A Study of the Growth of Particles in Silica Sol and Hydrogel as a Factor Determining the Final Structure of Silica Gel

By Hiroshi OTOUMA and Hiroshi UKIHASHI

(Received February 2, 1965)

Many investigations have been made of the polymerization of silicic acid. However, few studies have been undertaken of the systems with relatively high concentrations and of the changes in the turbidity of the silicic acid sol in relation to the growth of the ultimate particles comprising the sol after its gelation.

The purpose of the present work is to gain new information, by the light scattering method, about the growth of particles at a relatively high concentration of silicic acid before and after the gelation of its sol, which is prepared by adding sodium silicate solutions to sulfuric acid; we also eventually hope to find some relationship with the final structure of dried silica gel.

In the sol state the changes in particle size with time was indirectly determined by the weight-average molecular weights obtained by the dilution method. After gelation, the dissymmetry, which is especially related to the size of the large particles, and the turbidity were measured at frequent intervals in pursuit of the growth of primary particles and the state of their aggregation. The surface area of dried gel was measured in seeking its relationship with the size of the primary particles as determined by light scattering. The light scattering behavior of the sol and hydrogel will be consistently discussed in connection with the growth of the primary and secondary produced particles by aggregation.

Experimental

The Preparation of the Silica Sol and the Gel.—Samples with various pH values were prepared by controlling the addition of sodium silicate solutions ($SiO_2 : Na_2O = 3.22$) to sulfuric acid. The concentrations and other experimental conditions are listed in Table I. The sodium silicate solutions, sulfuric acid and sols prepared were purified by the use of glass filters (No. 4 and No. 5) and a solvent filtration apparatus. The sols which were used for determination of the particle size were filtered with great care. The turbidity of the distilled water used in the dilution was below 5×10^{-5} cm^{-1}. Silica hydrosol changed into hydrogel after a definite time. Both the sols and the hydrogels were always kept at 30°C in a thermostat except when measurements were being made.

Light Scattering Measurement and Equipment.—Light scattering measurements were made on a Shimadzu Photoelectric Light-Scattering Photometer Model-21 type, with a green light (546 mμ). The turbidity was evaluated against the incident beam from the scattering intensity at a direction of 90 degrees. The calibration of the turbidity was made by using a glass block. In the sol state small portions of samples, immediately after being taken up at definite intervals after their formation, were diluted to a concentration of 10^{-3} g./ml. in distilled water maintained at 30°C, then they were measured.

By using Eq. 1,[1] the weight-averge molecular weight, $\overline{M}_w$, was determined from the reciprocal of the intercept on the Hc/τ axis. Particle sizes were obtained by assuming the spheres to have the uniform density 2.2 g./cm^3.[2]

$$\frac{Hc}{\tau}=\frac{1}{\overline{M}_w}+Ac \qquad (1)$$

where :

---

[1] P. Debye, *J. Phys. Chem.*, 51, 18 (1947).

[2] R. K. Iler, "Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y. (1955).

$$H=\frac{32\pi^3}{3\lambda^4 \boldsymbol{N}}\cdot n_0^2\cdot\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2$$

c: the concentration of solute in g./ml.
τ: the turbidity
$\overline{M}_w$: the weight-average molecular weight
A: a constant
$\boldsymbol{N}$: Avogadro's number
λ: the wavelength of the light in vacuum
n_0: the refractive index of the solvent
$\frac{\mathrm{d}n}{\mathrm{d}c}$: the refractive index increment

$$\frac{\mathrm{d}n}{\mathrm{d}c}=0.151 \text{ (determined by the differential refractometery)}$$

After gelation, the change in the dissymmetry Z, the ratio of the intensity of the scattered light at 45° to that at 135°, was sought together with the intensity of the scattered light at 90°. For the measurement of the surface area, parts of the hydrogel were taken out at appropriate intervals after gelation and then repeatedly washed and dried at 200°C for 2 hr. Surface area was determined after calcination at 540°C for 4 hr. by the BET method.

Results and Discussion

Figure 1 shows the variation, with time, of the particle diameters in the sol state as calculated from the weight-average molecular weights.

The variation in the intensity of scattered light, and that in the dissymmetry, with the time elapsed after gelation are shown in Fig. 2 and Fig. 3 respectively. The curves of the scattering intensity are of the sigmoid type, with a maximum slope immediately after gelation. An almost constant value (not shown in Fig. 2) was reached in every case after a long period. In the curves in Fig. 3, on the other hand, the dissymmetry increases rapidly near the gelation point and finally reaches a constant value after only about two hours. The relations between the increase in the scattering intensity and the decrease in the surface area are shown in Fig. 4.

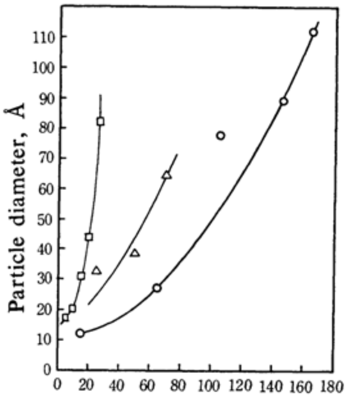


Fig. 1. Variation of particle size as a function of time.
□ Sample I △ Sample II ○ Sample III

TABLE I. THE PREPARATION OF THE SILICA HYDROSOL

Sample	Concn.	pH for preparation	Time of gelation* (at 30°C)
I	6N H_2SO_4+8.5% (as SiO_2) $Na_2O\cdot 3.22SiO_2$	4.05	32 min.
II	6N H_2SO_4+8.5% (as SiO_2) $Na_2O\cdot 3.22SiO_2$	3.53	100 min.
III	6N H_2SO_4+8.5% (as SiO_2) $Na_2O\cdot 3.22SiO_2$	3.25	175 min.
IV	2.1N H_2SO_4+3.0% (as SiO_2) $Na_2O\cdot 3.22SiO_2$	10.40	10 day**

* The time of gelation was taken as the earliest time at which the samples in the beaker became stiff enough not to move when the beaker was tilted.

** The surface area (274 m²/g.) was obtained of silica xerogel which had been prepared from hydrogel taken out immediately after gelation.

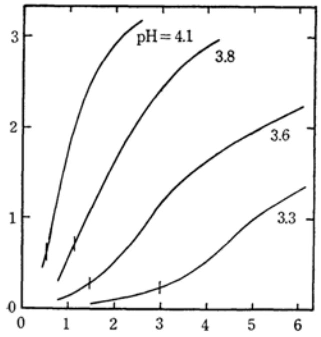


Fig. 2. Variation of scattering intensity with time. The vertical lines show the period of gelation.
I_0: incident beam, I_{90}: scattering light at 90° to the incident beam.

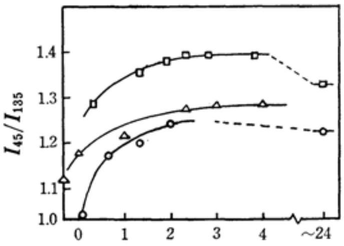


Fig. 3. Variation of dissymmetry for hydrogels.
pH: □ 3.8, △ 3.3, ○ 3.6

The experimental data on the changes in particle diameters in the sol state indicate

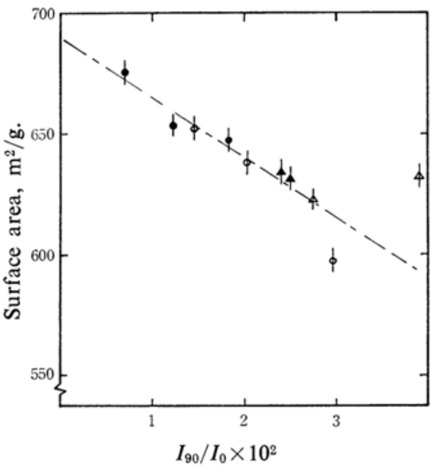
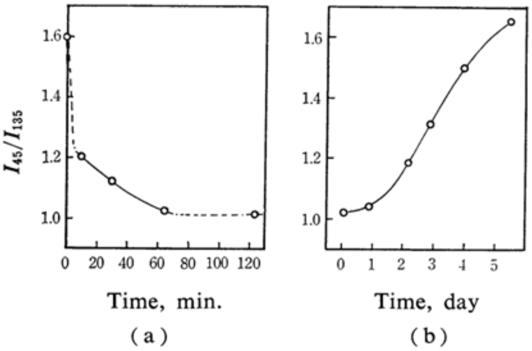


Fig. 4. Decrease of the surface area of silica gel with increasing scattering intensity of hydrogel from which the gels were prepared. pH: ▲ 3.5, ○ 3.6, ● 4.0, △ 4.1



(a) (b)

Figs. 5(a), 5(b). Variation of dissymmetry for sample IV.

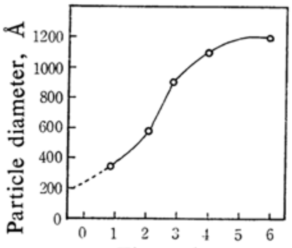


Fig. 6. Change of particle size with time determined from dissymmetry.

that it is likely that the following changes are likely when sodium silicate solutions are added to sulfuric acid.

First of all, particles with diameters of about 10—20Å rapidly appear in the mixture, as is estimated from Fig. 1, where three curves extrapolated to time zero intercept the coordinate at about 10—20Å, though their exact values in the initial stage could not be obtained because of the undue light scattering caused by impurities. The rapid growth of particles at the start, as seen in the results of sample IV (Fig. 5a), has also been predicted by Greenberg's[3)] and Debye's[4)] experiments. As Fig. 5a shows the large dissymmetry at $t=0$ is possibly due to impurities included rapidly decreased during the initial one hundred minutes, and then slowly increased with the growth of the particles, until gelation is completed ten days after. The interpretation of the rapid decrease in the dissymmetry in the initial stage would be: the light scattering arising from rapidly-growing particles after mixing surpassed that of impurities. Therefore, the decreased dissymmetry observed after one hundred minutes or so was due largely to the particles thus grown; these, however, were not so large as to make the dissymmetry deviate greatly from unity, so a value of around unity was obtained. Thus, the rapid decrease in the dissymmetry gives evidence of the rapid growth of particles at the start.

Greenberg obtained the particle diameter, at $t=0$, of approximately 200Å from his dissymmetry measurements. A similar observation has been reported elsewhere.[4)]

In view of these facts, it may be concluded that the rapid growth occurred soon after mixing.

In the initial stage, as has been mentioned in the literature,[4)] the association of particles seems to occur to a minor extent. According to Greenberg's experiment, the diameter of the particles at zero time is approximately 200Å. We, however, obtained the corresponding value of 10—20Å. This marked discrepancy can only be ascribed to the association-dissociation process, in which particles of 10—20Å are very weakly bounded together to form associated particles in a "highly solvated state"[3)] and in which, upon progressive dilution, the aggregates dissociate into smaller particles 10—20Å in diameter.

This is also suggested by the negative value of A (a constant in Eq. 1) being obtained only in the initial stage.

In the final stage, in turn, bonds between primary particles became stronger to such an extent that aggregates no longer dissociated into components upon dilution. This would be the reason why the particle size obtained in the final stage (Fig. 1) was substantially larger than that (only 40—45Å) which could be presumed from the BET surface area of dried gel[2)] (Fig. 4). In this connection the data on sample IV are very interesting, in this

---

3) S. A. Greenberg and D. Sinclair, *J. Phys. Chem.*, **59**, 435 (1955).

4) P. Debye and R. V. Nauman, ibid., **65**, 10 (1961).

case the change in particles size was followed by the measurements of the dissymmetry. A particle size of approximately 1200Å before gelation is shown in Fig. 6. Dried gel after gelation, however, shows a surface area of 274 m^2/g., which may indicate a primary particle only 110Å in diameter.[2]

These observations suggest that, in the final stage of the sol, not only the continued growth of ultimate particles but also association and partial gelation occur.

So far discussions have been made on primary and secondary particles and their growth in the sol state. Our further remarks will be centered upon the continued polymerization, resulting in the growth of primary particles, and upon the continued aggregation in the gel state.

Although the value of the dissymmetry and the scattering intensity are measures of the growth of particles, their behaviors with time in the same sample are markedly different from each other (Figs. 2 and 3). A possible explanation may be based on the fact that the increase in dissymmetry shows an increase in the size of secondary particles and that gel is built up as a result of three-dimensional linkages of such secondary particles. Though hydrogel is seemingly of a solid state at the gelation point, the networks are not completed. It takes still more time for the gel to form a complete network. Therefore, the time would be shown by the point of constant dissymmetry, when the net works are finished, since the aggregation accompanies gelation. The final diameter of the secondary particles in this experiment may be of the order of 800Å as calculated from the final dissymmetry uncorrected for concentrations.

A slight fall in the dissymmetry observed after a long time would be the result of a decrease in the size of secondary particles by dehydration condensation.

The change in scattering intensity is, on the other hand, due not only to the growth of primary particles but also to that of secondary particles. The increase in the earlier parts of the curves is probably due to the light scattering from secondary particles. While the dissymmetry reached a constant about two hours after gelation, the intensity of the scattered light continuously increased. Accordingly, the growth in the size of secondary particles would stop at the time given above. The fact that the intensity of scattered light exhibits a continuous increase furnishes evidence of the continued growth of primary particles as a result of the reaction of primary particles with the silicate ions remaining unreacted in gel. This reaction or polymerization certainly accompanies the change in the weight of secondary particle, but it does not accompany the change in size.

A series of surface area measurements of samples after gelation elucidated the light scattering behavior in connection with the internal change in the gel. The increase in the scattering intensity was clearly shown to be accompanied by an increase in the size of primary particles as determined from the surface area measurement. Accordingly, a decrease in the surface area will be related to an increase in the intensity of light scattering.

Although it seemed difficult to obtain a priori the relationship from the light scattering data because of the effects of secondary particles in gel and of the relatively high concentrations, resulting in interference between particles, nevertheless the following equation was derived from the straight line shown in Fig. 4 within a limited pH range:

$$S=690-21.5\cdot(I_{90}/I_0\times10^{-2})$$

where S is the surface area in m^2/g.

Summary

The growth of particles in the polymerization of silicic acid has been investigated by means of light scattering. The following results were obtained:

1) Polymerization does occur for a long period, even after gelation.

2) While the aggregation is predominant near the gelation point, it seems to occur to a lesser extent even in the initial stage. The aggregate finally grows to as much as 800Å in diameter. It is of a porous and sponge-like structure, including the solvent in it.

3) Hydrogel must be understood as an entity built up of secondary particles which also consist of primary ones. Consequently, hydrogel has prime structure and a substructure, by the former three-dimensional linkages among secondary particles are meant, while by the latter are meant those among primary particles.

4) There is a linear relationship between the scattering intensity of the hydrogel and the surface area of dried gel.

Research Laboratory
Asahi Glass Co., Ltd.
Kanagawa-ku, Yokohama