446. *The Polymerization of Silicic Acid.*

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Light-scattering, ultracentrifugation, and viscosity measurements have been made, over a wide range of degrees of polymerization, on a polymerizing solution of silicic acid. Molecular weights calculated from light scattering and the Archibald method of ultracentrifugation were in good agreement. Sedimentation-coefficient distributions indicated a broad and continuous distribution of molecular sizes, even at low degrees of polymerization, and a rapidly increasing degree of polydispersity with increase in average molecular weight. Weight-average molecular weights in reasonable agreement with the light-scattering values were obtained, by assuming spherical silica particles, from the sedimentation distribution curves. The kinetics of the polymerization have been interpreted on the basis of a bifunctional monomer unit and a random condensation between all polymeric species.

Early work on the gelation times of silicic acid prepared by neutralization of sodium silicate established that the reaction is reversible [1,2] and catalysed by acids, fluoride, or hydroxyl ions. More recent work [3,4] has been concentrated on the kinetics of the polymerization but no quantitative data covering a wide range of degrees of polymerization are available as a source of information on the mechanism of the reaction. This lack of data is not surprising on consideration of the experimental difficulties attached to the measurement of molecular weights on a continuously polymerizing system. Thus, the only two methods likely to be applicable, namely, light scattering and sedimentation, suffer from the disadvantage that measurements must be made over a range of concentrations and the results extrapolated to zero concentration. This is of no consequence in the study of a stable system, but the number of polysilicic acid concentrations which can be studied is limited by the need to make the measurements during a time interval such that the increase in molecular weight between observations at different concentrations is less than the standard deviation of the separate measurements.

Although the light-scattering technique is well established for the measurement of weight-average molecular weights M_w, the extension of the Archibald method of ultracentrifugation [5] to the rapid measurement of M_w is of comparatively recent origin.[6]

It was thus decided to make measurements of M_w on a sample of polymerizing silicic acid by both the Archibald and the light-scattering method and to compare these results with each other and with the values of M_w calculated from sedimentation coefficient distribution curves obtained by the method of Baldwin *et al.*[7]

Experimental

Preparation of Silicic Acid.—Sodium metasilicate was twice recrystallized from 5% sodium hydroxide solution, to give a product of composition $(Na_2O)_{1\cdot06}(SiO_2)_{1\cdot00},12\cdot3H_2O$. A sample of this material was checked for purity by passing a M-solution through a cation-exchange column in the hydrogen form and establishing that the effluent was free from strong acids and that the residue from evaporation of the solution was completely volatile in hydrofluoric acid.

Finely powdered sodium metasilicate was added to a cold, stirred slurry of cation-exchange resin in the hydrogen form (Zeo-Karb 225; 100—200 mesh; 2% cross-linking) in just sufficient dilute hydrochloric acid at pH 1·3 to produce a fluid suspension. The addition was stopped

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[1] Hurd, *Chem. Rev.*, 1939, **22**, 403.
[2] Hurd, Smith, Witzel, and Glam, *J. Phys. Chem.*, 1933, **57**, 678.
[3] Greenberg and Sinclair, *J. Phys. Chem.*, 1955, **59**, 435.
[4] Bechtold, *J. Phys. Chem.*, 1955, **59**, 532.
[5] Archibald, *J. Phys. Colloid Chem.*, 1947, **51**, 1204.
[6] Ginsberg, Appel, and Schachman, *Arch. Biochem. Biophys.*, 1956, **65**, 545.
[7] Williams, Baldwin, Saunders, and Squire, *J. Amer. Chem. Soc.*, 1952, **74**, 1542.

when the pH had increased to 2·8, by which time the temperature had risen from 0° to 4°. The resulting solution was filtered and passed through a column of cation-exchange resin in the hydrogen form to remove sodium ions, and then partly de-ionized by addition of De-Acidite FF (OH^- form) until the pH had increased to 2·10. This solution was then stirred with ashless filter floc and filtered, first through a Whatman 542 paper and then through an " Oxoid " membrane filter (pore size 0·5—1·0 micron) to remove possible traces of dust, colloidal silica, and finely divided resin. The filtrate, which contained 21·90 g. of silica per l. of solution, was stored in a Polythene bottle at 24·5°.

Light Scattering.—Light-scattering measurements were made with a Brice–Phœnix model 100 photometer with green light (5461 Å). The calibration of the opal reference standard supplied with the instrument had been previously checked by using pure toluene and a standard sample of polystyrene. A cylindrical light-scattering cell with flat entrance and exit windows was used throughout but, because of the relatively small dissymmetry of the solution, measurements were made only at 45°, 90°, and 135° and the molecular weights evaluated by the dissymmetry method. Measurements of the depolarization factor, Pu, at the beginning and end of the polymerization indicated that the corrections involved were about 2—3% of the observed molecular weight but, because the time available for each set of measurements was of necessity limited, no corrections for depolarization were in fact made.

Refractive-index increments were measured by a Hilger Rayleigh-type interferometer.

The " Oxoid " membrane filters used to clarify the solutions and solvent were found to be superior to ultrafine $\frac{5}{3}$-grade sintered-glass filters or to high-speed centrifugation. Refractive-index measurements before and after filtration showed that after a polymerization time of 18 days some silica was removed from the solution by this procedure and subsequent measurements were made on unfiltered solutions. However, turbidity measurements on the initial solution, before and after filtration, indicated that the light scattered by dust particles present in the aged solution was negligible in relation to that scattered by polysilicic acid.

Sedimentation.—A " Spinco " model E analytical ultracentrifuge equipped with automatic temperature control and low-speed attachment was used. The diaphragm of the Schlieren optics was replaced by the standard phase plate supplied by the manufacturers and green monochromatic light (5461 Å) was used. A 12-mm. synthetic boundary cell with a rubber valve as supplied with the instrument was used for all the runs. The rotor temperature was maintained at 20° and the speed was increased at the maximum permitted rate (limited by a drive current of 14 amp.), the time of commencement of sedimentation being taken as that at which the rotor reached 70% of its operating speed. The pictures obtained were projected on to graph paper by means of a photographic enlarger and ×40 drawings were made of the refractive-index gradient curves. The areas under the curves were measured with a mechanical planimeter.

Viscosity.—An Ostwald viscometer with a flow time for water of 287·0 sec. was used for the viscosity measurements. The temperature was 30° ± 0·005° and the kinetic energy correction, evaluated from the flow times of sucrose solutions of known viscosity, was found to be negligible.

SYMBOLS

A	Area between meniscus, boundary curve, and base line on the Schlieren picture.
A_s	Area between synthetic boundary curve and base line.
B	Interaction constant.
D	Diffusion coefficient.
M	Molecular weight of a single species.
M_0	Molecular weight of monomeric silica.
M_w	Weight-average molecular weight.
$\mathbf{N}$	Avogadro's number.
$P_{(90)}$	Dissymmetry correction factor.
$\mathbf{R}$	Gas constant.
T	Absolute temperature.
c	Concentration, units as specified in text.
c_0	Concentration of original solution in equation (8).
f	Frictional coefficient.
$g(s)$	Distribution function for the sedimentation coefficient of a sample.

k	Bimolecular rate constant.
n	Refractive index of solution.
n_0	Refractive index of solvent.
r	Radius of sphere.
s	Sedimentation coefficient.
$\bar{s}$	Mean sedimentation coefficient.
t	Time.
$\bar{v}$	Partial specific volume of solute.
x	Radius of rotation of a given point in the solution.
$\bar{x}$	Square root of second moment of the distribution curve.
x_m	Radius of rotation of the meniscus.
x_p	Radius of rotation of some point in the " plateau " region where $dc/dx = 0$.
y	Distance from base line to intersection of boundary curve and meniscus.
α	Exponent in equation (3).
η	Viscosity of the solution.
η_0	Viscosity of solvent.
$[\eta]$	Limiting viscosity number of the solute.
η_{sp}	Specific viscosity of the solute.
λ_0	Wavelength of light in equation (2).
ρ	Density of the solution.
τ	Turbidity.
ϕ	Volume fraction of solute.
ω	Angular velocity of rotor.

DISCUSSION

Light Scattering.—Zimm [8] showed that, to a good approximation, the excess turbidity of a solution over the solvent is related to the weight-average molecular weight of the solute by

$$HcP_{(90)}/\tau = 2BP_{(90)}c + 1/M_w, \qquad (1)$$

where

$$H = 32\pi^3 n_0^2 (dn/dc)^2 / 3N\lambda_0^4, \qquad (2)$$

and c is the concentration in g./ml.

The specific refractive-index increment (dn/dc) is assumed to be constant for a homologous series of polymers. Fig. 1 shows that dn/dc does vary during the early stages of the polymerization but approaches a constant value of 0·65: this value was used to calculate H in equation (2) for polymerization times greater than six days although for shorter times the values shown in Fig. 1 were used. The dissymmetry correction factor $P_{(90)}$ was obtained from the measured scattering dissymmetry with the aid of Table VI of ref. 9. The silica particles were assumed to be spherical although the correction factor is almost independent of particle shape for all points except that for a polymerization time of 23 days. Plots of $HcP_{(90)}/\tau$ against c are shown in Figs. 2 and 3, and the values of M_w obtained from the reciprocals of the intercepts on the $HcP_{(90)}/\tau$ axis are shown in Fig. 4 as a function of time.

Viscosity.—The limiting viscosity numbers of the solution were obtained by linear extrapolation of plots of η_{sp}/c (where c is the silica concentration in g./100 ml.) in the usual manner. The results for various degrees of polymerization are shown in Fig. 5. Fig. 6 shows the increase of limiting viscosity number with time and Fig. 7 is a plot of log $[\eta]$ against log M_w obtained by light scattering.

In general, when the logarithms of the limiting viscosity numbers of a series of fractionated polymer homologues are plotted against the logarithms of their molecular weights, linear relations are usually obtained of the form

$$[\eta] = KM^{\alpha}, \qquad (3)$$

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[8] Zimm, *J. Chem. Phys.*, 1948, **16**, 1093.

[9] Doty and Steiner, *J. Chem. Phys.*, 1950, **18**, 1211.

where K and α are constants, with α lying between 0·5 and 0·8 for linear non-electrolytes. The equation of the line drawn through the lower-molecular-weight points of Fig. 7 is

$$[\eta] = 1{\cdot}79 \times 10^{-3} M_{\mathrm{w}}^{0{\cdot}290}, \tag{4}$$

and the value of α is thus substantially less than that expected for a linear polymer. It is true that this value of α is obtained from weight-average molecular weights of polydisperse samples instead of from a narrow fraction, but M_{w} is often close to M_{v}, the viscosity-average molecular weight[10] which should be used in equation (3) for polydisperse solutes.

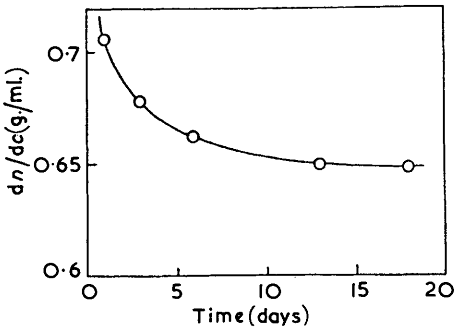

FIG. 1. Variation of specific refractive-index increment with time.

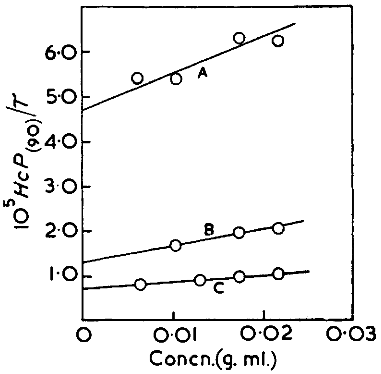

FIG. 2. Plot of $HcP_{(90)}/\tau$ against concentration for polymerization times of (A) 3, (B) 6, and (C) 8 days.

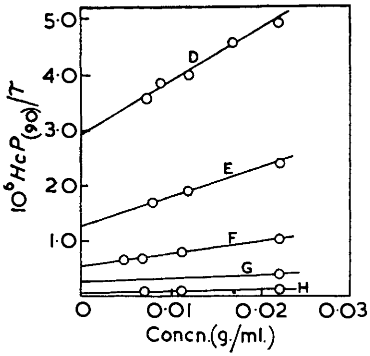

FIG. 3. As Fig. 2 for times of (D) 10, (E) 12·3, (F) 13, (G) 18, and (H) 23 days.

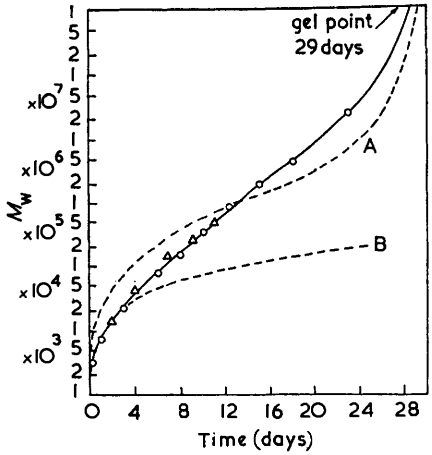

FIG. 4. Plot of molecular weight against time of polymerization.

○ Light-scattering values. △ Ultracentrifuge values. Broken curves: A, Calc. for $f = 2{\cdot}0001$, $k = 472$; *B*, Calc. for $f = 2{\cdot}000$, $k = 85{\cdot}5$.

Cheng and Schachman[11] have shown that Einstein's viscosity equation (5), derived for dilute suspensions of spherical particles, is applicable at least down to particle sizes

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[10] Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, New York, 1953.

[11] Cheng and Schachman, *J. Polymer Sci.*, 1955, **16**, 19.

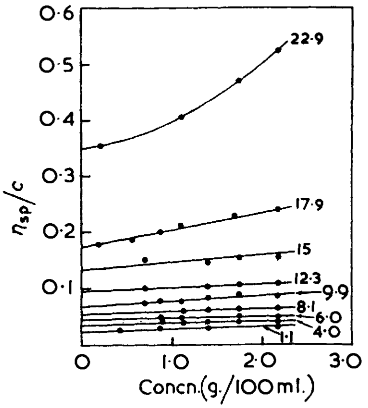

FIG. 5. Variations of specific viscosity with concentration. (Numerals on the lines refer to days. *c* are in g./100 ml.)

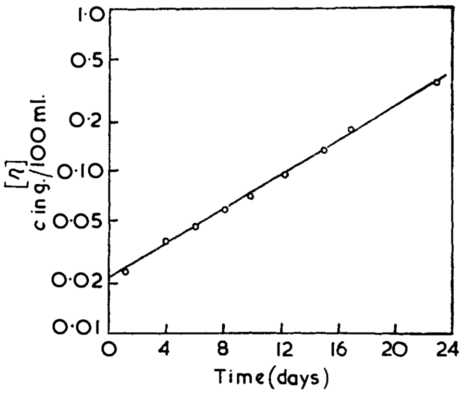

FIG. 6. Variation of limiting viscosity number with time.

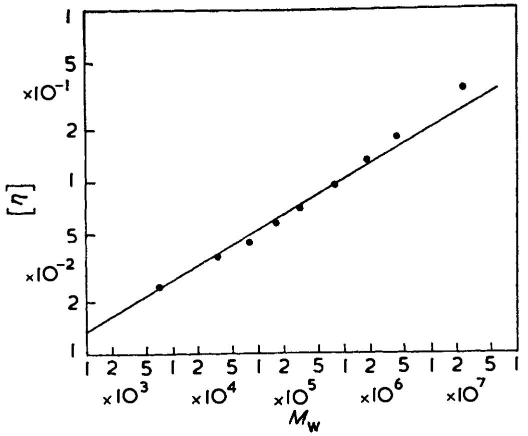

FIG. 7. Variation of limiting viscosity number with weight-average molecular weight.

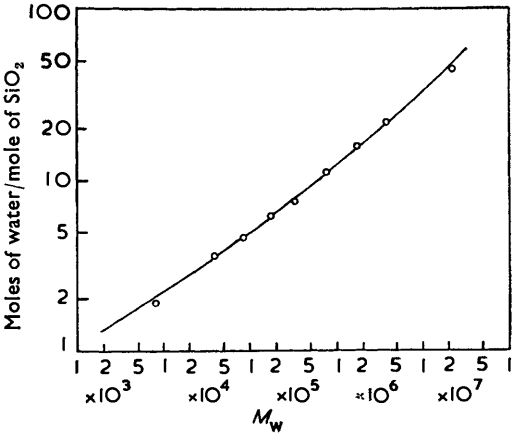

FIG. 8. Variation of hydration of silica polymers with weight-average molecular weight of the polymer.

of 0·2 micron. Thus, if the silica particles are spherical with a constant degree of hydration, then according to equation (5) the limiting viscosity number should be independent of molecular weight:

$$\eta_{sp} = \tfrac{5}{2}\phi. \qquad (5)$$

However, at the gel point of the solution, ϕ is equal to unity and it appears probable that, for intermediate stages of the polymerization, the hydrodynamically effective volume fractions of the silica must increase with molecular weight. The slow increase in limiting viscosity number of silica solutions with molecular weight, compared with that observed for extended-chain polymers and also predicted by Flory's theory,[10] is thus interpreted as being due to an increase in hydration of the effectively spherical particles. The term " hydration " in the present context refers to the total water associated with the molecule, both chemically bound and physically trapped; this hydration, calculated from the limiting viscosity numbers on the assumption that Einstein's equation is valid, is shown as a function of molecular weight in Fig. 8. A further assumption made is that the volume occupied by the " bound " water [*i.e.*, in $Si(OH)_4$] is the same as the equivalent weight of water in the free state. As the chemically bound water represents only a small proportion of the total over the range of molecular weights for which equation (5) is valid, the error involved is negligible.

Ultracentrifugation.—The Archibald method. Weight-average molecular weights were also calculated from the approach to sedimentation—diffusion equilibrium according to Archibald's method.[5] Rotational speeds varied from 25,980 r.p.m. for $M_w = 13{,}000$ down to 5100 r.p.m. at a molecular weight of 500,000 which represented an upper limit set by hunting of the rotor at lower rotational speeds.

The Archibald method was applied according to Ehrenberg's procedure [12] in which the ratio of sedimentation coefficient to diffusion coefficient obtained directly from equation

$$s/D = y/[w^2 x_m k_2 (A_s - A)], \qquad (6)$$

(where k_2 is the inverse of photographic enlargement) is used in Svedberg's equation

$$M = \frac{s}{D}\,\frac{RT}{(1 - \bar{v}\rho)}. \qquad (7)$$

The Svedberg equation is strictly applicable only to ideal uncharged solutes, but it will hold approximately for charged polymers for which the ratio of charge to molecular weight is low if a supporting electrolyte is added to depress the potential gradient created by the sedimenting polymer. Similar considerations apply to the light-scattering and viscosity equations. Although in the present work the concentration of supporting electrolyte (0·01M-hydrochloric acid) is not high, it should serve to depress the ionization of the extremely weak silicic acid and, on the assumption that no chloride-complexing occurs, equation (7) and the corresponding light-scattering equation should be applicable.

This is confirmed to some extent by the fact that the specific viscosity at the three highest concentrations shown in Fig. 5 for the 17·9-day solution were identical both in 0·01M-sodium chloride–0·01M-hydrochloric acid and in the dilute acid alone.

For a polydisperse system it can be shown [6] that equations (6) and (7) give M_w for the solute at the meniscus; this will decrease with time of centrifugation since the large molecules will be preferentially concentrated toward the bottom of the cell, and to obtain the weight-average molecular weight before redistribution of the solute occurs it is necessary to extrapolate M_w at the meniscus to zero time of sedimentation. Moreover, the concentration dependence of s is in general greater than that of D for non-ideal systems and the value of s/D will increase with dilution; thus, a further extrapolation to zero concentration is sometimes necessary. Both these extrapolations were found to be best performed logarithmically. The results are shown in Fig. 9; the plots -■-, -●-, -○- are

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[12] Ehrenberg, *Acta Chem. Scand.*, 1957, 1257.

extrapolations of the apparent molecular weights at the meniscus to zero time and the plots –▽– are extrapolations of the intercepts of the former plots to zero concentration. The latter procedure is somewhat doubtful because of the limited range and number of concentrations available.

The apparent specific volume of the polysilicic acid (after 8 days' polymerization) measured from solution-density data in the usual way was found to be independent of concentration up to 2·19% of silica, the mean value for $\bar{v}$ being 0·38 ml.

The values of M_w obtained from the extrapolations of Fig. 9 are shown, together with the light-scattering values, in Fig. 4 as a function of polymerization time. The agreement between the two methods is considered satisfactory in view of the limitation imposed by the few concentrations available.

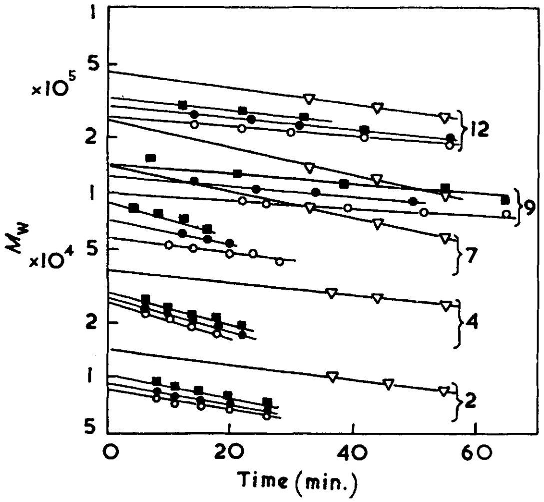

FIG. 9 Effect of variation of concentration and time on apparent M_w for various stages of polymerization. (Numerals on the lines refer to days.)

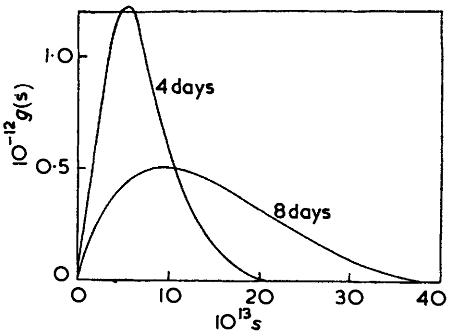

FIG. 10. Weight-distribution curve of sedimentation coefficients.

Molecular-weight Distributions.—Signer and Gross[13] showed that if the spreading of the boundary between solution and solvent is due entirely to the variation of sedimentation coefficients of the components, then the experimental refractive-index gradient curves can be transformed into sedimentation distribution curves and a function $g(s)$ plotted such that the weight fraction of solute with sedimentation coefficient between s and $s + ds$ found directly as $g(s)\,ds$. The equation took the form

$$g(s) = \frac{1}{c_0} \cdot \frac{dc_0}{ds} = \frac{1}{c_0} \cdot \frac{dc}{dx} \cdot \left(\frac{x}{x_m}\right)^2 \cdot x\omega^2 t. \tag{8}$$

In practice dn/dx (in arbitrary units) is substituted for dc/dx, and c_0 is taken as equal to the area between the base line and the boundary curve when the same ordinate units are used. Williams *et al.*[7] suggested that when additional boundary spreading is caused by diffusion such curves should be considered as apparent distribution curves $g^*(s)$, and they showed that whereas the boundary spreading due to polydispersity is proportional to time, t, the contribution due to diffusion is proportional to $t^{\frac{1}{2}}$ and thus becomes vanishingly small compared with the effect of polydispersity at infinite time. The apparent distribution curves are therefore extrapolated to infinite time, and the resulting curves for a given

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[13] Signer and Gross, *Helv. Chim. Acta,* **1934, 17,** 726.

concentration are extrapolated to zero concentration, to eliminate the self-sharpening effect of the boundaries due to the concentration dependence of the sedimentation coefficient. The apparent distributions $g^*(s)$ are then grouped about a mean sedimentation coefficient $\bar{s}$ given by

$$\bar{s} = [\mathrm{d}\,(\log_e \bar{x})/\mathrm{d}t]/\omega^2, \tag{9}$$

where $\bar{x}$ is the square root of the second moment of the distribution curve,

$$\bar{x}^2 = \frac{\int_{x_\mathrm{m}}^{x_\mathrm{p}} x^2 \cdot \frac{\partial c}{\partial x} \cdot \mathrm{d}x}{\int_{x_\mathrm{m}}^{x_\mathrm{p}} \frac{\partial c}{\partial x} \cdot \mathrm{d}x}. \tag{10}$$

The distance in the boundary from a point x to $\bar{x}$ is then related to a difference in sedimentation coefficients by the relation,

$$s - \bar{s} = \frac{2(x - \bar{x})}{\omega^2 t\,(x + \bar{x})}. \tag{11}$$

This procedure was followed for the polysilicic acid solution for polymerization times of 4 and 8 days. As with the Archibald results, the limited number and range of concentrations made the extrapolation to zero concentration uncertain. However, the immediate qualitative conclusion which can be drawn from these curves (Fig. 10) is that the observed increase in the value of M_w between 4 and 8 days (Fig. 4) arises from a general broadening of the molecular-weight distribution curve rather than a displacement of the curve to a region of higher molecular weight.

A quantitative relationship between s and M is needed to convert these sedimentation distributions into molecular-weight distributions. This can often be found experimentally if a series of stable polymer fractions of known molecular weight is available; this is not feasible at present for silicic acid and a theoretical approach becomes necessary.

If the particles are assumed to be spherical and large enough for both Stokes's and Einstein's equations to be valid, then by Stokes's law the frictional coefficient of a molecule is proportional to its radius (12),

$$f = 6\pi\eta_0 r. \tag{12}$$

From Einstein's equation the specific viscosity of a solute is (for spherical particles) equal to $\frac{5}{2}$ times its volume fraction as c approaches zero (13)

$$\phi = \tfrac{2}{5}\eta_\mathrm{sp} = \tfrac{2}{5}[\eta]c = \tfrac{4}{3}\pi r^3 \boldsymbol{N} \cdot \frac{c}{100M}, \tag{13}$$

where $\frac{4}{3}\pi r^3\boldsymbol{N}$ is the volume of one mole of solute and c is the concentration in g./100 ml.

The Svedberg equation (7) may be written in the form

$$M = sf\boldsymbol{N}/(1 - v\rho), \tag{14}$$

and elimination of c, f, and r from equations (12), (13), and (14) yields finally

$$\frac{s\eta_0[\eta]^{\frac{1}{3}}\boldsymbol{N}}{M^{\frac{2}{3}}(1 - \bar{v}\rho)} = \frac{\boldsymbol{N}^{\frac{1}{3}}}{6}\pi^{-\frac{2}{3}}30^{-\frac{1}{3}}. \tag{15}$$

It has also been shown that for the lower degrees of polymerization of silicic acid

$$[\eta] = 1{\cdot}79 \times 10^{-3} M_\mathrm{w}{}^{0{\cdot}290}. \tag{4}$$

Hence, substituting for $[\eta]$ in equation (15) and equating logarithmically, we obtain

$$\log_{10} M = 1{\cdot}754 \log_{10} s + 25{\cdot}868. \qquad (16)$$

The molecular-weight distribution curves obtained from the sedimentation coefficient distributions when using equation (16) are shown in Fig. 11. Weight-average molecular weights of $5{\cdot}49 \times 10^4$ and $1{\cdot}84 \times 10^5$ are obtained from the appropriate summations of the distribution curves, compared with values of $4{\cdot}0 \times 10^4$ and $1{\cdot}8 \times 10^5$ obtained from Fig. 4; the excellent agreement in the latter instance is, no doubt, fortuitous in view of the difficult extrapolations involved.

The treatment has been extended by Sheraga and Mandelkern [14] who used the Perrin [15] and Simha [16] equations to calculate the frictional coefficient and viscosity increment of ellipsoids as a function of axial ratio. These calculations also indicated that s should be proportional to $M^{\frac{2}{3}}$ and inversely proportional to $[\eta]^{\frac{1}{3}}$ at constant $\eta\bar{v}$ and ρ with the proportionality constants varying only slowly with axial ratio and approaching the value given in equation (15) as the axial ratio approaches unity. This lends confidence in the reliability of the curves in Fig. 11 although is a disadvantage in that the agreement between M_w calculated from the curve and that obtained by light scattering does not necessarily prove that the silicic acid particles are in fact spherical.

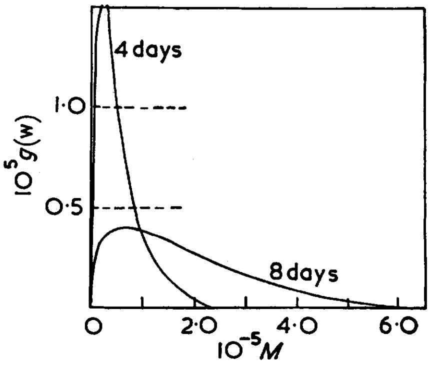

FIG. 11. Molecular-weight distribution curves for silicic acid.

Kinetics and Mechanism of Polymerization.—The kinetics of condensation polymerization have been studied theoretically by Flory [17,18] and more recently by Stockmayer [19] who used a different mathematical method but reached the same general conclusions. Both workers made the following assumptions: (1) Ring closure resulting from intramolecular reaction is negligible. (2) At any stage during the polymerizations all the functional groups that have not yet reacted are regarded as equally reactive, irrespective of the size of the molecule to which they are attached or the fate of the other functional groups on the same molecule. For example, it has been demonstrated experimentally that these assumptions are valid for polyesterifications in which the functional groups of a monomer unit are similar and sufficiently far apart.[20]

Bechtold [21] combined Stockmayer's statistical and kinetic derivation of the formulæ in order to eliminate α, the fraction of functional groups which have reacted, and expressed

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[14] Scheraga and Mandelkern, *J. Amer. Chem. Soc.*, 1953, **75**, 179.
[15] Perrin, *J. Phys. Radium*, 1936, **7**, 1.
[16] Sinha, *J. Phys. Chem.*, 1940, **44**, 25.
[17] Flory, *J. Amer. Chem. Soc.*, 1941, **63**, 3083, 3091, 3096.
[18] Flory, *J. Phys. Chem.*, 1942, **46**, 132.
[19] Stockmayer, *J. Chem. Phys.*, 1943, **11**, 45.
[20] Flory, *J. Amer. Chem. Soc.*, 1939, **61**, 3334.
[21] Bechtold, *J. Polymer Sci.*, 1949, **4**, 219.

the rate of change of M_w with time in terms of the functionality f and an ideal bimolecular rate constant k to give

$$\frac{M_w}{M_0} = \frac{1 + 2fckt}{1 + (2f - f^2)ckt}, \qquad (17)$$

where c is the silica concentration in moles (monomeric SiO_2) per litre. According to equation (17), for low degrees of polymerization with $(2f - f^2)ckt$ small compared with unity, M_w should be a linear function of t. However, at longer times, $(2f - f^2)ckt$ becomes increasingly negative for $f > 2$ and the polymerization increases more rapidly than predicted on a linear basis and is asymptotic to infinity at the gel point.

Although the general shape of the experimental curve conforms with this prediction, it was found impossible to fit it to equation (17) for any integral value of f. Thus, one or both of the assumptions made in the derivation of equation (17) is not valid for silicic acid. For polyesterifications, only about 5% of the reaction up to the gel point appears to be intramolecular[17] and no large errors would be expected if the first assumption were invalid. Conversely, polyesterifications involving glycerol in which the secondary hydroxyl group is known to be less reactive than the two primary hydroxyls would not be expected to follow the kinetics predicted by equation (17) and silicic acid appears to be a somewhat analogous example, the third and fourth hydroxyl groups being much less reactive than the first two. The fit of the experimental curve to that predicted for $f = 2$ during the early stages of the polymerization is in keeping with this hypothesis although the actual functionality must be greater than two to account for the eventual gelation. The best fit over the whole range of polymerization up to the gel point can be made by putting $f = 2{\cdot}0001$, whereas attempts to fit the experimental data for any two points by putting $f = 3$ or 4 results in gross deviations from the theoretical curve over the whole of the remaining range of molecular weights.

Further information on the mechanism is provided by the shapes of the molecular-weight distribution curves. It has been shown by Flory[22] that polymerization by monomer addition, for example, polymerization of ethylene oxide, is unique in that a very narrow distribution of molecular sizes occurs and that the relative breadth decreases as the average degree of polymerization increases. This is in sharp contrast to the observed behaviour, and mechanisms involving only addition of monosilicic acid or a silicate ion to a polymer molecule can be rejected. It seems reasonable to assume, therefore, that the broad distribution of molecular sizes, indicated by the molecular-weight distribution curves, arises from a random condensation with each other of all the polymeric species. The kinetics indicate that the monomer is apparently bifunctional during the early stages of the polymerization although the real functionality will be greater than two since the third and subsequent hydroxyl groups are much less reactive than the first two. However, the viscosity results are inconsistent with the idea that the polysilicic acid molecule exists in solution as an extended chain and it appears either that the chain is sufficiently contracted, or that the small amount of branching which occurs is enough, for the polysilicic acid molecule to be treated as spherical.

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[22] Flory, *J. Amer. Chem. Soc.*, 1940, **62**, 1561.