Colloid Polym Sci (2007) 285:967–975
DOI 10.1007/s00396-007-1642-8

ORIGINAL CONTRIBUTION

Sedimentation and drying dissipative patterns of colloidal silica (305 nm in diameter) suspensions in a glass dish and a watch glass

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Received: 2 October 2006 / Accepted: 26 December 2006 / Published online: 7 February 2007

Abstract Sedimentation and drying dissipative structural patterns formed in the course of drying colloidal silica spheres (305 nm in diameter) in aqueous suspension have been studied in a glass dish and a watch glass. The broad ring sedimentation patterns formed within several tenth minutes in suspension state by the convectional flow of water and colloidal spheres. The sedimentary spheres always moved by the convectional flow of water, and the broad ring patterns became sharp with time. The width of the broad rings was sensitive to the change in the room temperature and/or humidity. In other words, the patterns became sharp or vague when the room parameters decreased or increased. Colorful macroscopic drying structures were composed of a broad ring and the wave-formed patterns. Iridescent colored fine patterns formed in the solidification processes on the bases of the sedimentation patterns. Beautiful drying patterns were observed for the suspension mixtures of CS300 and NaCl, and were different from the structures of CS300 or NaCl individuals, which support the synchronous cooperative interactions between the colloidal spheres and the salt.

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Keywords Sedimentation dissipative structure · Drying dissipative structure · Colloidal silica spheres · Broad ring pattern · Wave-like pattern

Introduction

Generally speaking, most structural patterns in nature form via self-organization accompanied with the *dissipation* of free energy and in the nonequilibrium state. Among several factors in the free energy dissipation of aqueous colloidal suspensions, evaporation of water molecules at the air–water interface and the gravitational convection are very important. To understand the mechanisms of the dissipative self-organization of the simple model systems instead of the much complex nature itself, the authors have studied the *convectional*, *sedimentation*, and *drying* dissipative patterns of colloidal suspensions as systematically as possible.

Drying dissipative patterns have been studied for suspensions and solutions of many kinds of colloidal particles [1–13], linear-type polyelectrolytes [14], polymers [15, 16], ionic and nonionic detergents [17–19], and gels [20] mainly on a cover glass. The macroscopic broad ring patterns of the hill accumulated with the solutes in the outside edges always formed. For the nonspherical particles the round hill was formed in the center area in addition to the broad ring. Macroscopic spoke-like cracks or fine hills including flickering spoke-like ones were also observed for many solutes. The convection of water and the solutes at the different rates under gravity and the translational Brownian movement of the latter were important for the macroscopic pattern formation. Furthermore, beautiful fractal patterns such as branch-like, arc-like, block-like, star-like, cross-like, and string-like ones were observed in the microscopic scale. These microscopic drying patterns

were reflected from the *shape*, *size*, and/or *flexibility* of the solutes themselves. Microscopic patterns also formed by the translational Brownian diffusion of the solutes and the electrostatic and/or the hydrophobic interactions between solutes and/or between the solutes and the substrate in the course of the solidification. One of the very important findings in our experiments is that the primitive vague patterns were formed already in the concentrated suspensions or solutions before dryness and they grew toward fine structures in the process of solidification.

Quite recently, *sedimentation* dissipative patterns in the course of drying suspensions of colloidal silica spheres (1.2 μm in diameter) and green tea (Ocha) have been studied in a glass dish, a watch glass, and others [21–23]. The broad ring patterns were formed within several 10 min in suspension state by the convectional flow of water and the colloidal particles. The sedimentary particles were suspended above the substrate and always moved by the external force fields including convectional flow.

Convectional dissipative structures, which were formed in the initial course of dryness, were studied for the Chinese black ink and the 100% ethanol suspensions of colloidal silica spheres in our laboratory [10, 24]. Vigorous cell convectional flow was observed with the naked eyes, and the convectional patterns changed dynamically with time. The existence of the small circle-like *cell convections* proposed by Terada et al. [25–27], for the first time, was strongly supported.

In this work, sedimentation and drying dissipative patterns of colloidal crystals of silica spheres (350 nm in diameter) have been studied in the macroscopic and microscopic scales. Main purposes of this work are the clarification of the colloidal size effect on the dissipative patterns and the understanding of the dynamics of the sedimentary particles in suspension state.

Experimental

Materials

CS300 silica spheres were kindly donated from Catalysts and Chemicals Ind. (Tokyo). The diameter, standard deviation from the mean diameter, and the polydispersity index of the spheres were 305, 9.1, and 0.030, respectively. These size parameters were determined on an electron microscope in Gifu University. The spheres were carefully purified by repeated decantation more than thirty times. Then the sample was treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, AG501-X8(D), 20-50 mesh] for 6 years before use because newly produced silica spheres always released a considerable amount of alkali ions from the porous sphere surfaces for a long time. Water used for the sample purification and preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA, USA). Standard aqueous solution of sodium chloride at 0.1 mol/l (M) was purchased from Wako Chemicals (Osaka).

Observation of the dissipative structures

Ten or 4 ml of the aqueous suspension of CS300 spheres was put carefully and gently into a glass dish (42 mm in inner diameter and 15 mm in height, code 305-02, TOP, Tokyo) or a medium size watch glass (70 mm in diameter, TOP, Tokyo), respectively. Observation of the sedimentation and drying patterns was made for the suspensions set on a desk until the suspensions were dried up completely in a room air-conditioned at 27 °C. The humidity of the room air of the laboratory was between 64–69%, which was not regulated. Concentrations of CS300 and NaCl ranged from 0.00038 to 0.0152 in volume fraction and from 0.0001 to 0.03 M, respectively.

Macroscopic dissipative structures were observed on a Canon EOS 10D digital camera (Canon, Tokyo) with a lens (EF 28–200 mm, f=3.5–5.6 USM, Canon). Microscopic structures were observed with a metallurgical microscope (PME-3, Olympus, Tokyo). Reflection spectra of the dried film were recorded on a High-sensitivity Spectro Multichannel Photo-detector (MCPD-7000 G3, Otsuka Electronics, Osaka).

Results and discussion

Sedimentation and drying dissipative patterns in a glass dish

Figure 1 shows the sedimentation (a to e) and drying patterns (f) of CS300 spheres when sphere concentration is very low, 0.00038 in volume fraction. Clearly, broad ring patterns were observed within several 10 min for the suspensions without cap in the suspension phase, and the suspensions dried up after 8.4 days. It should be recalled that the broad ring patterns did not appear in a dish with cap for colloidal silica spheres, 1.2 μm in diameter [21]. Ten milliliter of the aqueous suspensions of CS300 silica spheres at 0.00228 in volume fraction, in a glass dish with a cap was dried up after 110 days at room temperature. The same suspension without cap was dried up after 8.4 days as is shown in Fig. 1f. In suspension state with cap they also exhibited the broad ring patterns, and dried film showed very strong iridescent colors. These results show that the shielding effect of a glass dish with a cap was not so complete for preventing the evaporation of water. However, evaporation and the resulted convectional flow were

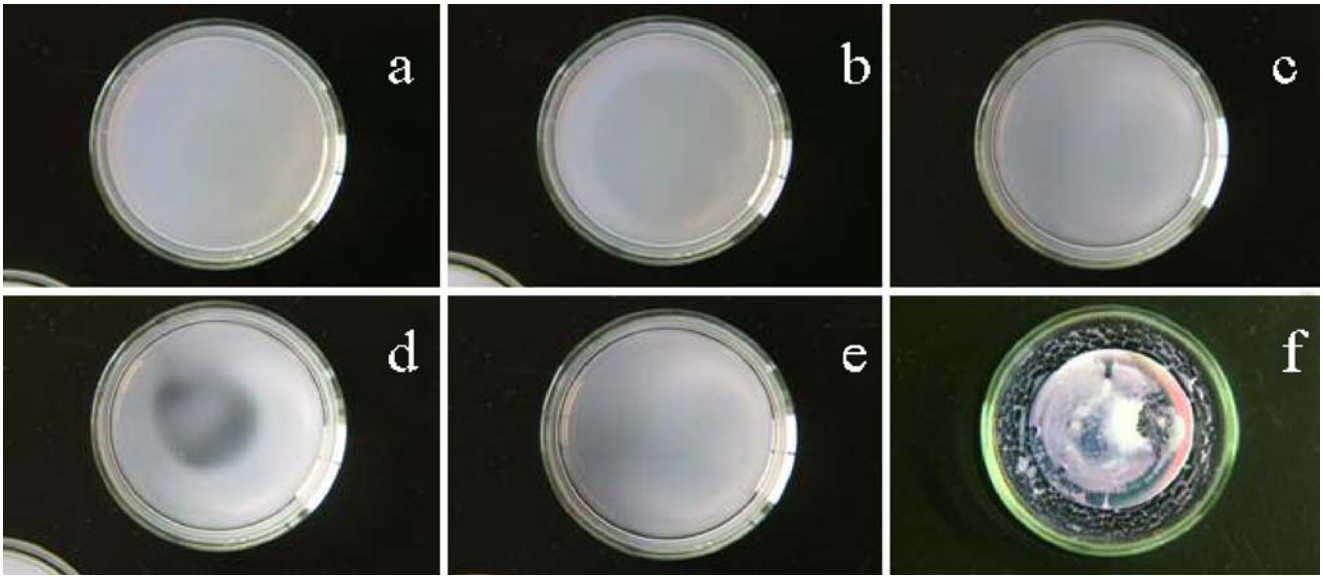

Fig. 1 Sedimentation and drying patterns of CS300 silica suspensions in a watch glass at 27 °C. ϕ=0.00038, 10 ml, code 241, (**a**) after 20 min, (**b**) 2 h, (**c**) 19.3 h, (**d**) 29.5 h, (**e**) 45 h, and (**f**) 8.4 day, dry

retarded efficiently with a cap. It should be noted that the broad rings formed rather quickly within several tenth minutes after suspension was set and even in the stage of the incomplete sedimentation of spheres, which shows the convections of water and spheres are vigorous even at room temperature.

A main cause for the broad ring formation is due to the convectional flow of water and CS300 spheres in the different rates, where the rate of the latter is slower than that of the former under gravity. Especially, flow of the spheres from the center area toward the outside edges in the lower layers of the liquid, which was observed on a digital HD microscope directly from the movement of the very rarely occurred aggregates of the colloidal particles of Chinese black ink in a glass dish, is important [10]. Clearly, the convectional flow is enhanced by the evaporation of water at the liquid surface, resulting to lowering of the suspension temperature in the upper region of the suspension. When the colloidal spheres reach the edge wall of the dish at the outside region of the liquid, a part of the spheres will turn upward and go back to the center region. However, many large and heavy spheres may drop downward on the cell bottom close to the outside cell wall, where the effective horizontal flow of the spheres may stop temporarily. This process must be followed by the broad ring accumulation of the spheres near the round outside edges.

It should be noted here that the formation of the broad ring patterns in the liquid phase reported in this study were observed first in a previous paper from the author's laboratory [22] as the author knows. However, the broad ring formation in the dried film has been observed so often for most of the solutions and suspensions examined by our group [7–14, 16–24] and further by other researchers [1–6]. Recently, microgravity experiments were made for the observation of the drying dissipative patterns of deionized suspension of colloidal silica spheres [28]. Surprisingly, the broad ring patterns did not disappear even in microgravity. This supports strongly that both the gravitational and the Marangoni convections contribute to the broad ring formation on earth, and the latter is still important in microgravity.

We should note further that the broad ring patterns, which were generally observed for all the drying patterns of suspensions and solutions including the present paper, were formed already in the process of convectional flow of water and solutes in suspension state. The broad ring sedimentation structures have been observed also in a polystyrene dish [21], in a watch glass [22], and even in a deep bowl [23] in our laboratory.

Figure 2 shows the macroscopic drying patterns of CS300 spheres in a glass dish at the initial sphere concentrations ranging from 0.00038 to 0.0152 in volume fraction 8.4 days after the suspensions were set. The macroscopic drying patterns were a bit different from those on a cover glass. The broad rings formed at the outside edges of the dried film, but within the inner wall of the glass dish. The size of the broad ring increased as the initial sphere concentration increased as clearly shown in the figure. All the dried films were colorful with the iridescent Bragg diffraction of light by the crystal-like array of the colloidal spheres in the film. Figure 2 also shows that the spoke-like fine cracks appeared especially in the areas of the broad rings. It is interesting to note that the wave-shaped beautiful and fine structures formed in the areas between the outside edges of the film and the inner-wall of the glass dish. It should be mentioned in this study that the

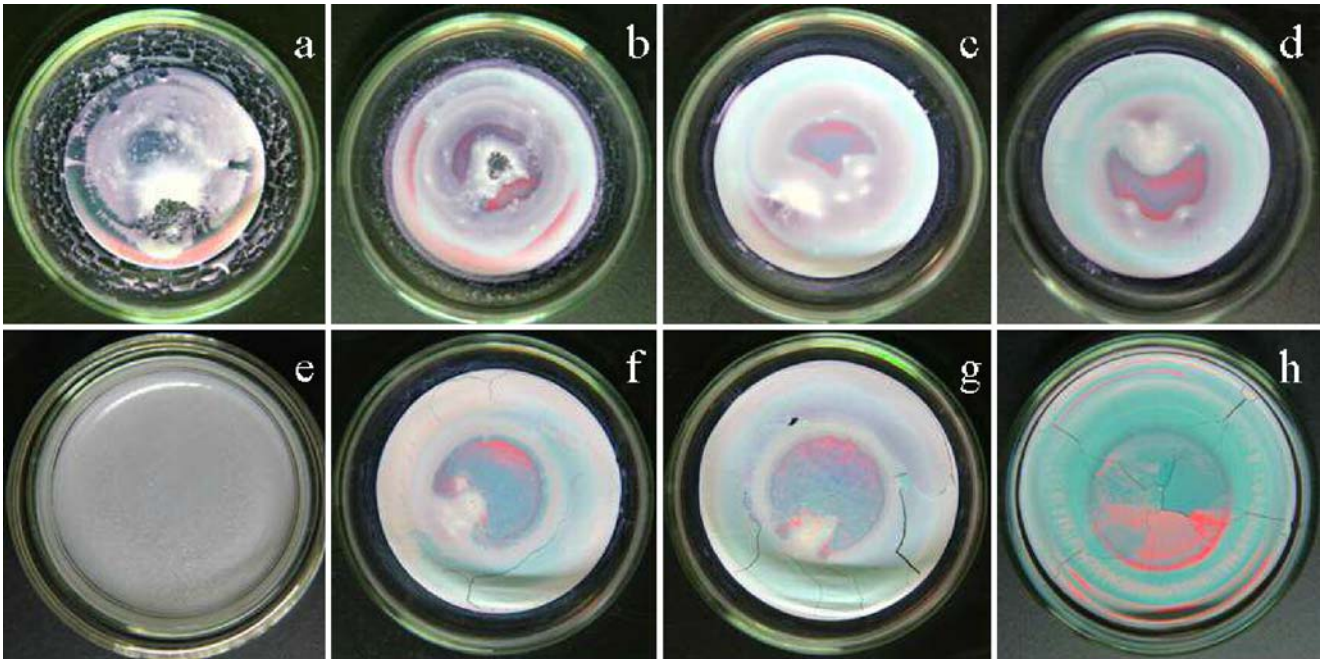

Fig. 2 Drying patterns of CS300 silica suspensions in a glass dish at 27 °C. 10 ml, after 8.4 days, dry, (**a**) ϕ=0.00038, (**b**) 0.00076, (**c**) 0.00152, (**d**) 0.00228, (**e**) 0.00228, with cap, (**f**) 0.00455, (**g**) 0.0076, and (**h**) 0.0152

drying frontier started at the center of the glass dish and moved toward the outer cell wall with time. This direction of the frontier movement was just opposite to that on a cover glass, where the frontier moved from the outside edges of suspension to the center [7, 8, 11].

Figure 3 shows the macroscopic drying patterns of CS300 suspensions in the presence of NaCl and in their absence at the dried state, 98.7 h after suspensions were set. Distinct differences were not observed among the broad ring patterns in the suspension state containing different amounts of sodium chloride, though the pictures showing these were omitted in this paper. However, it looks with the naked eyes that the broad rings were slightly sharp for the salt containing suspensions. The electrical double layers around the spheres are thin when the ionic concentration is high. Thus, the translational diffusion of the spheres will be much vigorous because the effective size of spheres including the double layers decreases. Macroscopic drying broad-ring patterns were observed clearly for all the samples and size of the broad ring increased as the salt

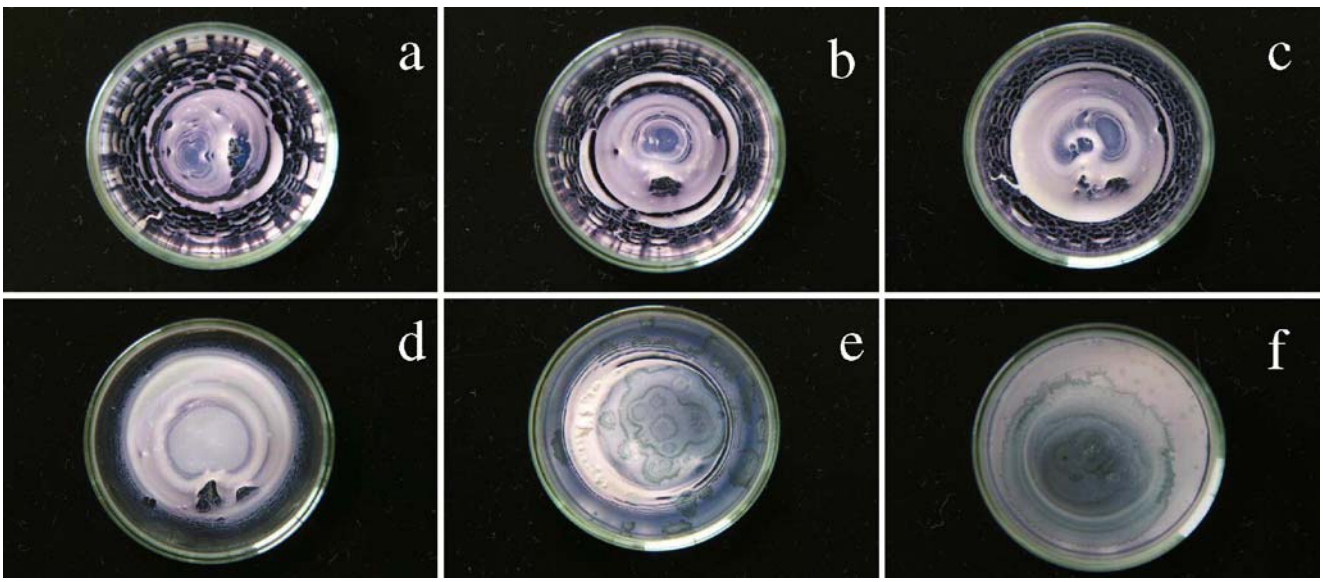

Fig. 3 Drying patterns of CS300 silica suspensions in a glass dish at 27 °C. ϕ=0.00038, 10 ml, 98.7 h, dry, (**a**) [NaCl] = 0 M, (**b**) 0.0001 M, (**c**) 0.0003 M, (**d**) 0.001 M, (**e**) 0.003 M, and (**f**) 0.01 M

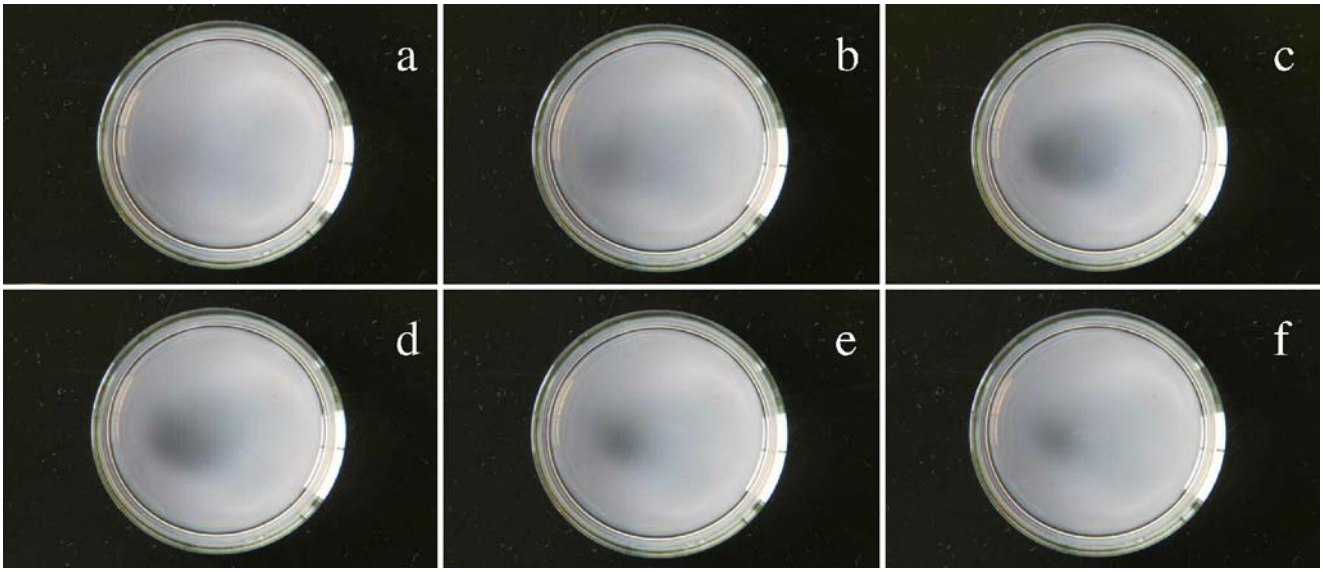

Fig. 4 Change in the sedimentation patterns of CS300 silica suspensions in a glass dish 45 h after setting at 27 °C. ϕ=0.00038, 10 ml, code 241, (**a**) 0 min, 27.0 °C, 67%, ON, (**b**) 15 min, 26.6 °C, 65 %, (**c**) 35 min, 25.5 °C, 61 %, (**d**) 45 min, 25.2 °C, 60%, OFF, (**e**) 67 min, 25.2 °C, 63%, and (**f**) 70 min, 25.1 °C, 66%

concentration increased as is clear in the figure. Surprisingly, quite different macroscopic patterns appeared for the suspensions containing sodium chloride higher than 0.001 M. Furthermore, the cooperative microscopic structures were also observed for CS300 spheres as was observed for CS1000A spheres [21], which will be

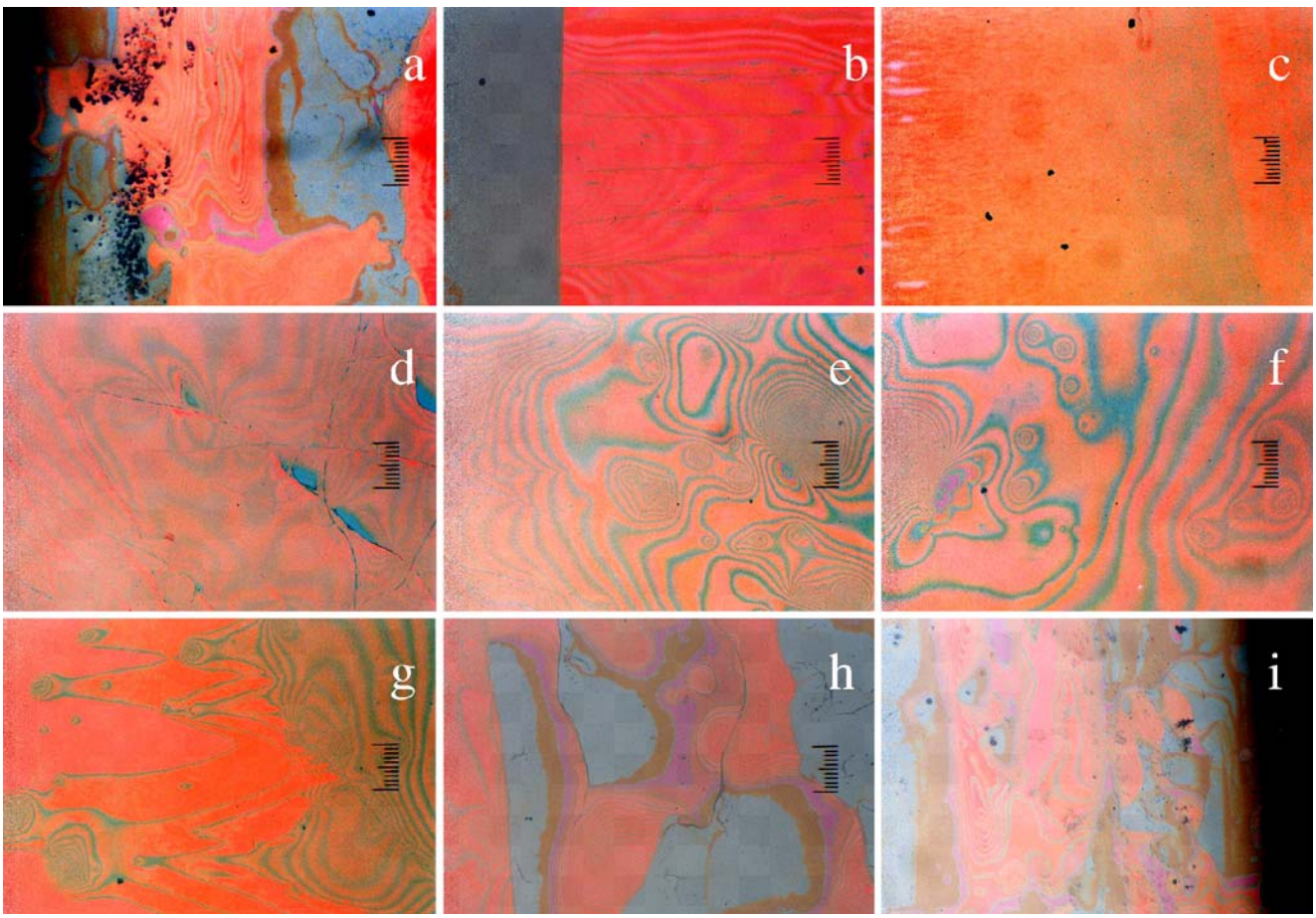

Fig. 5 Microscopic drying patterns of CS300 silica suspensions in a glass dish at 27 °C. ϕ=0.00038, 10 ml, dry, code 241, from left edge (**a**) to right (**i**), full scale=0.2 mm

described in detail below using the microscopic pictures shown in Fig. 6.

Figure 4 shows the sedimentation patterns of the deionized suspensions of CS300 spheres, when the temperature and the humidity changed by keeping switch of the compressor on or off. The experiments started 45 h after the suspensions were set, where the stable sedimentation state was achieved. After the picture was taken at 27 °C and 68% in humidity, the switch of the compressor was kept on. After 15, 35, and 45 min, pictures b, c, and d were taken. At these times, the values of the room temperature and humidity decreased to 26.6 °C and 65%, 25.5 °C and 61%, and then 25.2 °C and 60%, and the sedimentation patterns became sharp with time. After taking picture d, the compressor was switched off. Now, the patterns became vague after 67 and 70 min, respectively, where the temperature and the humidity of the laboratory decreased only slightly and increased, respectively. The convectional flow of spheres and water should become fast, when the temperature and also humidity above the air-suspension interface decreases. Thus, it is supported strongly that the convectional flow of spheres and water is the main cause for the broad ring sedimentation pattern. It should be noted in this study that the slopes, not the absolute values, of the temperature and/or humidity with time are important for the rates of the convectional flows.

Figure 5 shows the microscopic patterns of the dried film observed in Fig. 1, where the extended pictures were taken from the left-hand side outside edge to the right-hand side. Beautiful and colorful microstructures were observed. These iridescent colors are due to the Bragg diffraction of light by the crystal array of the colloidal spheres in the dried film. It should be mentioned further that the main cause of the microstructures will be the traces of the convectional flow of spheres and water molecules on a glass dish.

Figure 6 shows the microscopic pictures of the dried film of CS300 spheres containing 0.01 M of sodium chloride. The macroscopic picture of the film was shown already in Fig. 3f. The black or bluish patterns in these pictures are composed of the silica spheres and the whitish patterns are sodium chloride salt. These beautiful branch-like patterns demonstrate clearly that the synchronous cooperative interactions between the spheres and the salt molecules in the processes of solidification of the solutes play an important role for the pattern formation.

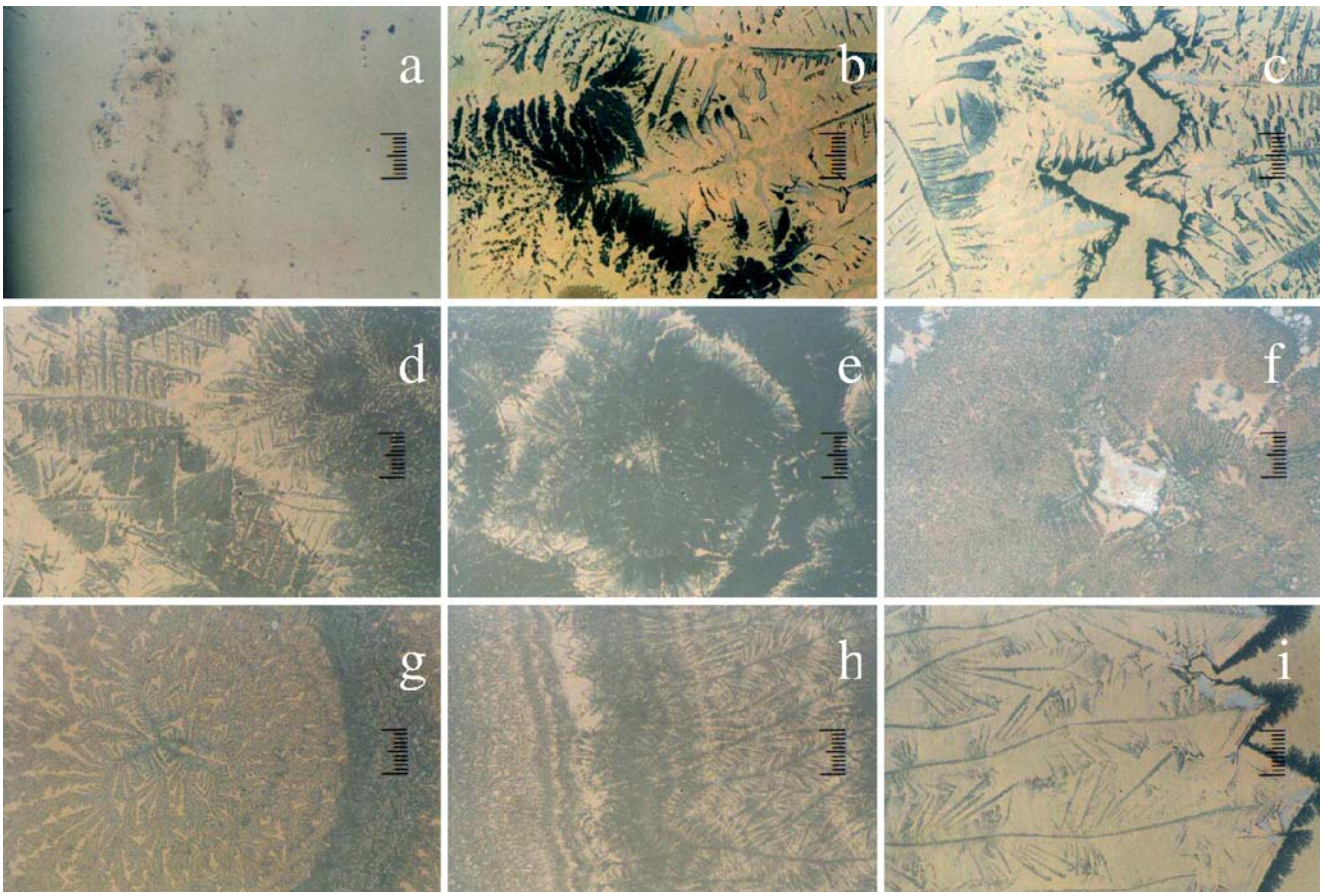

Fig. 6 Microscopic drying patterns of CS300 silica suspensions in a glass dish at 27 °C. ϕ=0.00038, [NaCl] = 0.01 M, 10 ml, dry, code 257, from left edge (**a**) to right (**i**), full scale=0.2 mm

Table 1 Reflection peak wavelengths (λ_p) and the nearest-neighbored intersphere distances (D) of the dried film from the reflection spectroscopy

Code	ϕ	[NaCl]	λ_p (nm)	D (nm)
241	0.000380	0	660	300
242	0.00076	0	652	292
243	0.00152	0	649	290
244	0.00228	0	647	289
246	0.00455	0	633	283
247	0.0076	0	629	281
248	0.0152	0	624	279
251	0.000380	0	661	301
252	0.000380	0.0001	700	313
253	0.000380	0.0003	658	294
254	0.000380	0.0005	647	289
256	0.000380	0.003	660 (broad)	300
257	0.000380	0.01	640 (broad)	290
258	0.000380	0.03	630 (broad)	280

Table 1 compiles the peak wavelengths (λ_p) of the reflection spectra of the dried films without and with sodium chloride and the nearest-neighbored intersphere distance (D) estimated. The D values were estimated from λ_p and using Eq. 1 [29, 30].

$$D = 0.6124\lambda_p/n \quad (1)$$

$$n = [\text{refractive index of silica}] \times 0.74 + [\text{refractive index of air}] \times 0.26 \quad (2)$$

In this study, refractive indices of silica and air were assumed to be 1.5 and 1.00, respectively. The reflection spectra of the dried film without salt and with salt lower than 0.0005 M of NaCl at the initial suspension state were sharp, though the graphs demonstrating these were omitted

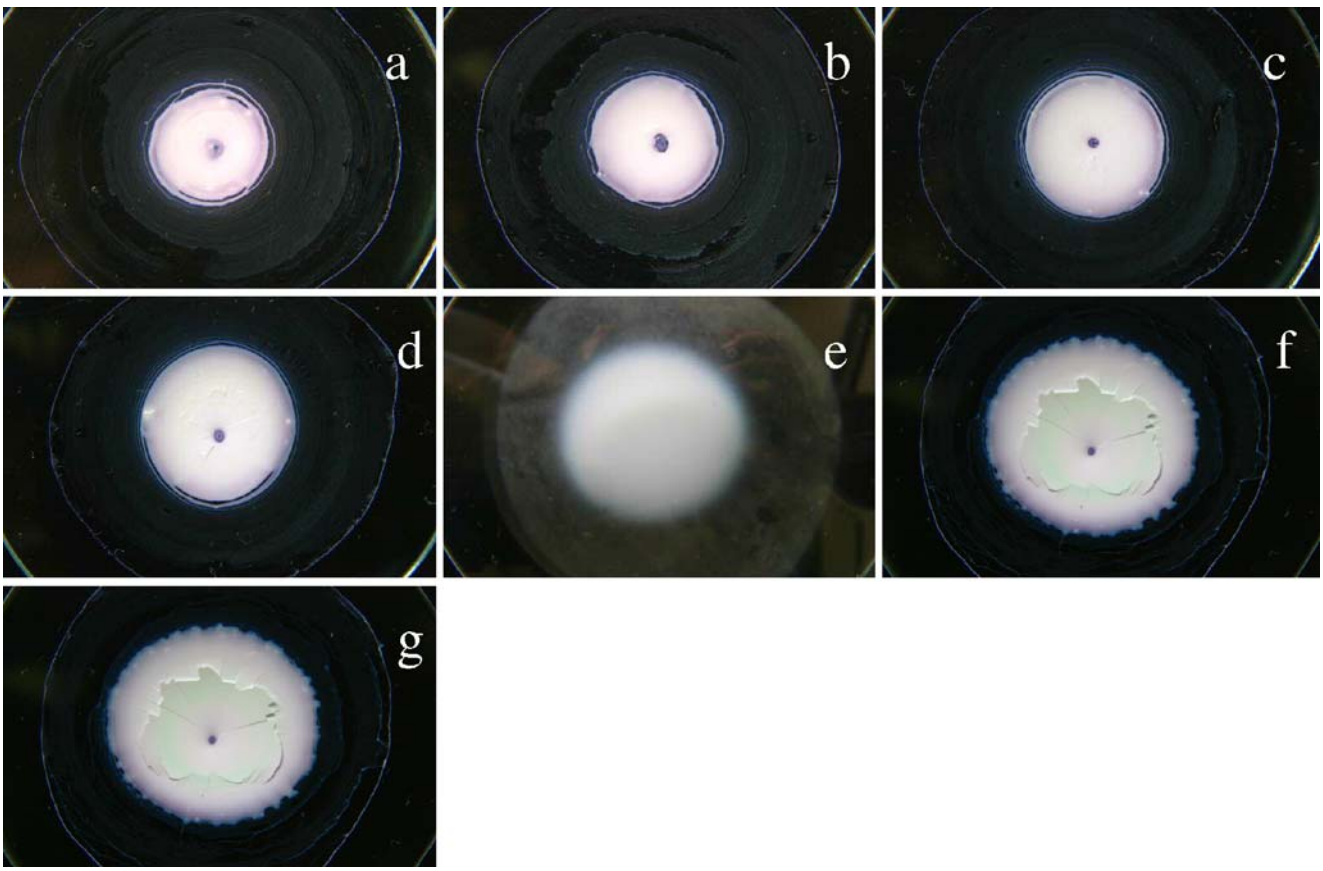

Fig. 7 Drying patterns of CS300 silica suspensions in a watch glass at 27 °C. 4 ml, 23.8 h after setting, dry except (**e**), (**a**) ϕ=0.00038, (**b**) 0.00076, (**c**) 0.00152, (**d**) 0.00228, (**e**) 0.00228 with cap, (**f**) 0.0046, and (**g**) 0.0076

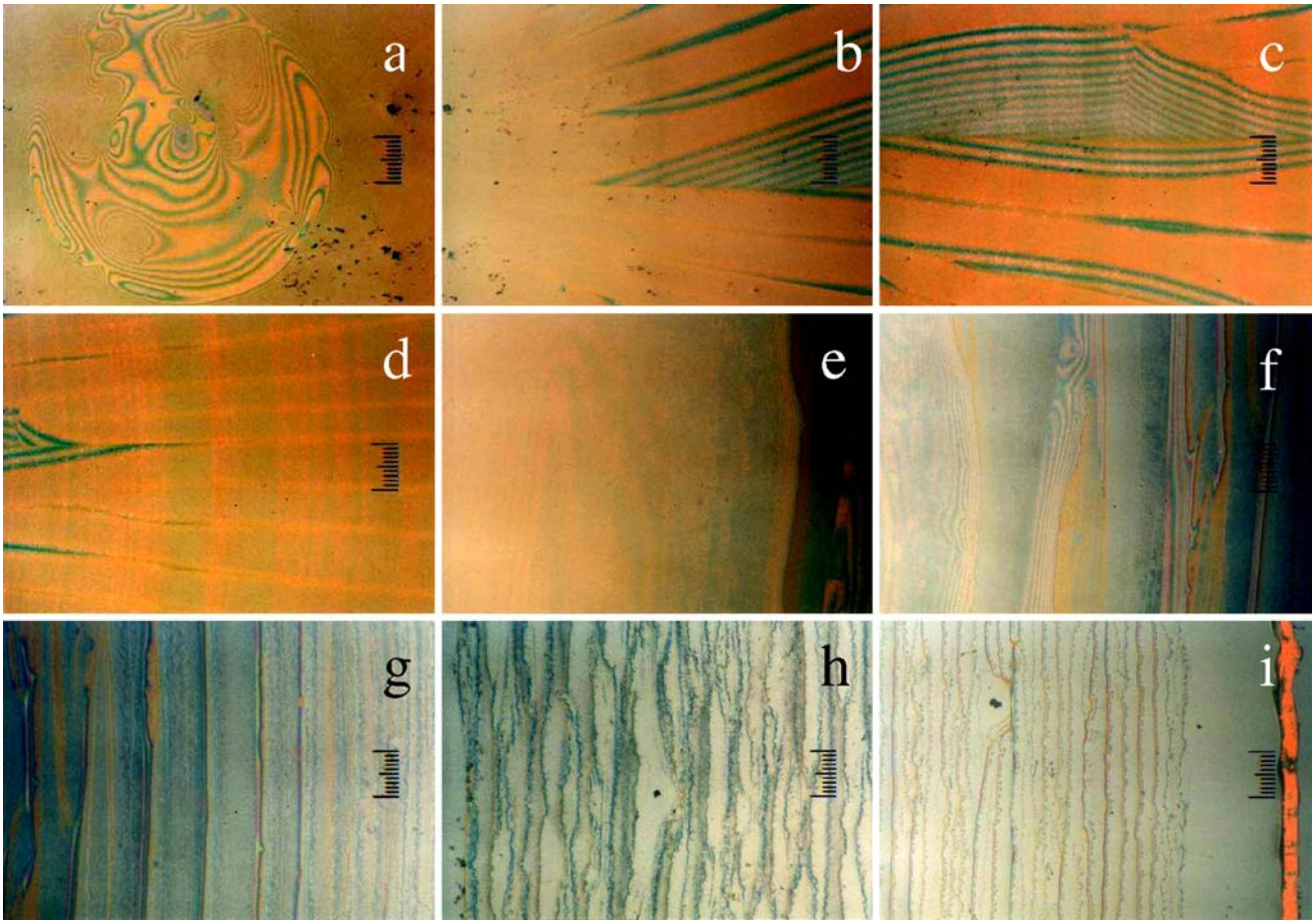

Fig. 8 Microscopic drying patterns of CS300 silica suspensions in a watch glass at 27 °C. ϕ=0.00152, 4 ml, dry, code 263, from center (**a**) to right edge (**i**), full scale=0.2 mm

in this article. This supports that the films are composed with the crystal arrays of CS300 spheres even in the presence of a tiny amount of salt. The reflection peaks of the films from the suspensions containing NaCl higher than 0.003 M were broad. These salt effects show that the crystal structures remained but distorted slightly by a large amount of salt. It should be noted in this study that the D values were very close to the diameter of CS300 spheres, 305 nm, which indicates the neighbored spheres almost contact each other. The spheres in the dried film have been reported to distribute in the closest-packed structure from the transmitted-light intensity measurements [29]. λ_p values and then D values shifted toward the shorter wavelengths as the initial sphere concentrations increased. This supports the idea that the nearest-neighbored spheres contact each other more tightly as the sphere concentration increases by the thinning effect of the electrical double layers formed around the spheres with increasing sphere concentration. Slight decrease in the D values by the addition of sodium chloride and the distortion of the crystal structures are also explained beautifully by the thinning of the double layers with salt addition. It should be mentioned in this study that the refractive indices of the dried film containing sodium chloride were assumed to be the same as that of the film containing no salt.

Sedimentation and drying dissipative patterns in a watch glass

When the colloidal suspension of CS300 spheres was kept still in a watch glass, sedimentation of the spheres took place within 2 h especially at the upper layers of suspension and a broad ring pattern was observed clearly at the central area of the watch glass with the naked eyes. The suspensions dried up after 23.8 h, though the pictures showing the course of dryness were omitted in this report. A main cause for the broad ring formation is again the convectional flow of water and CS300 spheres in the different rates and due to the evaporation of water from the outer edges. The flow of spheres from the center area toward the outside edges in the lower layer of the liquid is especially important [10]. Enhancement of the convectional flow by the evaporation of water must be followed by the broad ring accumulation of the spheres near the round outside edges.

Figure 7 shows the drying patterns of CS300 suspensions without cap shielding (a to d and f to g) and with cap (e) at different sphere concentrations from 0.00038 to 0.0076 in volume fraction. These pictures show clearly that the sphere accumulation at the deepest central point did not take place compared with the upper colorful broad ring area. Picture 7e shows the pattern when the same suspension as Fig. 7d was capped with the reversed large watch glass and 23.8 h after suspension was set. During 23.8 h, the colloidal spheres in the capped watch glass sedimented and moved toward central area. However, the broad ring patterns, which were observed in the uncapped watch glass, did not appear as is clearly shown in Fig. 7e. Comparison of the patterns between capped and uncapped experiments support the fact that strength of the convectional flow of spheres and water without cap is not strong enough to prevent the sedimentation of the spheres along the sloped wall of the watch glass, but certainly strong enough to make broad ring patterns with a vacant hole of the spheres in the center.

Figure 8 shows the microscopic pictures of the drying patterns of CS300 suspensions at ϕ=0.00152 from the central area (a) to right-hand side edge (i). Three different types of patterns appeared from the central area to the outside edge regions, (1) round fine circle-like patterns (a), (2) spoke-like patterns in the radial direction (b and c), and (3) multistrings circle-like patterns (e to i). It should be noted that the patterns of type (3) were observed for the suspensions of the large silica spheres (1.2 μm in diameter) in a watch glass [22]. These three types of the microstructures support the existence of the three different modes of convectional flows of water and solutes as a function of the distance from the center of the watch glass. It should be noted again that the iridescent and colored pictures are due to the Bragg diffraction of light by the crystal array of CS300 spheres in the dried film.

Acknowledgments Financial supports from the Ministry of Education, Culture, Sports, Science and Technology, Japan and Japan Society for the Promotion of Science are greatly acknowledged for Grants-in-Aid for Exploratory Research (17655046) and Scientific Research (B) (18350057 and 16350124), respectively. Catalysts and Chemicals is thanked deeply for his providing the colloidal silica sphere samples used in this work.

References

1. Vanderhoff JW (1973) J Polymer Sci Polym Symp 41:155
2. Nicolis G, Prigogine I (1977) Self-organization in non-equilibrium systems. Wiley, New York
3. Ohara PC, Heath JR, Gelbart WM (1997) Angew Chem 109:1120
4. Maenosono S, Dushkin CD, Saita S, Yamaguchi Y (1999) Langmuir 15:957
5. Nikoobakht B, Wang ZL, El-Sayed MA (2000) J Phys Chem 104:8635
6. Ung T, Litz-Marzan LM, Mulvaney P (2001) J Phys Chem B 105:3441
7. Okubo T, Okuda S, Kimura H (2002) Colloid Polym Sci 280:454
8. Okubo T, Kimura K, Kimura H (2002) Colloid Polym Sci 280:1001
9. Okubo T, Kanayama S, Kimura K (2004) Colloid Polym Sci 282:486
10. Okubo T, Kimura H, Kimura T, Hayakawa F, Shibata T, Kimura K (2005) Colloid Polym Sci 283:1
11. Okubo T, Yamada T, Kimura K, Tsuchida A (2005) Colloid Polym Sci 283:1007
12. Yamaguchi T, Kimura K, Tsuchida A, Okubo T, Matsumoto M (2005) Colloid Polym Sci 283:1123
13. Okubo T, Nozawa M, Tsuchida A (2006) Colloid Polym Sci (in press). DOI 10.1007/s00396-006-1626-0
14. Okubo T, Kanayama S, Ogawa H, Hibino M, Kimura K (2004) Colloid Polym Sci 282:230
15. Shimomura M, Sawadaishi T (2001) Curr Opin Colloid Interface Sci 6:11
16. Okubo T, Yamada T, Kimura K, Tsuchida A (2006) Colloid Polym Sci 284:396
17. Okubo T, Kanayama S, Kimura K (2004) Colloid Polym Sci 282:486
18. Kimura K, Kanayama S, Tsuchida A, Okubo T (2005) Colloid Polym Sci 283:898
19. Okubo T, Shinoda C, Kimura K, Tsuchida A (2005) Langmuir 21:9889
20. Okubo T, Itoh E, Tsuchida A, Kokufuta E (2006) Colloid Polym Sci 285:339
21. Okubo T (2006) Colloid Polym Sci 284:1395
22. Okubo T (2006) Colloid Polym Sci 284:1191
23. Okubo T (2006) Colloid Polym Sci 285:331
24. Okubo T (2006) Colloid Polym Sci 285:225
25. Terada T, Yamamoto R, Watanabe T (1934) Sci Pap Inst Phys Chem Res (Japan) 27:173, Proc Imper Acad Tokyo 10:10
26. Terada T, Yamamoto R, Watanabe T (1934) Sci Pap Inst Phys Chem Res (Japan) 27:75
27. Terada T, Yamamoto R (1935) Proc Imp Acad (Tokyo) 11:214
28. Tsuchida A, Okubo T (2003) Sen'I Gakkaishi 59:264
29. Okubo T (1986) J Chem Soc Faraday Trans 1(82):3175
30. Okubo T (1986) J Chem Soc Faraday Trans 1(82):3185