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## STUDY OF THE POLYMERIZATION OF SILICIC ACID IN AQUEOUS SOLUTION BY TRIMETHYLSILYLATION-GAS CHROMATOGRAPHY

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### SUMMARY

The effects of pH, concentration of monosilicic acid and temperature on the formation of low-molecular-weight silicic acid species in the early stages of polymerization were studied by trimethylsilylation-gas chromatography (TMS-GC). The change with time in the distribution of silicic acid species up to the hexamer was measured. The results obtained by TMS-GC are compared with those obtained by colorimetry. In solutions of initial monosilicic acid concentration of 600 ppm SiO<sub>2</sub> at pH 1.8, 20°C and at pH 8.5, 90°C, it was found that a temporary equilibrium is set up among SiO<sub>4</sub><sup>4-</sup>, Si<sub>2</sub>O<sub>7</sub><sup>6-</sup> and Si<sub>3</sub>O<sub>10</sub><sup>8-</sup> during the induction period. On the other hand, for 2500 and 5000 ppm SiO<sub>2</sub> solutions at pH 1.8, 20°C, higher-molecular-weight silicic acid species than Si<sub>3</sub>O<sub>10</sub><sup>8-</sup> were formed during the induction period, and the distribution of these species changed with time. All of the silicic acid species formed during the induction period, and the distribution of these species changed with time. All of the silicic acid species formed during the induction period were determined by colorimetry.

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### INTRODUCTION

When the concentration of monosilicic acid in aqueous solution is higher than the solubility of amorphous silica, monosilicic acid polymerizes. The rate of polymerization is slower at pH 2–3 than at pH 7–9. The kinetics of the polymerization of silicic acid have been studied by colorimetry<sup>1–3</sup>. However, no information is available on the change in molecular (particle) size of the polymers with time.

Light scattering, ultracentrifugation and viscosity measurements have been employed to determine the number average molecular weights of polymers<sup>4</sup>. Gel chromatography has been applied to separation of silicic acid polymers<sup>5</sup> and the mechanism of growth of polymer particles has been discussed<sup>6</sup>.

Trimethylsilylation was first employed for the study of mineral silicate structures by Lentz<sup>7</sup>. In previous papers, we reported suitable methods for the determi-

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nation of trimethylsilyl (TMS) derivatives of silicic acids by gas chromatography (GC)<sup>8</sup> and for the trimethylsilylation of silicic acids in aqueous solution<sup>9</sup>. These methods can be applied to the study of the early stage of polymerization of silicic acid.

In this work, the effects of pH, concentration of silicic acid and temperature on the formation of low-molecular-weight silicic acid species in the early stage of polymerization were studied by trimethylsilylation-gas chromatography (TMS-GC). The results obtained are compared with those obtained by colorimetry.

## EXPERIMENTAL

### *Sample solutions and reagents*

Hexamethyldisiloxane (HMDS) was purchased from Tokyo Kasei Kogyo and purified by distillation four times at 120°C. All the other chemicals used were of reagent grade.

Monosilicic acid solution for the experiments at 20°C was prepared by hydrolysis of tetramethoxysilane in 0.01 *M* hydrochloric acid solution, and that for the experiment at 90°C was prepared by dissolution of anhydrous silica in 2 *M* sodium hydroxide solution.

### *Procedure*

Monosilicic acid solution was adjusted to the desired pH with 0.5 *M* sodium carbonate solution or 0.5 *M* hydrochloric acid. At appropriate intervals, 5 ml of the sample solution were withdrawn by pipette and immediately added to a mixture of water (5 ml), concentrated hydrochloric acid (7.5 ml), *n*-propanol (15 ml) and HMDS (12 ml) which had been stirred for 1 h at 28°C. The mixture was then stirred for 45 min at 28°C. The siloxane layer was treated as described previously<sup>9</sup>.

TMS derivatives of silicic acids were determined by GC<sup>8</sup>.

The change of concentration of silicic acid with time was measured by colorimetry.

## RESULTS AND DISCUSSION

### *Effect of pH*

The variation of the concentrations of silicic acid species with time in solutions of initial monosilicic acid concentration of 600 ppm (as SiO<sub>2</sub>) was examined at pH 1.8, 4.0, 6.0 and 8.5 at 20°C. The results are shown in Figs. 1-4. Each silicic acid species is expressed in its anionic form and the concentration of each species is given in terms of SiO<sub>2</sub>. The Si(T) value is the sum of the concentrations of each silicic acid species whose TMS derivatives can be determined by GC. The difference between the initial concentration of monosilicic acid and the Si(T) value can be regarded as the amount of GC-undeterminable silicic acid species.

At pH 1.8 (Fig. 1), Si<sub>2</sub>O<sub>7</sub><sup>6-</sup> and Si<sub>3</sub>O<sub>10</sub><sup>8-</sup> are formed. During the first hour, the amounts of Si<sub>2</sub>O<sub>7</sub><sup>6-</sup> and Si<sub>3</sub>O<sub>10</sub><sup>8-</sup> increased with rapid decrease in the amount of SiO<sub>4</sub><sup>4-</sup> but then did not vary up to 13 h. This shows that, after 1 h, a temporary equilibrium is set up among three silicic acid species. The Si(T) value did not change with time and was equal to the initial concentration of silicic acid. This indicates that no GC-undeterminable silicic acid species were formed.

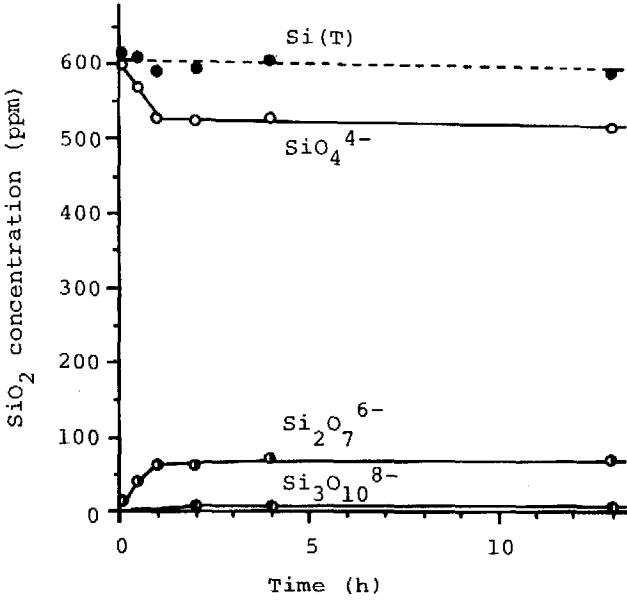


Fig. 1. Changes in the concentration of silicic acid species with time for a 600 ppm SiO<sub>2</sub> solution at pH 1.8.

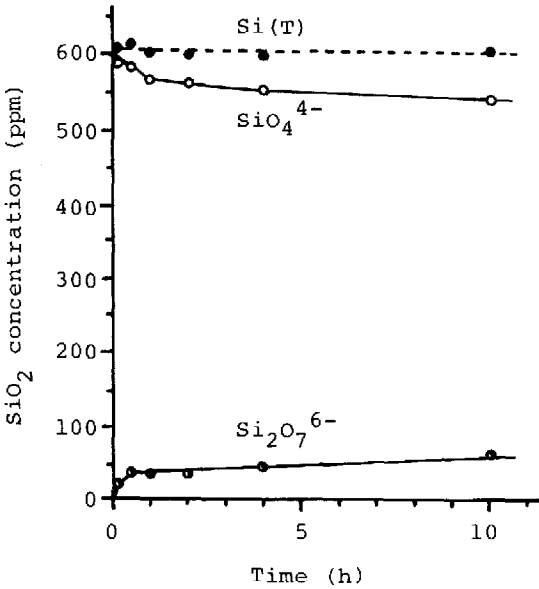


Fig. 2. Changes in the concentration of silicic acid species with time for a 600 ppm SiO<sub>2</sub> solution at pH 4.0.

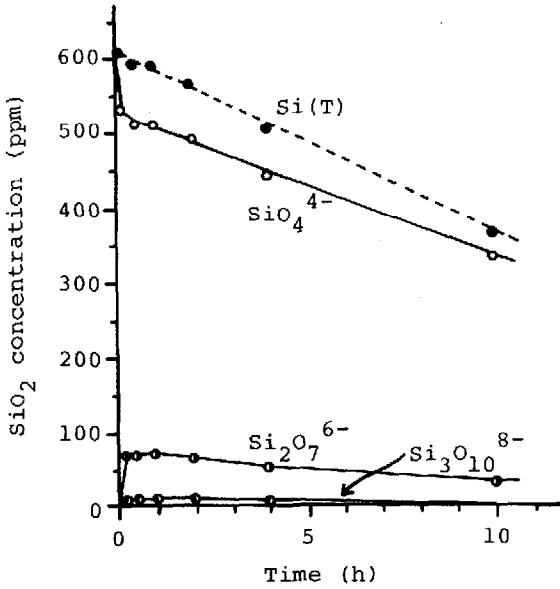


Fig. 3. Changes in the concentration of silicic acid species with time for a 600 ppm  $\text{SiO}_2$  solution at pH 6.0.

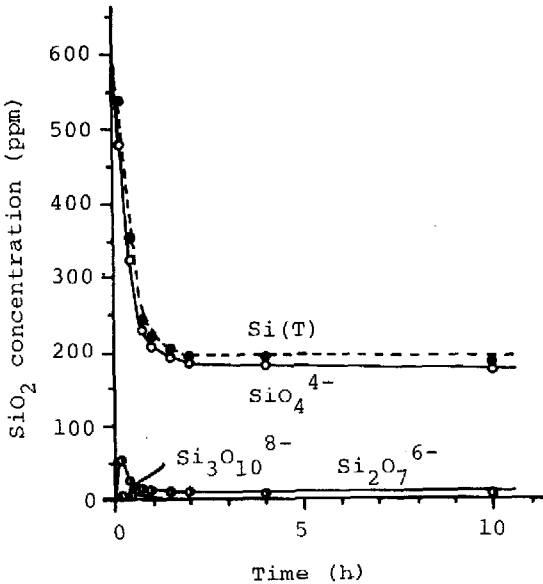


Fig. 4. Changes in the concentration of silicic acid species with time for a 600 ppm  $\text{SiO}_2$  solution at pH 8.5.

At pH 4.0 (Fig. 2), only  $\text{Si}_2\text{O}_7^{6-}$  formed as the polymeric species and its amount gradually increased with decreasing amount of  $\text{SiO}_4^{4-}$ . The Si(T) value did not change with time.

At pH 6 (Fig. 3), the amounts of  $\text{Si}_2\text{O}_7^{6-}$  and  $\text{Si}_3\text{O}_{10}^{8-}$  initially rapidly increased and then gradually decreased. The amount of  $\text{SiO}_4^{4-}$  and the Si(T) value also decreased with time.

At pH 8.5 (Fig. 4), the amounts of  $\text{SiO}_4^{4-}$ ,  $\text{Si}_2\text{O}_7^{6-}$  and  $\text{Si}_3\text{O}_{10}^{8-}$ , and the Si(T) value rapidly decreased in 1 h. This demonstrates the rapid polymerization of silicic acid. After 2 h, the Si(T) value only decreased very slowly.

#### Effect of monosilicic acid concentration

The effect of the concentration of monosilicic acid on the change in silicic acid species with time was examined using 600, 2500 and 5000 ppm monosilicic acid solutions at pH 1.8 and 20°C. The results are shown in Figs. 1, 5 and 6.

In the 600-ppm solution (Fig. 1), only two polymeric species,  $\text{Si}_2\text{O}_7^{6-}$  and  $\text{Si}_3\text{O}_{10}^{8-}$ , are formed and the Si(T) value did not vary within 13 h. On the other hand, in the 2500-ppm solution (Fig. 5), silicic acid species other than  $\text{Si}_2\text{O}_7^{6-}$  and  $\text{Si}_3\text{O}_{10}^{8-}$ , such as  $\text{Si}_3\text{O}_9^{6-}$ ,  $\text{Si}_4\text{O}_{12}^{8-}$ ,  $\text{Si}_4\text{O}_{13}^{10-}$ ,  $\text{Si}_5\text{O}_{15}^{10-}$  and  $\text{Si}_6\text{O}_{17}^{10-}$ , formed progressively. The Si(T) value gradually decreased. The progress of the polymerization is shown more clearly by the 5000-ppm solution (Fig. 6). Although  $\text{Si}_3\text{O}_9^{6-}$  and  $\text{Si}_4\text{O}_{13}^{10-}$  are formed in the solutions of 2500 and 5000 ppm, they were not plotted in the figures because of their small amounts.

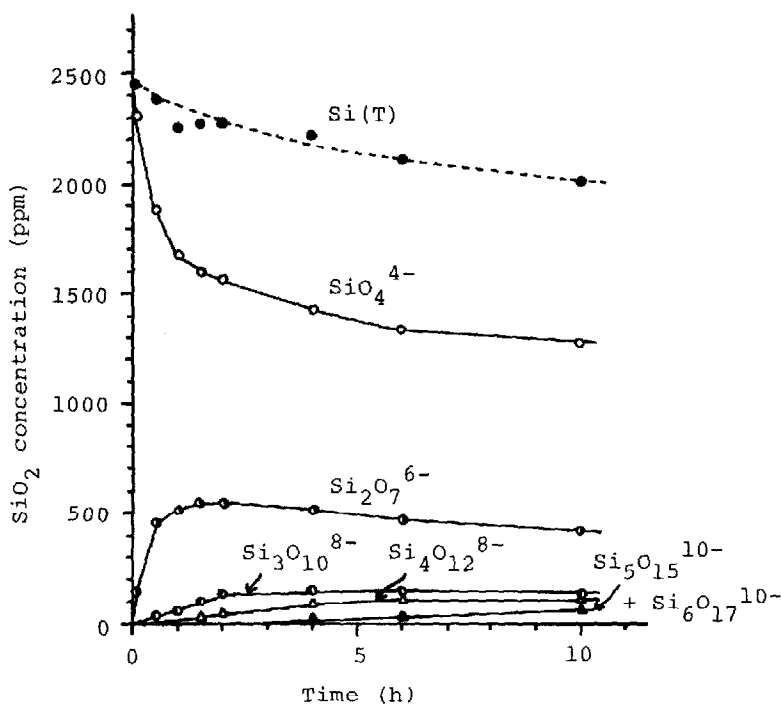


Fig. 5. Changes in the concentration of silicic acid species with time for a 2500 ppm  $\text{SiO}_2$  solution at pH 1.8.

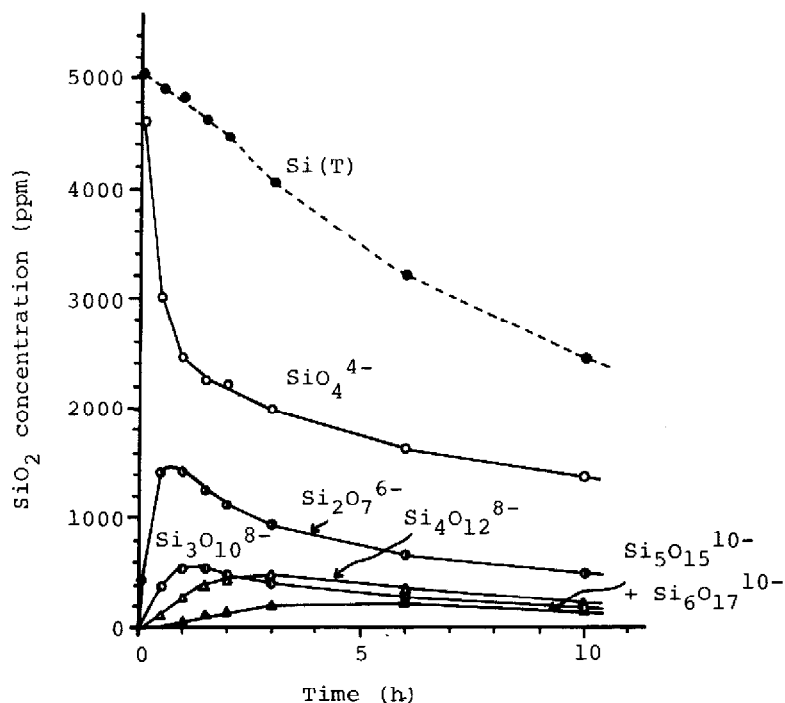


Fig. 6. Changes in the concentration of silicic acid species with time for a 5000 ppm  $\text{SiO}_2$  solution at pH 1.8.

### Effect of temperature

The polymerization of silicic acid was studied at  $90^\circ\text{C}$  for the monosilicic acid solution of 600 ppm at pH 8.5. The results are shown in Fig. 7, as is the variation with time of the concentration of silicic acid determined by colorimetry. The  $\text{Si(T)}$  value and the concentration of silicic acid determined by colorimetry were identical with the initial monosilicic acid concentration until 4 h and then suddenly began to decrease. There is an induction period during which there is no change in the concentration of silicic acid as determined by colorimetry. The induction period is greater at higher temperatures and decreases with increasing degree of supersaturation of monosilicic acid<sup>10</sup>. As is seen from Fig. 7,  $\text{Si}_2\text{O}_7^{6-}$  and  $\text{Si}_3\text{O}_{10}^{8-}$  formed in the early stages of the induction period and then a temporary equilibrium was set up among  $\text{SiO}_4^{4-}$ ,  $\text{Si}_2\text{O}_7^{6-}$  and  $\text{Si}_3\text{O}_{10}^{8-}$  during 1–4 h. As soon as the induction period was over, the concentrations of these species began to decrease.

### Comparison of the results obtained by TMS-GC and colorimetry

The variation with time of the concentration of silicic acid as determined by colorimetry at  $20^\circ\text{C}$  for solutions of initial monosilicic acid concentrations of 600, 2500 and 4700 ppm at pH 1.8 and for that of 600 ppm at pH 8.5 is shown in Fig. 8. The results indicate that the concentration of silicic acid in each solution of pH 1.8 did not change during 10 h regardless of the difference in the initial concentration of monosilicic acid. As is seen from Figs. 5 and 6, silicic acid species up to the hexamer were determined, and the decrease in the  $\text{Si(T)}$  value with time indicates the formation

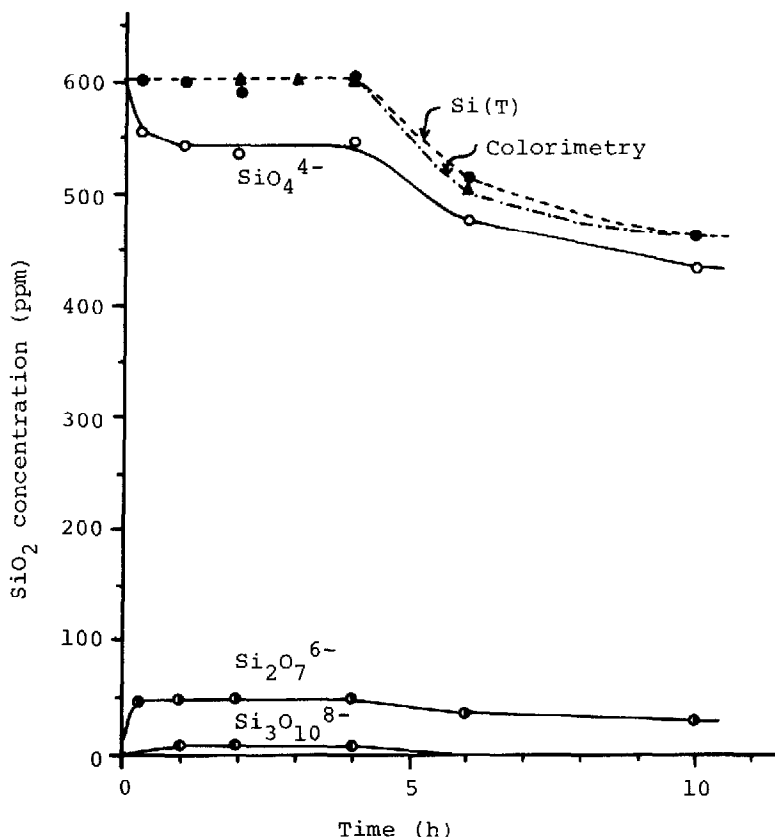


Fig. 7. Changes in the concentration of silicic acid species with time and in the concentration of silicic acid as determined by colorimetry at 90°C for a 600 ppm SiO<sub>2</sub> solution at pH 8.5.

of GC-undeterminable silicic acid species. As the concentration of silicic acid determined by colorimetry is identical with the initial monosilicic acid concentration, it is clear that all of the GC-determinable and -undeterminable silicic acid species formed were determined by colorimetry. On the contrary, for the 600 ppm silicic acid solution of pH 8.5, the concentration of silicic acid determined by colorimetry varied with time in a similar manner to that of the Si(T) value (Figs. 4 and 8). These results show that the GC-undeterminable silicic acid species formed could not be determined by colorimetry.

The colour development in colorimetry is based on the formation of molybdosilicic acid and only monosilicic acid contributes to this. Therefore, to be determinable by colorimetry, polysilicic acids must depolymerize to monosilicic acid. It is suggested that the polysilicic acids formed at pH 1.8 have small sizes and easily depolymerize, because the rate of particle growth of polysilicic acids is very slow at about pH 2 (ref. 6). On the other hand, it has been shown that in the 600 ppm silicic acid solution of pH 8 at 20°C the particles of polysilicic acids grow rapidly<sup>6</sup>. The results obtained for the 600 ppm SiO<sub>2</sub> solution of pH 8.5 shown in Figs. 4 and 8

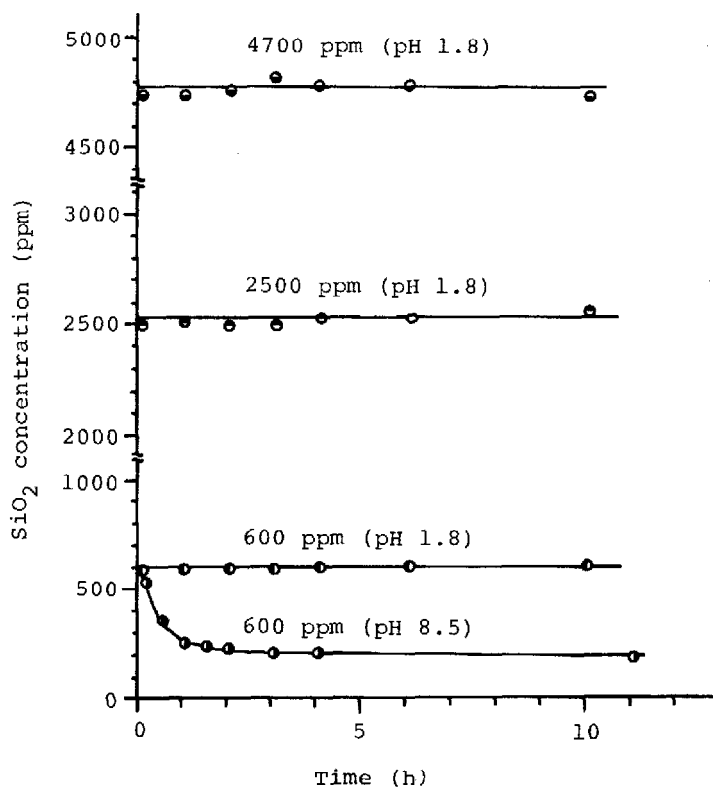


Fig. 8. Changes in the concentration of silicic acid with time as determined by colorimetry.

indicate the rapid formation of large polysilicic acids which do not easily depolymerize.

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