Colloid Polym Sci 277:474–478 (1999)

SHORT COMMUNICATION

T. Okubo
A. Tsuchida
K. Kobayashi
A. Kuno
T. Morita
M. Fujishima
Y. Kohno

Kinetic study of the formation reaction of colloidal silica spheres in microgravity using aircraft

Received: 10 November 1998
Accepted in revised form: 12 January 1999

T. Okubo (✉) · A. Tsuchida
K. Kobayashi · A. Kuno
Department of Applied Chemistry
Gifu University
Gifu 501-1193, Japan
e-mail: okubotsu@apchem.gifu-u.ac.jp
Fax: +81-58-2932628

T. Morita · M. Fujishima
Japan Space Utilization Promotion Center
Tokyo 169-0051, Japan

Y. Kohno
Kobe Shipyard & Machinery Works
Mitsubishi Heavy Industries Co. Ltd.
Kobe 652-0854, Japan

Abstract Polymerization reactions of colloidal silica spheres via the hydrolysis and dehydration processes of tetraethyl orthosilicate with ammonia and a tiny amount of water in ethyl alcohol have been studied in microgravity by the parabolic flights of a MU-300 rear-jet aircraft. Induction periods and polymerization rates are determined by fast-scanning transmitted-light-intensity measurements and the fast-scanning dynamic light-scattering method. Direct observation of the reaction mixtures is also made with a charge-coupled device video camera. Reproducible and reliable data are obtained in microgravity compared with those in gravity. Increases in the induction times and decreases in the polymerization rates are observed in microgravity compared with those in gravity. One of the main reasons for these observations is the fact that the translational Brownian movement of the reactants and/or product spheres is free from downward translational movement in microgravity. Very weak convection of the reaction suspensions in microgravity is another important factor.

Key words Reaction kinetics in microgravity – Colloidal silica spheres – Polymerization – Transmitted-light intensity – Dynamic light scattering

Introduction

Recently, keen attention has been paid to chemical reactions, especially polymerization reactions in microgravity as a new technology in space [1–3]. In microgravity using a space shuttle Vanderhoff et al. [1] succeeded in preparing monodisperse polystyrene spheres 5–18 μm in diameter with narrower particle size distributions than those prepared in gravity. A series of polyacrylamide gels have been synthesized in microgravity [3]. All these microgravity experiments are, however, restricted to studies on the morphologies (such as size and shape) of the polymers and gels formed and their reaction yields. Kinetic analyses of the polymerization reactions such as rate constants and the reaction mechanisms have not been reported yet.

Our group has performed several microgravity experiments hitherto on the colloidal crystallization kinetics [4, 5] and the rotational relaxation times [6] of anisotropic-shaped colloidal particles of tungstic acid by the aircraft and the free-fall techniques, respectively. In this report, polymerization reactions of colloidal silica spheres from ethyl silicate, ammonia and water are studied kinetically in microgravity for about 20 s duration using aircraft. The specific gravity of colloidal silica spheres is about 2.2, high enough compared with that of solvent ethanol of 0.82. Thus, the reactants and the product spheres are sedimented in gravity and the reaction mixtures must be agitated vigorously in most cases throughout the polymerization processes. In microgravity, on the other hand, the reactants and the products do not sediment and the reaction proceeds homogeneously without stirring. Another advantage of the microgravity experiments is the substantial reduction in the convection of reaction mixtures. For example, it is observed clearly by charge-coupled device camera observations that the movement of the small air bubbles in the mixtures stops completely in the microgravity of ±0.01 *G* produced by the parabolic flight of an aircraft.

In another paper, the kinetic analyses of the formation reactions of colloidal silica spheres have been reported in gravity by the transmitted-light-intensity and the dynamic light-scattering techniques [7]. The colloidal spheres were synthesized from ethyl silicate (EtSi), ammonia (NH_3) and a trace of water in ethanol solvent. The reaction mechanisms are determined to be the formation of the small preliminary particles followed by their coalescence to the final size of colloidal silica spheres, and are given by Eqs. (1) and (2) [7].

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \qquad (1)$$

$$\equiv Si{-}OH + HO{-}Si\equiv \rightarrow \equiv Si{-}O{-}Si\equiv + H_2O \qquad (2)$$

The polymerization starts after a certain induction time (t_i) ranging from several tens of seconds to several hours, and t_i increases as the concentrations of NH_3, EtSi and/or H_2O decrease. Furthermore the apparent rates of reaction, v', were evaluated. Log v' increased linearly with slopes of 1, 2 and 0.5 as the logarithms of the concentrations of EtSi, NH_3 and H_2O increased, respectively.

Experimental

Materials

Tetraethyl orthosilicate was guaranteed grade purchased from Wako Pure Chemicals (Osaka). Ethyl alcohol (99.5%) and ammonia (25%) were the most purified grade reagents commercially available and were obtained from Wako Chemicals. The water used for the sample preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore Co., Bedford, Mass.).

Fast-scanning transmitted-light intensity (FTLI) and fast-scanning dynamic light-scattering (FDLS) spectroscopies

Time-resolved transmitted-light intensity and dynamic light-scattering measurements were made on a fast-scanning spectrophotometer type MCPD-2000, Otsuka Electronics, Osaka) and a fast-scanning dynamic light-scattering spectrophotometer (type ALV-5000, ALV Langen, Germany), respectively. A stopped-flow type mixer was purchased from Otsuka Electronics (type MX-10, Hirakata, Osaka) and the observation cell was a flow-type quartz glass tube. Two ethanol solutions of EtSi and NH_3 were purified by filtering separately using Millipore membranes (0.2 mm), and were then mixed with the mixer. The reaction mixture was introduced into the flow cell and its flow stopped several milliseconds after mixing.

A Mitsubishi MU-300 jet aircraft was used to achieve a microgravity of about ±0.01 *G* for 20–22 s. This period was not long enough to follow the whole process of the formation reactions of colloidal silica spheres, which takes between 30 s and 2 min. In this work, therefore, the kinetic measurements in microgravity started 0, 15, and 30 s after the rapid mixing of the reactant solutions. These kinds of measurements are able to provide information on the influences of microgravity on the initial, medium and final stages of the reactions.

The phase diagram of the reaction mixtures, where aqueous NH_3 was replaced with H_2O is shown in Fig. 1. The upper and lower regions of the curve given by crosses are homogeneous (transparent) and heterogeneous (turbid) regions, respectively. Open circles show the components of the reaction mixtures used for the microgravity experiments. The reaction mixtures shown by four open circles at high concentrations of EtSi are a bit turbid. Therefore, the reference experiments were always carried out by mixing the ethanol solutions of EtSi and H_2O (instead of aqueous NH_3) both in microgravity and in gravity for the FTLI measurements. The corrected absorbances were obtained from the differences between the absorbances measured in the reaction experiments and the corresponding reference measurements.

Results and discussion

Figure 2 shows a typical example of the changes in the absorbances of the reaction mixtures (shown by triangles), those of the corresponding reference solutions containing no NH_3 (crosses), and the differences, the corrected absorbances (open circles). The reaction starts at $t = 0$. In this experiment, 0 *G* ranges from $t = 14$ s (arrow a) to 35 s (arrow b). From $t = 0$ to arrow a, from arrows b to c and after arrow c, the reaction mixtures are in 2 *G*, 1.5 *G* and 1 *G*, respectively. A slight decrease with time in the absorbance of the reference solution can be seen in the figure; this is ascribed to the fact that the initial turbid reaction mixture becomes only slightly transparent with time. The increase in the corrected absorbances shown by open circles clearly shows that the reaction mixture becomes turbid due to the colloidal spheres formed in the course of the polymerization reaction.

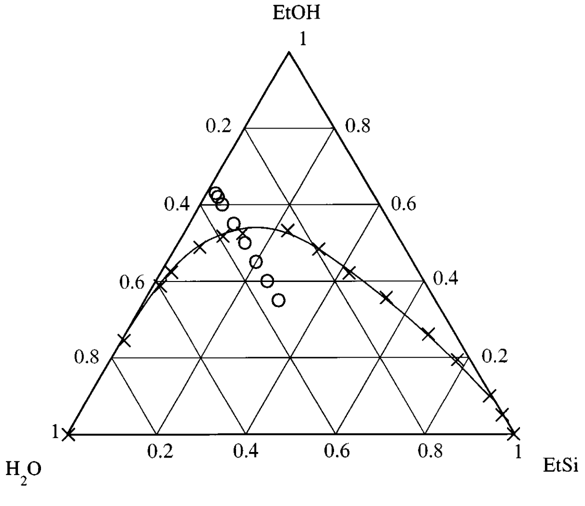

Fig. 1 Phase diagram of the reaction mixtures in volume fraction at 25 °C. *Open circles* shows the reaction mixtures studied

Traces of the corrected absorbances measured 5 times and their mean values at 1 *G* for the polymerization reaction are shown in Fig. 3. Clearly, the experimental errors look rather large. From our experience on microgravity experiments, this is believed to be caused mainly by the upward movement of the extremely small bubbles, which cannot be seen with the naked eye, formed in the reaction mixtures. Movement of dust can be safely neglected since the reaction mixtures are purified by filtering. Surprisingly, the reproducibility of the absorbances was raised substantially in microgravity as shown in Fig. 4, though the same experiments were performed only twice. Reliable and reproducible data are obtained clearly due to the fact that no bubbles move in microgravity.

Plots of the diameter of the spheres formed versus time for the 13 runs of FDLS measurements at 1 *G* are shown in Fig. 5. Clearly, the data scattered in gravity, though the reaction mixtures were free from dust larger than 0.2 μm as a result of filtering. It is well known that the reliability of dynamic light-scattering measurements is lowered significantly by only a tiny amount of dust and/or bubbles.

The FDLS results in microgravity are shown in Fig. 6. The scattering of the data reduced greatly. Clearly, the reliability of the measurements improved strikingly in microgravity. Fig. 6 shows the existence of

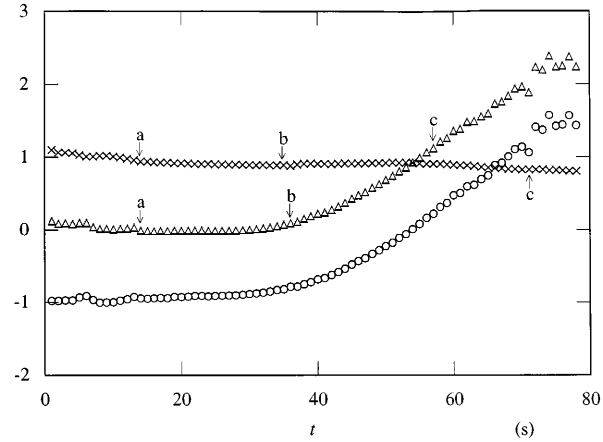

Fig. 2 Absorbance versus time plots from fast-scanning transmitted-light-intensity (*FTLI*) measurements in the course of colloidal silica formation at 25 °C. 0 *G* ranges from $t = 14$ to 35 s, [EtSi] = 15 vol%, $[NH_3]$ = 8.75 wt%, ○: corrected absorbances of the reaction mixtures, ×: references, △: raw data of absorbances, at 600 nm

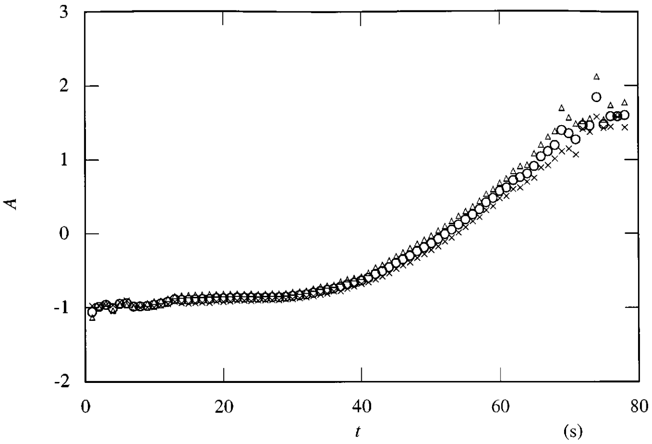

Fig. 4 Absorbance versus time plots from FTLI measurements in the course of colloidal silica formation at 25 °C. 0 *G* ranges from $t = 14$ to 32 s, [EtSi] = 15 vol%, $[NH_3]$ = 8.75 wt%, ○: mean values of the corrected absorbances, ×: 1st experiment, △: 2nd, at 600 nm

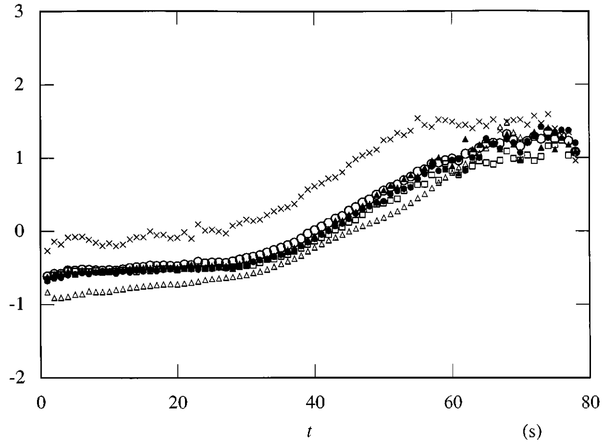

Fig. 3 Absorbance versus time plots from FTLI measurements in the course of colloidal silica formation at 25 °C. At 1 *G*, [EtSi] = 15 vol%, $[NH_3]$ = 8.75 wt%, ○: mean values of the corrected absorbances, ×: 1st experiment, △: 2nd, □: 3rd, ●: 4th, ▲: 5th, at 600 nm

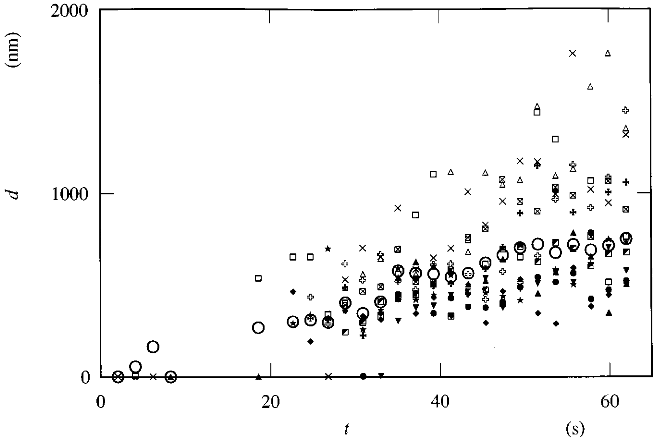

Fig. 5 Diameter versus time plots from fast-scanning dynamic light-scattering (*FDLS*) measurements in the course of colloidal silica formation at 25 °C. At 1 *G*, [EtSi] = 15 vol%, $[NH_3]$ = 8.75 wt%, ○: mean values of 13 sets of experiments

the induction times, where the primary and small-sized colloidal spheres are formed. Determination of the size of the primary spheres was, however, impossible by our FDLS technique, since their size of 10–20 nm was too small to be detected.

Figure 7 shows the induction times (t_i) at 0 *G*, where open circles, triangles and squares show the starting times of the microgravity at $t = 0$, 15 and 30 s, respectively. The data at 1 *G* are also given by solid circles in the figure. The t_i values increased in microgravity compared with gravity especially when the reaction mixtures experienced microgravity at the beginning of the formation reaction. One of the most plausible causes is the fact that both the number and the rate of formation of the primary spheres decrease due to substantial reduction in the convection of the reaction mixtures. It should be mentioned here that the induction periods in the colloidal crystallization processes have also been prolonged in microgravity [5].

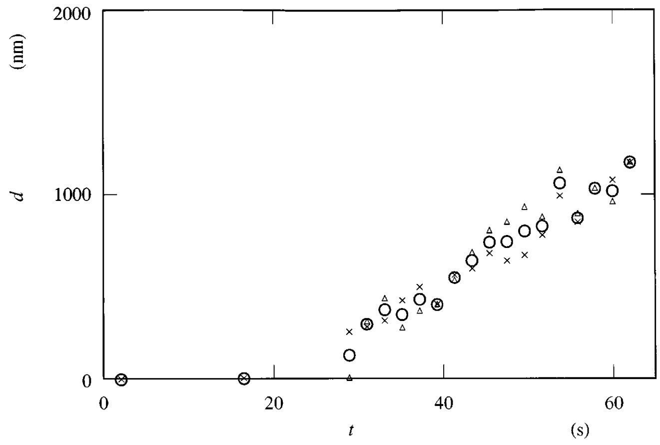

Fig. 6 Diameter versus time plots from FDLS measurements in the course of colloidal silica formation at 25 °C. 0 *G* ranges from $t = 14$ to 32 s, [EtSi] = 15 vol%, [NH$_3$] = 8.75 wt%, ○: mean values of two sets of experiments

As was discussed in a preceding paper [4], the absorbance (A) of the reaction mixtures is given by Eq. (3),

$$A = A_o + A_p - A_s \tag{3}$$

where A_o is the solvent absorption, A_p the particle absorption, and A_s the light-scattering term at θ (scattering angle) = 0. The A_p term arises from the colloidal spheres formed in the reaction mixtures and should increase linearly with increasing volume of the spheres as

$$A_p \propto Nd^3 \ , \tag{4}$$

where N is the number of spheres formed and d is the diameter of the spheres. The light scattering term, A_s is further given by Eq. (5),

$$A_s \propto \ln(I_p \times I_i + I_m) \ , \tag{5}$$

where I_p is the intensity of the scattered light from the particle-form factor at $\theta = 0$. I_i is the intensity of scattered light contributed from the interference factor at $\theta = 0$ and reflects the particle distribution in the reaction mixtures, and I_m is the multiple-scattering term and is important especially in the final stage of the polymerization reaction, where large-sized colloidal spheres grow. The diameter, d, of the colloidal silica spheres formed and their reaction rates, v, are, therefore, approximated very roughly by Eqs. (6) and (7) [4].

$$d \propto A_p^{1/3} \propto A^{1/3} \tag{6}$$

$$v = \mathrm{d}(d)/\mathrm{d}t \propto \mathrm{d}(A^{1/3})/\mathrm{d}t \tag{7}$$

The apparent reaction rates, v', of the colloidal formation reactions in microgravity and in gravity are shown

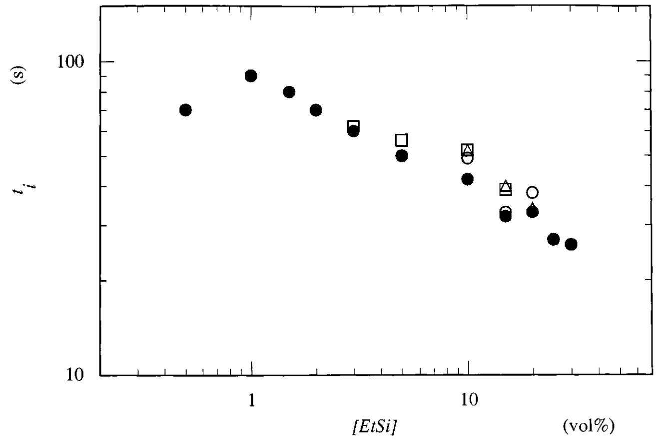

Fig. 7 Induction periods in the course of colloidal silica formation at 25 °C. [NH$_3$] = 8.75 wt%, ○: 0 *G* starts at $t = 0$ s, △: 15 s, □: 30 s, ●: at 1 *G*

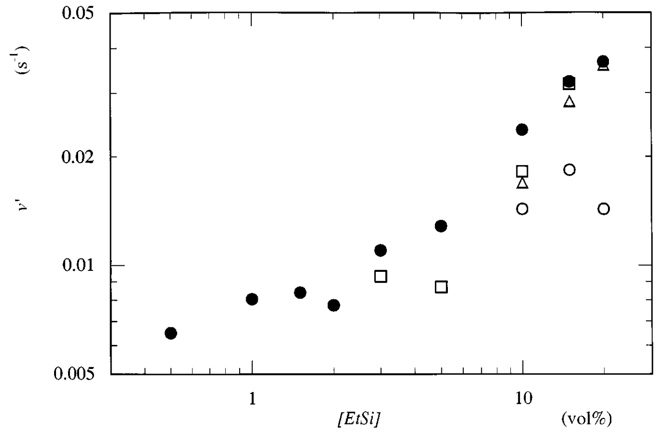

Fig. 8 Apparent rates in the course of colloidal silica formation at 25 °C. [NH$_3$] = 8.75 wt%, ○: 0 *G* starts at $t = 0$ s, △: 15 s, □: 30 s, ●: at 1 *G*

in Fig. 8. The v' values were determined from the reciprocal difference in the times, t_i and t_f, where the initial linear line of the $A^{1/3}$ versus t plots crosses the initial ($t = 0$) and final saturated horizontal lines, respectively. Surprisingly, the polymerization rates were greatly lowered when the reaction mixtures experienced microgravity at the beginning of the reaction. It is highly plausible that a decrease in the number of small primary particles and also a decrease in their size in microgravity influenced the polymerization rates.

In conclusion, the microgravity effect on the formation reactions of colloidal silica spheres was far more significant than expected. The thermodynamic activities of the reactant and product molecules in activated complex theory will change in microgravity due to the no-convection effect of reactant mixtures, for example. The role of microgravity itself on the kinetic parameters has not been clarified theoretically hitherto, and this must be studied in future. The microgravity effect on the final size of the silica spheres formed is not clear yet, because the duration of the microgravity (~20 s) was too short compared with the reaction time needed for the completion of sphere formation (60 s or more).

Acknowledgements The authors are grateful to the National Space Development Agency of Japan(NASDA) and the Japan Space Utilization Promotion Center (JSUP, "Frontier Reseach Project") for their financial and technical support. Diamond Air Service Co. Toyoyama, Aichi, is greatly acknowledged for carrying out the microgravity flights.

References

1. Vanderhoff JW, El-Aasser MS, Micale FJ, et al. (1986) PMSE Proc Am Chem Soc Div Polym Mater Sci Eng 54:587
2. Microgravity polymers (1986) NASA Conference Publication C-2392, Cleveland, Ohio, June 1985
3. Briskman V, Kostarev K, Leontyev V, Levkovich M, Mashinsky A, Nechitailo G (1977) In: Proceedings of the 48th International Astronaut. Congress Turin, Italy., International Astronaut Federation, pp 1–13
4. Okubo T, Tsuchida A, Okuda T, Fujitsuna K, Ishikawa M, Morita T, Tada T (1977) Parabolic flight (reports of microgravity experiments by air craft, NASDA), 7(No. 4):7
5. Okubo T, Tsuchida A, Okuda T, Fujitsuna K, Ishikawa M, Morita T, Tada T (1998) Colloids Surfaces (in press)
6. Okubo T, Tsuchida A, Yoshimi H, Maeda H (1999) Colloid Polym Sci (in press)
7. Okubo T, Kobayashi K, Kuno A, Tsuchida (1999) Colloid Polym Sci 277: 483–487