SiCl \longrightarrow nbHCl + [Si(OEt)_a(OSiMe_3)_bO_{0.5(4-a-b)}]_n \qquad (5)$$

in which product at time t, when $1/(1 + b)$ moles of the parent acid is capped, the total gram-atoms is $n(Si_1C_tH_tO_t)$. After calculation of C_t and O_t from analyses, a and b were determined by eq 6. The cap-

$$\begin{aligned} b + (1 + b)(4O_t - C_t) &= 8 \\ a &= 0.5[C_t(1 + b) - 3b] \end{aligned} \qquad (6)$$

ping reaction (eq 5) is fast and complete even in the presence of large amounts of alcohol and water. Of course, in the presence of excess H_2O in the hydrolysates, Me_3SiOH is generated and condenses with itself and with polysilicic acids. Apparently the capping of $\geqslant$SiOH is strongly dominant, since $Me_3SiOSiMe_3$ also can be used to cap silanol groups of polysilicic acids.[4] Large amounts of HCl apparently do not change the gross structure or molecular weight of silicates or silicic acids.[4]

Kinetic Equations for Condensation Polymerization and Gelation. To obtain information on the nature of the hydrolysates in the solutions, we have relied on the polymer capping experiments and molecular weight kinetics. The progress of molecular weight with time and gel time *vs.* concentration in condensation polymerizations[1] are shown in eq 7–10. Weight-average and

$$\bar{M}_w = M_0\left[\frac{1 + 2fC_0kt}{1 - (f^2 - 2f)C_0kt}\right] \qquad (7)$$

$$\bar{M}_n = M_0\left[\frac{2 + 2fC_0kt}{2 - (f^2 - 2f)C_0kt}\right] \qquad (8)$$

$$t_{gel} = \frac{1}{(f^2 - 2f)C_0k} \qquad (9)$$

$$\frac{\bar{M}_{n,gel}}{M_0} = \overline{DP}_{n,gel} = \frac{2f - 2}{f - 2} \qquad (10)$$

number-average molecular weights are $\bar{M}_w$ and $\bar{M}_n$, respectively. M_0 is the monomer molecular weight, f is the functionality of the condensing monomer of initial concentration C_0, k is the reaction rate constant, and t is reaction time. Equation 9 for gel time is derived from the definition of gelation as the time at which $M_w = \infty$, whence the denominator of eq 7 must equal 0. As derived from eq 8 and 9, $\overline{DP}_n$ at gelation depends only on the functionality of the polymerizing monomer (eq 10). Some restrictions for validity of these equations are that activity of functional groups is not affected by the size of the molecules to which they are attached, functional groups on the same molecule do not react with each other (no cyclization), and weight loss in the condensation is negligible.

Results

Hydrolysis and Hydrolysates. Exothermy. The temperature changes during the spontaneous hydrolyses and polymerizations help to describe the events taking place. Data showing hydrolysis to yield 15% SiO_2 solutions using a constant HCl concentration and increasing water are given in Table II. For the region 1.73–3.47 moles of H_2O/mole of $(EtO)_4Si$, ΔT increases, which probably means that the per cent of hydrolysis is increasing, although many other heat effects must be considered, such as heats of mixing, polymerization, and hydration.[3] In Table III are data for a similar series in which X represents the increasing weight of 0.1 N HCl used, along with the hydrolysis in which $Y = 44$. It should be noted that up to $X = 30$, both Tables II and III indicate homogeneous hydrolyses; *i.e.*, the initial ingredients and products are in complete solution. However, from $X = 30$ to 92 they are not, and appreciable time is required for hydrolysis to proceed and the temperature to rise to the point that the altered initial phases become mutually soluble. This initial heterogeneity may be responsible for slight interfacial hydrolysis and polymerization leading to very slight haze, then faint sedimentation, observed in hydrolysates in which $X \geqq 45$. This haze is less in the series with the

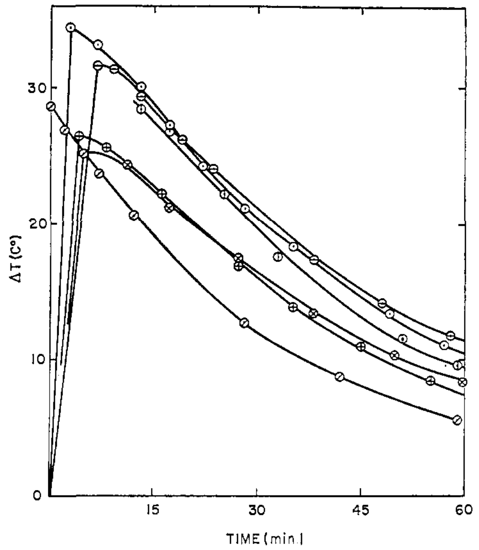


Figure 1. Hydrolysis of $(EtO)_4Si$, exotherm and cooling: ⊙, $X = 45$; ⊖, $X = 45$ (15 g of 0.1 N HCl); ○, after reheat of $X = 45$; ⊕, $X = 22.5$; ⊗, $X = 22.5$ (15 g of 0.1 N HCl); ∅, after reheat of $X = 22.5$.

increasing HCl. This is probably related to the speed of the reactions, and both initial compatibility and concentration of catalyst are probably involved in clarification time. The amount of catalyst (HCl) strongly affects the time required to reach the maximum temperature, since it is significantly shorter for the HCl-rich series in the region of $X = 20$ to 92.

Table II. Hydrolysis of $(EtO)_4Si$ (Constant HCl)

		Clarification		Maximum[a]		
X[b]	H_2O/ $(EtO)_4Si$[c]	Temp, °C	Time, min	Temp, °C	Time, min	ΔT, °C
15	1.73	25.5	0	42	6	16.5
17.5	2.02	26	0	47.5	6	21.5
20	2.31	26	0	50	8	24
22.5	2.60	26	0	51.5	8	25.5
30	3.47	27	0.2	54.5	6	27.5
45	5.20	35	3	55	6	26
60	6.94	41	6	54.5	8	25.5
92	10.64	48	27	53	28	26

[a] Initial temperature 25.5–29°. [b] Grams of H_2O plus 18 g of 0.1 N HCl. [c] In moles.

Table III. Hydrolysis of $(EtO)_4Si$ (Increasing HCl)

		Clarification		Maximum		
X[a]	H_2O/ Si[c]	Temp °C	Time, min	Temp, °C	Time, min	ΔT, °C
15	1.73	25	0	43	5.5	18
17.5	2.02	25	0	45.5	5.5	20.5
20	2.31	25	0	49	4.5	24
22.5	2.60	25	0	51.5	4.5	26.5
30	3.47	28	0.2	55	4	30
45	5.20	34	1	56.5	3	31.5
60	6.94	40	2	57	3	32
92	10.64	52	12	54	13	29
Y[b]						
44	5.09	43	9.5	68.7	10.0	29

[a] Grams of 0.1 N HCl. [b] Grams of 20% SiO_2. [c] In moles.

Thermal behavior during cooling of hydrolysates is also of interest. In Figure 1 are shown the ΔT's *vs.* time after mixing for four hydrolyses (192 g each), two each at $X = 22.5$ (one with 15 g of 0.1 N HCl and one with 22.5 g of 0.1 N HCl) and $X = 45$ (one with 15 g of 0.1 N HCl and one with 45 g of 0.1 N HCl). Also shown are the cooling curves for two similar hydrolysates reheated after advanced age (after exothermal effects are negligible), all in matched 160-g glass bottles. These qualitative data demonstrate that the X45 hydrolysates give off more heat in the early stages than the X22.5 hydrolysates, and in each of the cases the HCl-rich hydrolysates reach a higher ΔT more quickly than the HCl-poor hydrolysates. Furthermore, there is more delayed exotherm in the hydrolysates poorer in HCl, since their cooling curves eventually rise above the cooling curves for the HCl-rich hydrolysates.

Glpc and Nmr *vs.* Time after Hydrolysis. The rapidity of the hydrolysis was confirmed using methanol as a diluent in an X22.5 hydrolysis. The values under glpc peaks were corrected for nonvolatile Si-containing species. No volatile condensed silicates were detected. Within 55 sec the concentration of $(EtO)_4Si$ dropped from the input 52% to *ca.* 4%, and to *ca.* 0.2% in 36 min, while EtOH increased from 0 (input) to *ca.* 37% in 55 sec and to *ca.* 45% in 36 min. In other glpc and nmr experiments using EtOH diluent in the hydrolysis, the degree of hydrolysis increased with time and with increasing X; *i.e.*, EtOH increased and EtOSi$\lessdot$ groups diminished.

$\bar{M}_n$ from Vapor-Pressure Methods. Measurements of $\bar{M}_n$ by vapor-pressure methods confirmed that polymerization is occurring rapidly at room temperature, as shown in Table IV. These should be considered minimum values, since they represent the sum of the effects of polysilicic acids and impurities, which are most important at high $\bar{M}_n$.

Table IV. $\bar{M}_n$ of Polysilicic Acid (as SiO_2)

		Vapor pressure method	
Age, days	X	Ebullioscopy	Osmometry
0.04	22.5[c]		250
1.0	22.5		417
18	22.5	1040[a]	1330
18	22.5	990[b]	
18	45		2290

[a] Diluent, $EtOH/H_2O$ 99.8:0.2 by wt containing 5.62 mg of HCl/100 g. [b] Diluent, absolute EtOH. [c] pH 1.07–1.30 for X22.5 hydrolysates.

Polysilicic Acid Capping with Trimethylchlorosilane. The efficiency of the capping process was shown by hydrolyzing $(EtO)_4Si$ in the presence of an equivalent weight of Me_3SiCl. This procedure is substantially equivalent to capping during complete hydrolysis but with short condensation time. To a mixture of 50 g (0.24 mole) of $(EtO)_4Si$, 23.5 g of EtOH, and 108 g of Me_3SiCl (1 mole) was added, during 0.5 hr, 22.5 g of 0.1 N HCl (corresponding to $X = 45$). The mixture was stirred overnight, and the water-insoluble layer was separated, washed with H_2O, and dried (Na_2SO_4). There was obtained 78.9 g of a mixture of siloxanes. The major component (56 g, 62% conversion, bp 215–250°) was tetrakis(trimethylsilyl) silicate. The carbon and hydrogen analyses of a portion (bp 234–250°) were 38.08 and 9.52% found *vs.* 37.45 and 9.42% calculated,

Table V. Analyses of Capped Polysilicic Acids and Calculated Composition of the Parent Acids

Age, hr	Analyses,[a] % Si	C	H	O	Groups/Si (eq 6) OEt	OH	O
				$X = 17.2$			
1	32.41	36.315	8.77	22.505	0.974	1.768	0.629
24	32.41	33.98	8.17	25.44	0.892	1.216	0.946
115	32.17	32.375	7.645	27.81	0.888	0.908	1.102
312	32.82	30.905	7.26	29.015	0.783	0.798	1.210
				$X = 22.5$			
1	35.335	30.34	7.33	27.00	0.476	1.064	1.230
4	35.505	29.175	7.105	28.215	0.458	0.932	1.305
24	36.11	28.015	6.705	29.17	0.401	0.852	1.374
144	37.30	25.89	5.935	30.875	0.306	0.734	1.480
2184[b]	38.62	20.86	5.29	35.23	0.228	0.465	1.654
				$X = 45$			
0.5	38.285	27.06	6.645	28.01	0.149	1.006	1.423
23	38.705	24.705	5.99	30.60	0.160	0.779	1.530
48	38.98	23.995	5.87	31.155	0.193	0.675	1.566
480[b]	40.15	18.54	5.34	35.97	0.109	0.449	1.721

[a] Average of two; oxygen by difference. [b] CH_2Cl_2 used in separation.

Table VI. Properties of Capped Polysilicic Acids

Age, hr	Physical state	$\bar{M}_n$ (benzene)	$\overline{DP}_n$ of Si[b] (parent)	EtO/OH (Nmr)	(Table V)
		$X = 17.2$			
1	Liquid	559	2.3	0.78	0.55
24	Liquid	834	4.4	0.78	0.73
155	Liquid	1080	6.5	1.04	0.98
312	Liquid	1127	7.3	1.04	0.98
		$X = 22.5$			
1	Liquid	1260	7.7	0.6	0.45
4	Liquid	1390	9.1	0.6	0.49
24	Viscous liquid	1480	10.3	0.5	0.47
144	Solid[a]	2770	21.2	0.6	0.42
2184	Solid	3815	35.8	0.6	0.49
		$X = 45$			
0.5	Solid	2330	15.8	0.2	0.15
23	Solid	3190	24.7	0.2	0.20
48	Solid	4380	35.9	0.2	0.29
480	Solid	9020	89.0	0.1	0.24

[a] Mp = 90–100°. [b] Calculated from the $\bar{M}_n$ of capped acids, their formula weights from analyzed atom ratios (not shown), and the number of Si atoms in the parent acid, $1/(1 + b)$.

and molecular weight 382 (found) *vs.* 384.9 (calcd), indicating good correlation with tetrakis(trimethylsilyl) silicate. The infrared spectrum of the capped mixture was very similar to that of hexamethyldisiloxane and showed no absorption for $\geqslant$SiOH. This indicates substantially 100% capping efficiency.

The capping of polysilicic acids was carried out as described under Methods. As a check on purity, Cl analyses for the capped acids from an X17.2 hydrolysate ranged from 0.06 to 0.02%. DTA data on the capped materials showed no major endothermic and exothermic shifts up to 500°. A capped product from a young hydrolysate scanned by TGA (6°/min in N_2) showed no loss to 250°, 5% loss at 366°, and 45% loss at 600°. The infrared spectra of these samples resembled that of hexamethyldisiloxane and showed no hydroxyl absorption. Major bands were assigned to CH (3.37, 3.43 μ), $Si(CH_3)_3$ (7.96, 11.84, and 13.20 μ), and SiOC and SiOSi (9.25 μ broad). The nmr spectra were simple showing $SiCH_3$ (τ 9.91) and ethoxy groups attached to silicon (triplet τ 8.85, quadruplet τ 6.25). No hydroxyl resonance was observed. When a small amount of EtOH was introduced, a separate resonance for EtOH was observed along with the expected hydroxyl group showing that the initial ethyl group resonances were not due to this impurity. Integration of the nmr spectra allowed a measure of $SiOEt/SiOSiMe_3$, which reflects the ratio of SiOEt/SiOH present in the polysilicic acid at the time of capping.

The data of Table V for capped polysilicic acids are internally consistent. After the Si/OEt/OH/O ratios were calculated for the parent polymers, the back-calculation of the trimethylsilyl derivatives thereof led to ratios of C and H atoms to Si that deviated from the found ratios by an average of less than 0.1% for C and 1.9% for H.

The decrease of OH/Si with age is apparent in all hydrolysates as is the corresponding increase in shared O/Si. In the X17.2 and X22.5 hydrolysates, there is also a decline of EtO/Si, indicating progressive hydrolysis, but when $X = 45$, in the time investigated the EtO/Si ratio is nearly constant. The calculated degrees of hydrolysis attained at the greatest ages capped were 80.4, 94.3, and 97.3% for X17.2, X22.5, and X45 hydrolysates, respectively. In Table VI are summarized changes in the physical properties and $\bar{M}_n$ of the capped acids, which range from highly fluid to solid, and the $\overline{DP}_n$ calculated for the corresponding parent polysilicic acids. Also shown is a comparison of EtO/OH ratios derived from nmr of capped acids with those calculated from compositions of the parent acid. In the X17.2 hydrolysates, the EtO/OH ratios were determined from two measurements each of $CH_2/Si(Me)_3$ and $Me/Si(Me)_3$. Although the average deviation was less than 0.03, the nmr values did not overlap the analytical values.

Light Scattering. The results obtained from light-scattering experiments are shown in Table VII. The $\bar{M}_w$ values show good reproducibility and the decreasing B values indicate that the older polymers interact less with the solvent.

Gelation. A broad view of gelation time for both the X and Y series of hydrolysates is shown in Figure 2, which indicates faster gelation for the Y series, presumably because of higher concentration and different solvent environment. With regard to the influence of

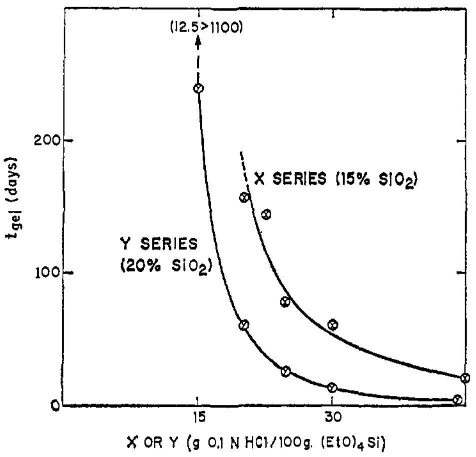


Figure 2. Gel time for $(EtO)_4Si$ hydrolysates: ⊗, *X* series (15% SiO_2; ⊗, *Y* series (20% SiO_2) (*cf.* Table I).

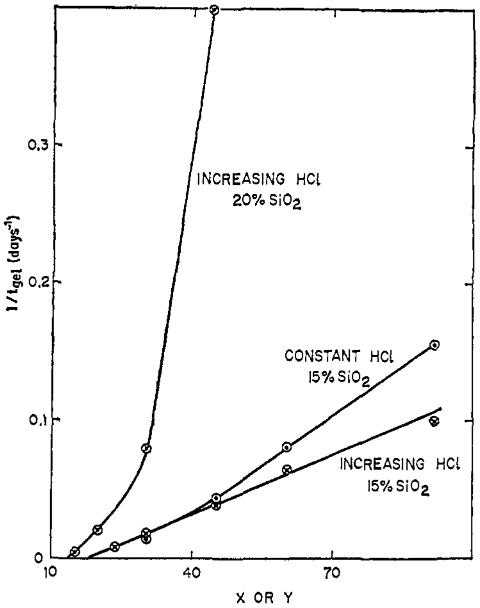


Figure 3. Dependence of $1/t_{gel}$ on $H_2O/(EtO)_4Si$ in hydrolysis: ⊗, *X* series, increasing HCl; ⊖, X series, constant HCl; ⊗, *Y* series.

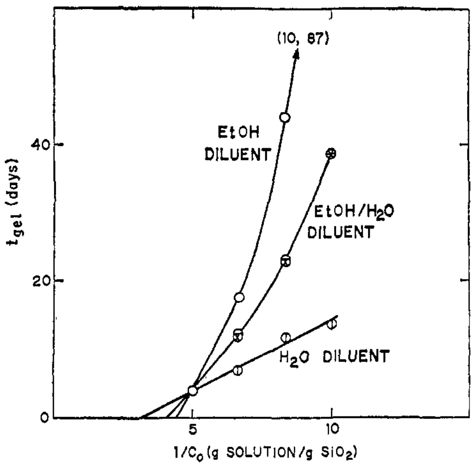


Figure 4. Dependence of gel time on dilution after $(EtO)_4Si$ hydrolysis. Diluents: ○, EtOH; ⦶, H_2O; ⊖, $EtOH/H_2O$ 76.8:232 (w/w); ⊗, EtOH/0.1 *N* HCl 76.8:23.2 (w/w).

H_2O and HCl concentration on polymerization rates, plots of $1/t_{gel}$ *vs.* *Y* and *X* (for both the constant HCl and increasing HCl series of Tables II and III) appear to intercept near 17, which is equivalent to about 2 moles of $H_2O/(EtO)_4Si$ (Figure 3). However, hydrolysates with lower *X* and *Y* values do gel, as discussed further.

Table VII. $\bar{M}_w$ and *B* from Light Scattering in $(EtO)_4Si$ Hydrolysates

Age, days	*X*45 hydrolysate[a] $\bar{M}_w$	B^f	*X*45 hydrolysate[b] $\bar{M}_w$	B^f
0.04	4,490	32.4		
0.25	4,915	8.6		
1.04	8,800	10.1	6,400	
6.04	47,000	1.3	48,600	1.2
9.04			127,200	0.76
13.04	591,000[c]	0.31	846,900[c]	0.16
17.04	6,959,000[d]	0.027	6,781,900[d]	0.027
17.2	∞[e]			
17.6			∞[e]	

[a] Hydrolysis of 100 g of $(EtO)_4Si$; $\Delta T = 33.9°$. [b] Hydrolysis of 600 g of $(EtO)_4Si$; $\Delta T = 36.8°$; pH 1.75 at age 17 days. [c] Dissymmetry measurements indicate these values to be 40–50% less than true $\bar{M}_w$. [d] Dissymmetry measurements indicate $\bar{M}_w$ to be 25–50 × 10^6 and *B*, *ca.* 0.043. [e] Inferred from gelation; no light-scattering measurements. [f] Osmotic slope (10^7 ergs cm^3 g^{-2}).

Many factors influence the rate of gelation (polymerization to $\bar{M}_w = \infty$), such as pH (slow at pH 2, fast at pH 5), fluoride and other ionic catalysis, solvent environment, and nature of the acid catalyst. As an example, *X*22.5 hydrolysates with tetramethylurea instead of ethanol as a diluent gel at about 400 *vs.* about 120 days for EtOH. Several other solvents, such as ketones and ethers, are also powerful stabilizers against gelation. No strong effort has been made to control all factors, but the effects of $EtOH-H_2O$ diluents on the gelation characteristics of a *Y*44 hydrolysate were further studied. Figure 4 shows t_{gel} *vs.* $1/C_0$ for EtOH dilutions. The apparent pH stayed within 1.55–1.80. This curve is compared with those for dilutions with H_2O and with curves for $EtOH/H_2O$ and EtOH/0.1 *N* HCl dilutions, both at 76.8/23.2 by weight. The latter two dilutions yield identical gel times, intermediate to those for H_2O and the EtOH dilutions. If the polymerizations at various dilutions were free of restrictions for the validity for eq 7–10 and effects due to changing environment, these plots would be straight lines intercepting the base line at $1/C_0 < 1$ instead of at 3–4.5. That is, the polysilicic acid should show a finite gel time even when 100% concentrated. Water as a diluent accelerates polymerization, even though it is a product of the condensation. However, other factors must be dominant, such as solvent effects and increased hydrolysis of EtOSi<.

Temperature affects the gel time as indicated in Table VIII.

Polysilicic Acid Concentrated by Extraction. When an *X*22.5 hydrolysate is shaken with 5–10 volumes of benzene (Triclene, chloroform, hexane, cyclohexane, and toluene are also operable), alcohol is extracted by the hydrocarbon and a viscous, colorless, liquid lower phase is obtained that gels within a few minutes or hours, depending on the specific hydrolysis and age prior to extraction. The acceleration in gelling is presumed due to increased concentration. Prior to gelation the concentrated polysilicic acid has wide compatibility with many solvents, such as alcohols, acetone, acetic acid, dioxane, glycol monoethyl ether, and methacrylate and acrylate esters. The viscosity of the concentrate increases with age of the hydrolysate until at advanced age the lower phase is a solid. For an *X*22.5 hydrolysate, the concentrate was found to contain 53% SiO_2 (by ignition) in *ca.* 82:18 EtOH/benzene solvent. Drying one of the viscous lower phases at room temperature yielded hard, glassy chips with densities as high as 1.87 g/cc, comparable to *ca.* 1.9 g/cc for opal containing 12% H_2O.

Polysilicic Acid Concentrated by Drying. When the hydrolysates are dried to equilibrium with room air, the nonvolatile proportion declines with age and increasing *X* or *Y* (Table IX). The behavior on ignition confirms the presence of organic material, such as EtO groups. The hardness increases with *X* and with increasing age. The hardness obtained from *X*45 hydrolysates, which attain high hardness most rapidly, exceeds that of glass. These results are consistent with the concentrations of H_2O, EtOH, and the changing polysilicic acids as polymerization progresses as calculated from the capping experiments (Table X). Thus, there is no apparent need to invoke water of hydration to explain the weights of these polysilicic acids. Since drying will serve to bring the already large molecules close together, it is reasonable that further cross-linking would soon occur and hardness would increase. The hydrolysates made with large $H_2O/(EtO)_4Si$ ratios are left with fewer EtO groups, which would interfere with cross-linking. When hydrolysates are dried during DTA determinations, a large endotherm is observed at 125-135°.

Table VIII. Effect of Temperature on Gelation Time

15% SiO_2 (*X* g of 0.1 *N* HCl/100 g of $(EtO)_4Si$)			
	t_{gel}, hr, at		
X	4.5°	Room temp	60.4°
45	4000	520 (23.1 av)	22
45		420 (25.5 av)	
22.5		3384 (23.9 av)	250
20		4836	
17.3			993
16			3096
20% SiO_2 (*Y* g of 0.1 *N* HCl/100 g of $(EtO)_4Si$)			
Y	4.5°	Room temp	60.4°
44	735	64 (24.7 av)	3.25, 3.75
33	1334	108 (25.9 av)	8.67
25.5			25
25			28
22.5	4572	649 (25.4 av)	49.5
20		1224 (25.1 av)	106
19		1692	161
18		2650	274
17.3		3696	420
16.43		5244	830, 941
15.56			1200
15.13			1692, 1776, 2194
14.75			3783
14.41			4668

Table IX. Properties of Polysilicic Acids Concentrated by Drying

X or *Y*	Age, days	% solids[a]	Ignition	Hardness (Moh)
		20% SiO_2 Input		
12.5	1090	27.73	Flames	<Calcite
		15% SiO_2 Input		
15	85	19.96	Glow, black char	<Calcite
17.5	85	19.75	Glow, black char	<Calcite
20	85	19.15	Glow, black char	= Calcite (3)
22.5	85	18.96	Glow, black char	= Fluorite (4)
45	0.1	18.76	Sl. glow, brown char	= Glass (5.5)
45	3	19.10[b]	Sl. glow, brown char	>Glass
45	16	18.39[c]	V. sl. glow, no char	≫Glass

[a] After 72 hr at 20% RH, 25°. [b] After 72 hr at 23% RH, 25°. [c] After 118 hr at 18% RH, 25°.

Table X. H_2O, EtOH, and Polysilicic Acid Concentration[a]

	Concentration, wt %			
Age, hr	$(EtO)_4Si$	H_2O	Polysilicic acid[b]	EtOH
		X = 17.2		
(0	52.08	8.96	0	38.96)
1	0	(−1.84)	28.03	73.81
24	0	(−0.78)	26.03	74.76
115	0	(−0.09)	25.30	74.81
312	0	(−0.08)	24.08	76.02
		X = 22.5		
(0	52.08	11.72	0	36.20)
1	0	1.39	21.83	76.79
4	0	1.65	21.37	76.98
24	0	1.70	20.66	77.65
144	0	1.74	19.51	78.74
2184	0	2.18	18.18	79.65
		X = 45		
(0	52.08	23.44	0	24.48)
0.5	0	12.50	18.67	68.84
23	0	13.04	18.26	68.71
48	0	13.35	18.33	68.33
480	0	13.67	17.04	69.29

[a] Calculated from eq 4 and Table V. [b] $[Si(OEt)_a(OH)_bO_{0.5(4-a-b)}]_n$.

The calculated data in Table X support the analyses of the capped acids, except that the *X*17.2 hydrolysates should all calculate to 0% H_2O. Thus, we may have disturbed slightly the very early equilibria or have lost some important low-molecular-weight materials. The results at 115 and 312 hr are satisfactorily close to 0. The water concentrations increase slightly after hydrolysis, while the concentrations of the nonvolatile polysilicic acids decline, except the 48-hr hydrolysate. It is most probable that, within experimental error, EtO/Si and EtOH concentrations are constant in the *X*45 series. Determinations of water by Fischer reagent averaged 12.4% for $X = 45$ at 3.5 days *vs.* expected >13%, and for *X*22.5 hydrolyzates, 4% H_2O at 1 hr and 2.27% at 1–96 hr compared with the expected average of 1.6%. Determination of water by glpc averaged 3% for *X*22.5 hydrolysates aged 1–24 hr. The technique may dehydrate $\gg$SiOH. The calculated values of 1.39–2.18% are preferred over these measured values.

Discussion

The thermal behavior during hydrolysis of $(EtO)_4Si$ and early vapor-pressure determinations of $\bar{M}_n$ indi-

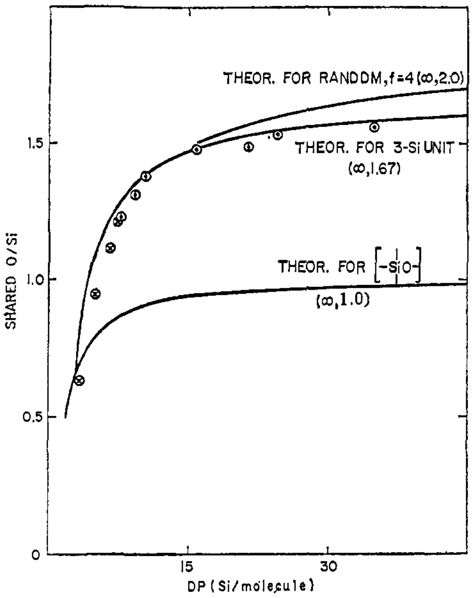
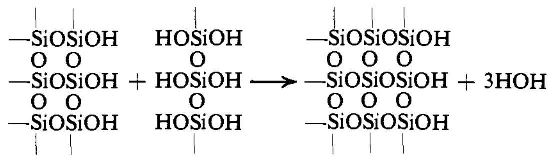


Figure 5. Increase of shared oxygen with degree of polymerization in $(EtO)_4Si$ hydrolysates: ⊗, $X = 17.2$; ⦶, $X = 22.5$; ⊙, $X = 45$ (Tables V and VI).

cate a high rate of hydrolysis compared with the rate of polymerization. Also, a rapid, limited condensation prior to the main polymerization under study and other effects are probably involved. The rapid hydrolysis is confirmed by glpc and nmr spectra. The exact course of all reactions during the highly exothermal stage will require careful study.

The data from the capping experiments appear to define well the average compositions of polysilicic acids being formed, and these calculated compositions conform with the EtO/OH ratio from nmr spectra of the acids as well as expected from integrations of the spectra. Decreasing EtO/Si *vs.* time indicates continuing hydrolysis in hydrolysates poor in water. Little further hydrolysis occurs during polymerization of the *X*45 hydrolysate. Over the whole range, OH/Si declines, and shared O/Si increases. Since the $\overline{DP}_n$ of the compositions also increases with age, condensation polymerization is highly probable. A plot of shared O/Si *vs.* DP is shown in Figure 5 for the hydrolysates of Tables V and VI. Those of ages 2184 hr and 480 hr were not included because their measured $\overline{DP}_n$ values, as shown later, are probably much too low. Their isolation and purification were also different and difficult because of high $\bar{M}_w$. However, since they are at 75–95% of their gelation time, the fact their average O/Si is 1.69 adds weight to arguments that follow. Shown also are theoretical curves for shared O/Si atom for various pertinent polymerizing units. It is seen that the data calculated from the capped polysilicic acids closely fit a three-Si unit, but are not close to a linear polymerization based on $\gg$SiO– units. If we consider a single growing molecule in a random, four-functional condensation polymerization, the upper curve asymptotic to the line for two shared oxygens/silicon is expected.

One could assume that soon after hydrolysis the bulk of the hydrolyzed $(EtO)_4Si$ condenses to a three-Si unit that polymerizes linearly, as exemplified by eq 11



$$\begin{array}{lcl} \text{—SiOSiOH} & \text{HOSiOH} & \text{—SiOSiOSiOH} \\ \text{O O} & \text{O} & \text{O O O} \\ \text{—SiOSiOH} + & \text{HOSiOH} \longrightarrow & \text{—SiOSiOSiOH} + 3\text{HOH} \\ \text{O O} & \text{O} & \text{O O O} \\ \text{—SiOSiOH} & \text{HOSiOH} & \text{—SiOSiOSiOH} \end{array} \qquad (11)$$

wherein the unsatisfied valences are EtO or OH groups. This hypothesis has the virtue that it leaves the total, real functionality of each Si atom at the usual value of 4, but permits polymerization to proceed at an apparent value of $f = 2$. If this situation prevails, a growing polymer with 0.667 EtO group per Si would never gel unless some additional H_2O was available. This degree of hydrolysis (83.33%) is theoretically attainable only when *X* or *Y* $\geqq$ 14.4. A *Y*12.5 hydrolysate has not gelled after 3 years at room temperature (Figure 2).

This hypothesis of three-chain ribbons leads, independent of polymerization mechanism, to a relation between DP and the ratio of shared O atoms to total Si atoms (eq 12). That is, it would not matter for eq 12

$$\text{DP} = 3/[1.6667 - (\text{O/Si})] \qquad (12)$$

whether each $\gg$SiO– unit added singly to the growing ribbon, as triple $\gg$SiO– units as shown in eq 11, or by condensation of larger units. For example, the water evolved (Table X) during polymerization of the *X*45 series conforms better with the condensation of units of DP = 15 than with units of DP = 3. Values of DP calculated from eq 12 using O/Si ratios from Table V are shown in Table XI and may be compared with the experimentally derived values of $\overline{DP}_n$ of Table VI.

Table XI. Degree of Polymerization from O/Si Ratio

$X = 17.2$		$X = 22.5$		$X = 45$	
Age, hr	DP (eq 12)	Age, hr	DP (eq 12)	Age, hr	DP (eq 12)
1	2.9	1	6.9	0.5	12.3
24	4.2	4	8.3	23	22.0
155	5.3	24	10.2	48	30.0
312	6.6	144	16.0	480	...
		2184	237		

The agreement is satisfactory with two notable exceptions. The calculated value of 237 for the 2184-hr hydrolysate is probably closer to reality, as will be seen later, than the questionable cryoscopically derived value of 35.8. The application of eq 12 to the 480-hr hydrolysate is not valid, since the analytically derived O/Si ratio already exceeds 1.667. This may be accounted for in part by shared O in cross-linking, which has been neglected in the discussion above. Another possibility is a four-chain ribbon, for which DP = 4/[1.75 – (O/Si)]. If one accepts the DP's of Table VI as real, including those of the older hydrolysates, the four-chain ribbon gives a better fit over-all than eq 12. The characterization of the capped polysilicic acids should be studied further.

In a plot of $\overline{DP}_n$ *vs.* time (from Tables V and VI), straight lines of different slopes are obtained for X = 22.5 and X = 45 (Figure 6). Since these hydrolysates do gel at *ca.* 110–150 days and *ca.* 17–22 days, respectively, these lines will eventually turn concave upward, and the functionality of the "monomer" involved must

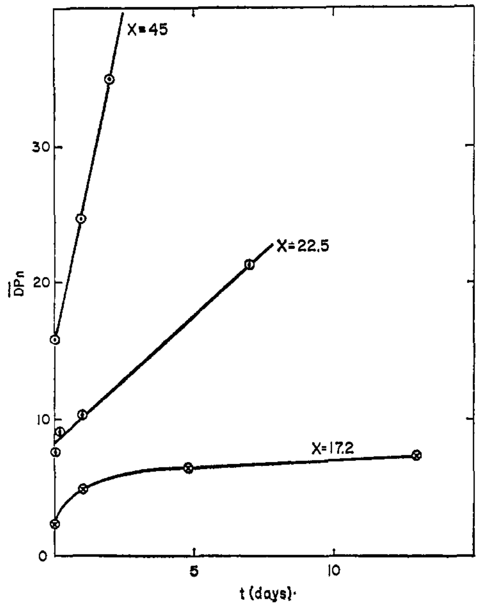


Figure 6. Increase of $\overline{\mathrm{DP}}_n$ with time after $(EtO)_4Si$ hydrolysis: ⊗, X = 17.2; ⦶, X = 22.5; ⊙, X = 45 (Table VI).

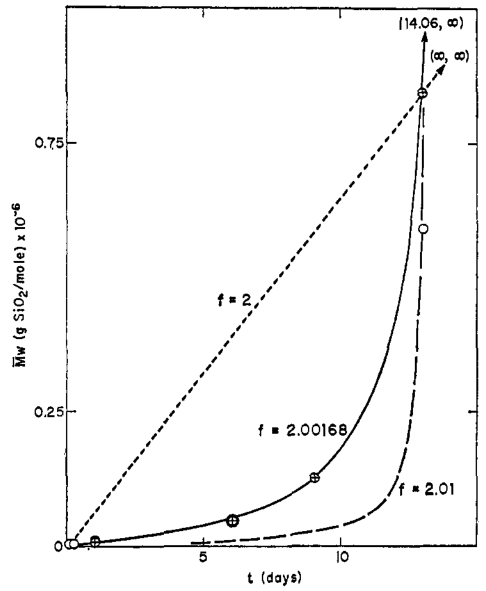


Figure 7. Increase of $\overline{M}_w$ with time after $(EtO)_4Si$ hydrolysis. ○, $\overline{M}_w$ for X = 45, set *a* (Table VII); ⊖, set *b*. Dotted line calculated for f = 2 and k = 1810; solid line calculated for f = 2.00168 and k = 141; dashed line calculated for f = 2.01 and k = 25.1

be >2. It is apparent that $\overline{\mathrm{DP}}_n$ at gelation should exceed the values of 295 and 217 obtained by straight-line extrapolation to the observed gel times. Even from these values we obtain for X = 22.5, $f < 2.0068$ and for the X45 hydrolysates, $f < 2.0093$ (eq 10). The corresponding k's (g of soln/g of SiO_2 × day) are >4 and >18 (eq 9). The fact that these plots do not extrapolate to $\overline{\mathrm{DP}}_n = 1$ at <1 hr supports a hypothesis of a rapid condensation to a multiple $\geqslant$SiO– unit during the exothermal stage. For the case of the X17.2 hydrolysate, the initial part of the curve is concave downward, indicating insufficient functionality for gelling. Another interpretation is that the early steep slope confirms a rapid precondensation and, as hydrolysis slowly increases, the polymerization will proceed to gelation.

Independent confirmation of the almost linear nature of the polymerization in the X45 hydrolysate is available by analysis of $\overline{M}_w$ measurements through eq 7. In Figure 7, we show a plot of experimental points of $\overline{M}_w$ *vs.* time that closely fits the theoretical curve for f = 2.00168 and k = 141, which yields a too short gel time of 14.1 days. The power of eq 7 for fixing the value of f, provided all restrictions on eq 7 are met, is clearly demonstrated by the large deviation of the experimental points from the strictly linear polymerization line and the curve representing f = 2.01. After determination of f and K, t_{gel} and $\overline{M}_n$ values can be calculated using eq 8–10. It should be emphasized that $\overline{M}_w$ results from light scattering are not reliable at low values because of insensitivity nor at high values unless dissymmetry corrections are made. Nevertheless, calculations from Table VII give values of f restricted to the range 2.0005–2.0017, including a calculation involving the actual gel time (17.6 days) and the corrected $\overline{M}_w$ at 17.04 days. Thus the limits deduced from $\overline{M}_n$ measurements ($2 < f < 2.01$) are met. Much more quantitative characterization of the polymerization is possible, but this is not warranted until the effects of the mixed solvents on dr/dC_0 and on light scattering upon dilution and the initial stages are better defined so that the actual polymerizing monomer, its changing environment, and its weight loss in condensation can be properly accommodated.

Gelation in hydrolysates with X and Y < 17.3 (Table VIII) is another strong indication that the condensation, if it is all in single phase, is not proceeding by random four-functional condensation of $Si(OH)_4$. For values of Y less than 17.3 (equivalent to $H_2O/(EtO)_4Si$ 2:1), where there must always be residual EtOSi$\leqslant$ groups, the cross-linking of ribbons composed of rows of $\geqslant$SiO– chains seems more plausible. This kind of hypothesis could also account for the almost linear polymerization and any gelation that might occur in hydrolysates down to X or Y = 8.65 ($H_2O/(EtO)_4Si$ 1:1), equivalent to a minimum possible 50% hydrolysis; this case would require cross-linking of linear single chains of $-O(OEt)_2$-Si– on which there is an occasional replacement of EtO by OH. Significantly, the data of Table VIII permit estimating the value of $H_2O/(EtO)_4Si$ below which the hydrolysates will not gel. For hydrolysates aging at room temperature and 60.4°, plots of $(1/t_{gel})^p$ *vs.* X or Y yield straight lines whose intercepts (by extrapolation) are at X_0 or Y_0 = 12.5–15. From the limited data (Table VIII), it appears that p = *ca.* 0.6 gives the best straight lines for the X series and p = *ca.* 0.4 for the Y hydrolysates. The two cases with the most data, Y at room temperature and Y at 60.4°, yield intercepts at *ca.* 13 when p = 0.5. The latter case, the only one for which temperature control was adequate, is shown in Figure 8. Data above Y = 25, which are not plotted, also fit the straight line extremely well. Although the data below Y = 16 become less dependable because of great dependence on very small deviations in $H_2O/(EtO)Si$ ratio, a divergence from an intercept of Y_0 = 14.4 toward an intercept of Y_0 = 13 is apparent. The data indicate that polymers above Y = 16 are entering a ribbon with a maximum of three chains, since the inter-

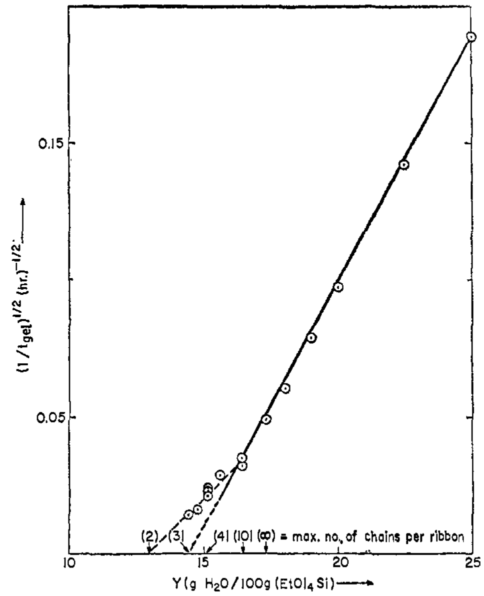


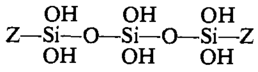
Figure 8. Estimation of number of chains per siloxane ribbon: ⊙, $(1/t_{gel})^{1/2}$ for Y hydrolysates at 60.4°.

cept for these is at Y_0 = 14.4. In general

$$(1/t_{gel})^p = D(Y - Y_0) \tag{13}$$

where D is a constant and Y_0 is the hydrolysate yielding infinite linear ribbons. This corresponds to the hypothesis of a three-chain ribbon when Y_0 = 14.4 and with a two-chain ribbon when Y_0 = 13.

The polymerization under consideration may not necessarily require any further assumptions to explain why ribbons in hydrolysates of high X or Y values, which must necessarily have a high concentration of peripheral OH groups, do not cross-link in solution more than they do. Preliminary study of molecular models shows that there are two or possibly three orientations that could be assumed by a condensing "monomer"



$$\mathrm{Z{-}\underset{OH}{\overset{OH}{Si}}{-}O{-}\underset{OH}{\overset{OH}{Si}}{-}O{-}\underset{OH}{\overset{OH}{Si}}{-}Z}$$

which is designated as Δ. For example, Δ could condense so that the terminal groups (Z = EtO or OH) are oriented toward the same side of the ribbon as the previously added ones or toward the opposite side. Assume that three consecutive peripheral OH groups must have the same orientation before they can be active in cross-linking (by the same mechanism that Δ adds to the growing chain) and that some of the peripheral groups are EtO. The statistics of this situation lead to values of excess functionality (>2) per Si atom that are within an order of magnitude of those obtained experimentally. They were estimated by Monte Carlo methods. For example, if 100% hydrolysis was attained and Δ added with two orientation choices of equal probability, the excess f per Δ is 0.29, equivalent to an apparent value of f = 2.097 per Si atom. For 95.83% hydrolysis, close to that for the X = 45 hydrolysate, which had a substantially constant degree of hydrolysis (96.2%) during polymerization, an estimate of f = 2.043 per Si atom is obtained. For a Δ representing 91.67% hydrolysis (one-half of the peripheral groups are EtO), we estimate f = 2.016 per Si atom and for 83.3% hydrolysis, no excess over 2. To account for the experimental values, especially f = 2.0005 to 2.0017 as estimated from light-scattering data, more orientation choices or random isolation of peripheral OH groups between neighboring cross-links could be assumed. However, it is preferred at this time to assume that there are forces favoring the addition of each Δ in an orientation opposite the previous one. If there were forces directing each adding Δ to the same orientation as the previous one, one might expect large cyclic structures of the postulated ribbons. The mechanics of a molecular model indicate that a ribbon of at least 13 similarly oriented Δ units would be required to permit a cyclic structure of low strain.

Further data will be required to determine more precisely the polymerization and cross-linking mechanisms in polysilicic acid solutions and whether the same mechanisms prevail during drying, accelerated by concentration changes and viscosity, or whether a mechanism involving single OH groups becomes prevalent.

Acknowledgments. We wish to thank our many colleagues who assisted with this work, especially Dr. D. D. Bly for the light-scattering data and helpful discussions and Dr. R. L. Postles for assistance with probability estimations.