Colloid Polym Sci (2008) 286:1527–1535
DOI 10.1007/s00396-008-1927-6

ORIGINAL CONTRIBUTION

Sedimentation and drying dissipative patterns of colloidal crystals of poly(methyl methacrylate) spheres in a glass dish

Tsuneo Okubo

Received: 27 July 2008 / Revised: 27 August 2008 / Accepted: 30 August 2008 / Published online: 13 September 2008

Abstract In a series of our studies on the dissipative structure formation, this work focused on the sedimentation and drying patterns of colloidal crystals of poly(methyl methacrylate) colloidal spheres with different sizes (100, 200, 300, and 1,000 nm in diameter) in a glass dish. During the course of dryness, the brilliant iridescent colors changed. Drying frontier grew from the central area of the cell toward the outside edge. Macroscopic and microscopic drying patterns of the resulting film from dried colloidal suspensions showed outer and inner broad rings. Size of the outer rings increased with increasing sphere concentration but did not altered sphere size, while these factors affected the inner ring size. These observations do not support the pinning effect proposed by Deegan et al.

Keywords Poly(methyl methacrylate) colloids · Glass dish · Sedimentation pattern · Drying pattern · Dissipative structure · Broad ring

Introduction

In general, most structural patterns in nature form via self-organization accompanied with the dissipation of free energy and in the non-equilibrium 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. In order 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 in the course of dryness of colloidal suspensions as systematically as possible, though the three kinds of patterns are correlated strongly and overlapped to each other.

The most famous convectional pattern is the hexagonal circulating ones, the Bernard cell, and has been observed when liquids contain plate-like colloidal particles as monitors and were heated homogeneously in a plain pan [1–3]. Another typical convectional dissipative pattern is the spoke-like one, observed in the Bernard cells, and also appeared in various substrates sometimes accompanied with the huge number of small cell convections. The spoke patterns with cell convections were observed formerly for the membranes of Chinese black ink on water by Terada et al. [4–7]. The author likes to call the spoke-like pattern as Terada cell. The convectional patterns, especially Terada cells, were observed directly in the initial course of dryness of the Chinese black ink in a glass dish [8], the 100% ethanol suspensions of colloidal silica spheres [9], a cup of miso soup (Okubo T, manuscript in preparation), coffee [10] (Okubo T, manuscript in preparation), or black tea (Okubo T, manuscript in preparation) and colloidal crystals of poly(methyl methacrylate) (PMMA) spheres on a cover glass and a watch glass [11, 12] in our laboratory. Distorted Bernard cells were often observed for miso soup, coffee, and black tea. For the 100% ethanol suspensions of colloidal silica spheres, Terada cell-type vigorous convectional flow was observed clearly with the naked eye, and the convectional patterns changed dynamically with time.

T. Okubo (✉)
Institute for Colloidal Organization,
Hatoyama, 3-1-112, Uji,
Kyoto 611-0012, Japan
e-mail: okubotsu@ybb.ne.jp

T. Okubo
Cooperative Research Center, Yamagata University,
Johnan 4-3-16,
Yonezawa 992-8510, Japan

Deegan et al. [10] have reported the traces of spoke-like patterns under a microscope. They introduced the capillary flow theory instead of the convectional flow of the liquid from the pinning effect of the contact line of the drying drop. From our series of drying experiments for suspensions and solutions, the pinning effect was not always supported for spherical colloidal suspensions on a cover glass. For anisotropic-shaped particles, broad ring at the outside edge disappeared and round hill appeared instead. The author believes that the convectional flow of solutes and solvent is essentially important for the dissipative pattern formation during the course of dryness. Furthermore, the pinning effect for the broad ring formation was not supported in a glass dish and a watch glass. It should be mentioned further that theoretical studies for the convectional patterns have been made mainly using Navier–Stokes equations, but these are not always successful yet [13–18]. The main cause for this is undoubtedly due to the insufficient experimental studies so far. It should be noted further that the size, shape, conformation, and/or flexibility information of particles and/or solutes (molecules) is transformed cooperatively and further accompanied with the amplification and selection into the succeeding sedimentation and drying patterns.

Sedimentation dissipative patterns in the course of drying suspensions of colloidal silica spheres (183 nm to1.2 μm in diameter) [19–24], size-fractionated bentonite particles [25], green tea (Ocha) [26], and miso soup (Okubo T, manuscript in preparation) have been studied in detail in a glass dish, a cover glass, a watch glass, and others, for the first time, in our laboratory. The broad ring patterns were formed within several 10 min in suspension state by the convectional flow of water and the colloidal particles. It was clarified that the sedimentary particles were suspended above the substrate and always moved by the external force fields, including convectional flow and sedimentation. The sharpness of the broad rings was sensitive to the change in the room temperature and/or humidity. The main cause for the broad ring formation is due to the convectional flow of water and colloidal particles at the different rates, where the rate of the latter is slower than that of the former. Quite recently, dynamic sedimentation patterns formed cooperatively from the distorted spoke-line convectional structures of colloidal particles were observed for coffee and black tea (Okubo T, manuscript in preparation).

Drying dissipative patterns have been studied for suspensions and solutions of many kinds of colloidal particles [8, 9, 11, 19–43] (Okubo T, manuscript in preparation), linear-type synthetic and bio-polyelectrolytes [44, 45], water-soluble neutral polymers [46, 47], ionic and non-ionic detergents [48–50], gels [51], and dyes [52] 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 non-spherical 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. Furthermore, fractal patterns such as branch-, arc-, block-, star-, cross-, 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 before dryness, and they grew toward fine structures in the process of solidification.

In this work, sedimentation and drying dissipative patterns of colloidal crystals of PMMA spheres in a glass dish have been studied in the macroscopic and microscopic scales. One of the main purposes of this work is the clarification of the colloidal size and concentration effects on the dissipative patterns in a glass dish. The other purpose is to compare the patterns in a glass dish with other substrates, a cover glass, and watch glass. The dryness starts from the central area in a glass dish, while drying frontiers on a cover glass and watch glass starts from the outside edge of the liquid. Furthermore, the author's group has studied morphology, crystallization kinetics, structures, and physico-chemical properties of colloidal crystals systematically hitherto [53–58]. However, colloidal crystals of PMMA spheres was not studied by our group and reported by the author quite recently [11, 12].

Experimental

Materials

PMMA spheres, GW1 (100±7 nm in diameter and polydispersity index), GW6 (200±10 nm), GW8 (300±12 nm), and PM1000 (1.0 μm±20 nm), were kindly donated from Soken Chemicals (Tokyo). These size parameters were determined on an electron microscope by the manufacturer. PM1000 spheres were carefully purified more than 30 times by decantation with pure water, since a large amount of the detergents used for sphere synthesis must be deleted from the stock suspension. Then, all the stock sample suspensions were treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, AG501-X8(D), 20–50 mesh] for more than 5 years before use. The stock suspensions from GW1 to PM1000 spheres thus obtained crystallized and emitted strong iridescent bluish to whitey colors, respectively. Water used for the sample preparation was purified by a Milli-Q

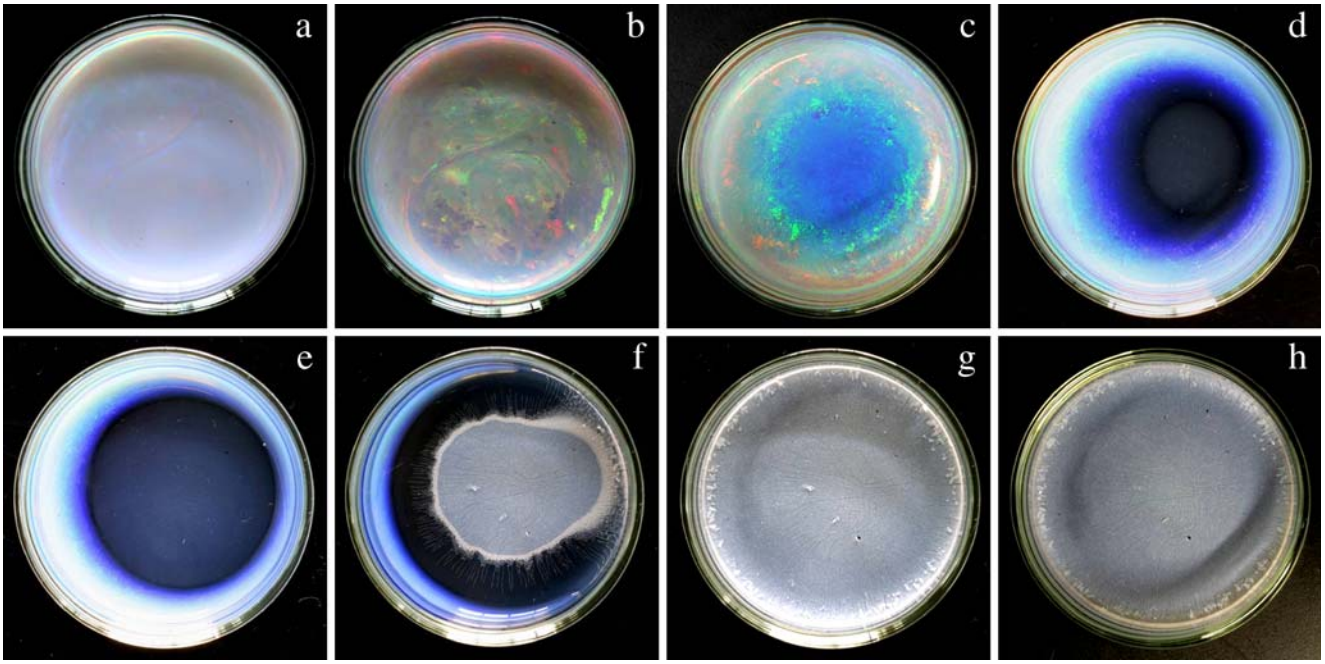

Fig. 1 Sedimentation and drying dissipative patterns of GW1 spheres in a glass dish at 26 °C. Code 576, ϕ=0.0318, 5 ml, **a** 20 min after setting, **b** 22 h and 20 m, **c** 32 h and 40 m, **d** 41 h and 40 m, **e** 45 h and 20 m, **f** 48 h and 30 m, **g** 52 h and 30 m, **h** 58 h

reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA, USA).

Observation of the dissipative structures

Five milliliters of the suspensions was put carefully and gently into a medium size glass dish (42 mm in inner diameter and 15 mm in height, code 305-02, TOP, Tokyo). A disposable serological pipet (10 ml, Corning Lab. Sci.) was used for putting the suspension in a glass dish. The sedimentation and drying patterns were observed for the suspensions on a desk covered with a black plastic sheet. The room temperature was regulated at 24 °C (for GW6 and GW8 suspensions), 25 °C (PM1000), or 26 °C (GW1).

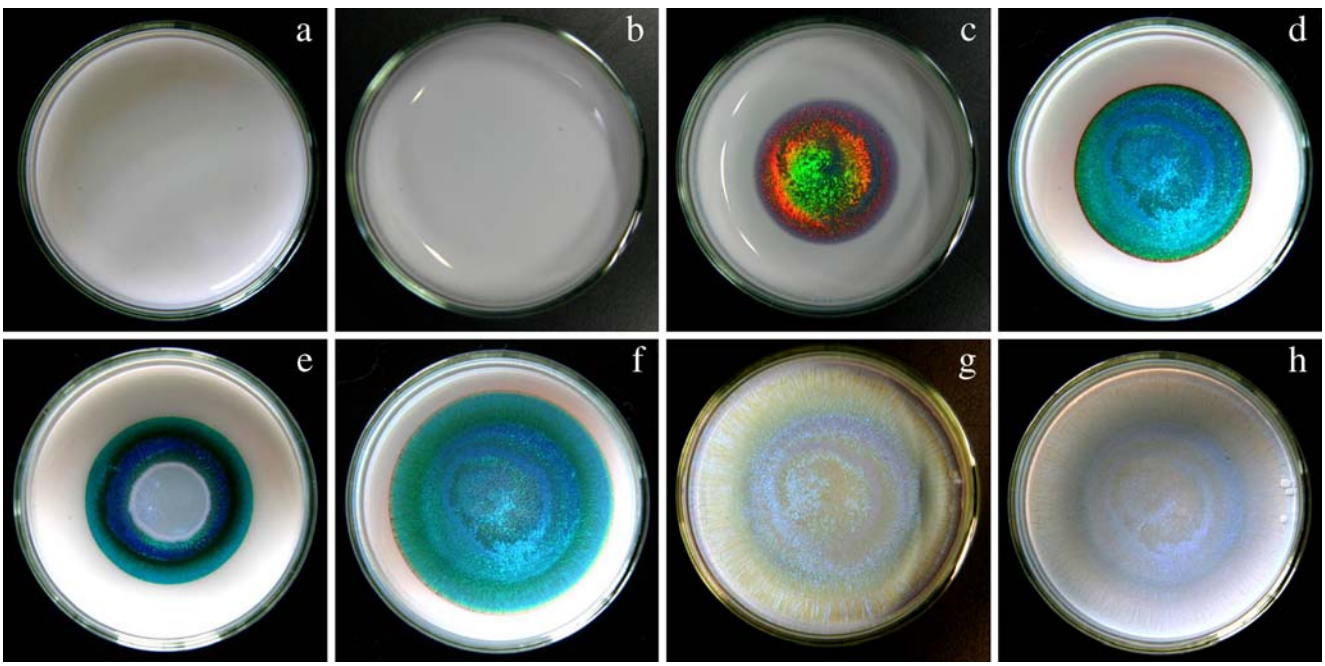

Fig. 2 Sedimentation and drying dissipative patterns of GW6 spheres in a glass dish at 24 °C. Code 487, ϕ=0.042, 5 ml, **a** 5 min after setting, **b** 4 h and 5 m, **c** 60 h and 10 m, **d** 64 h and 15 m, **e** 65 h and 55 m, **f** 68 h and 40 m, **g** 78 h and 55 m, **h** 89 h

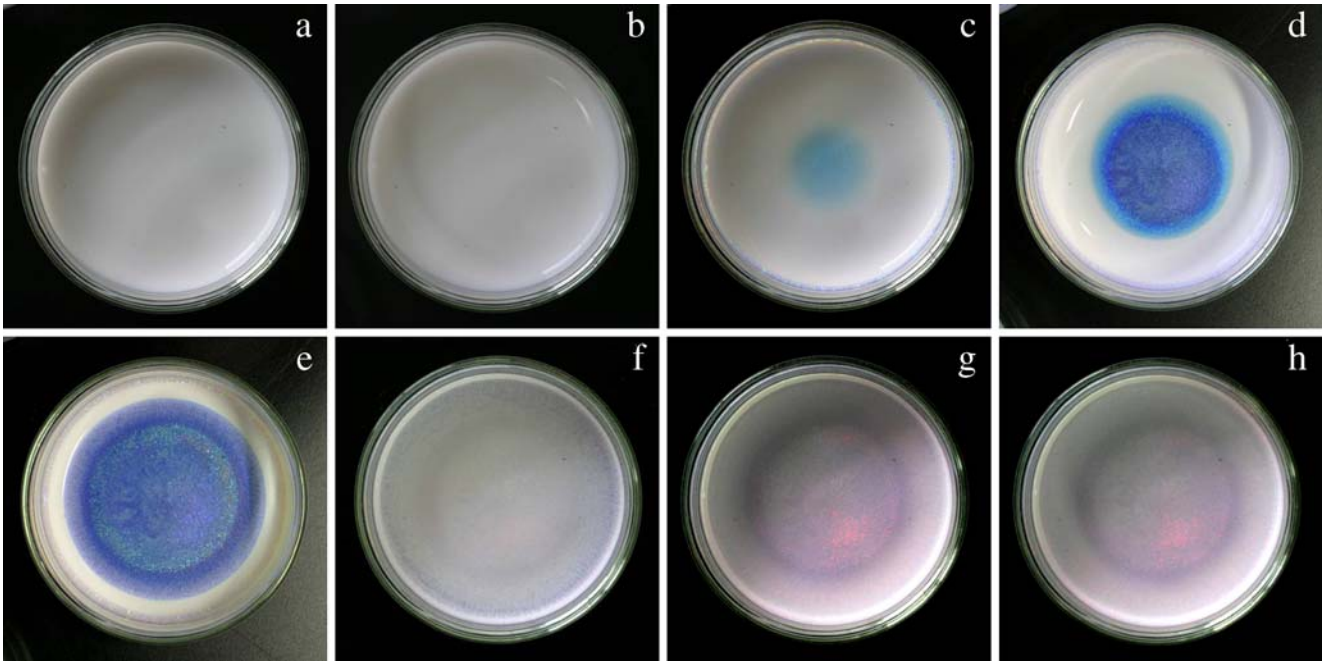

Fig. 3 Sedimentation and drying dissipative patterns of GW8 spheres in a glass dish at 24 °C. Code 557, ϕ=0.049, 5 ml, **a** 25 min after setting, **b** 5 h and 30 m, **c** 48 h and 5 m, **d** 52 h and 45 m, **e** 58 h and 45 m, **f** 65 h and 55 m, **g** 70 h and 35 m, **h** 72 h and 25 m

Humidity of the room was not regulated and was between 45% and 60%. Sphere concentrations were between 0.0002 and 0.1 in volume fraction.

Macroscopic patterns were observed on a Canon EOS 10 D digital camera with a macrolens (EF, 50 mm, f=2.5) and a life-size converter EF. Microscopic drying patterns were observed with a metallurgical microscope (PME-3, Olympus, Tokyo).

Results and discussion

Convectional patterns in a glass dish

Figures 1, 2, 3, and 4 show the typical examples of the pattern change during the course of dryness of colloidal crystal suspensions of GW1, GW6, GW8, and PM1000

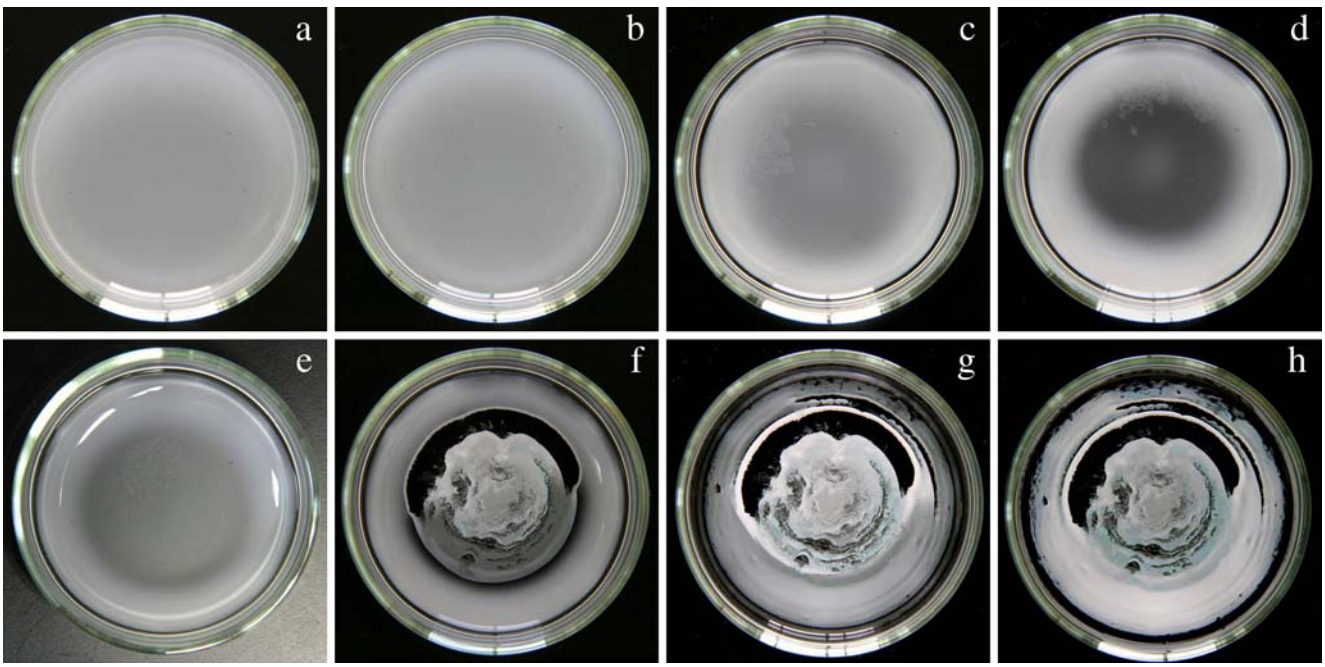

Fig. 4 Sedimentation and drying dissipative patterns of PM1000 spheres in a glass dish at 25 °C. Code 512, ϕ=0.000797, 5 ml, **a** 20 min after setting, **b** 1 h and 5 m, **c** 17 h and 50 m, **d** 45 h and 25 m, **e** 54 h and 40 m, **f** 61 h and 35 m, **g** 69 h and 45 m, **h** 71 h and 55 m

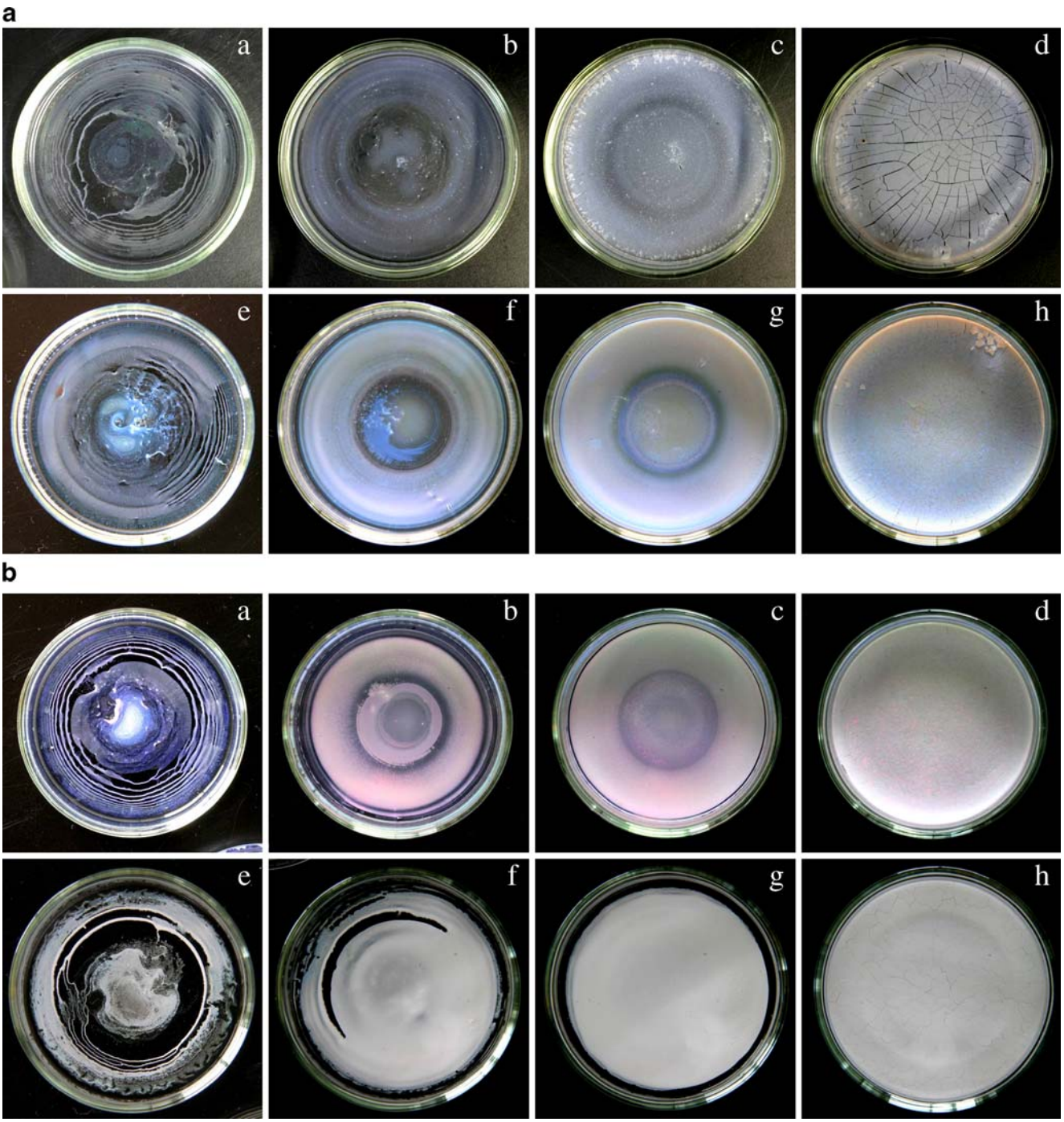

Fig. 5 ***a*** Drying dissipative patterns of GW1 (**a** ϕ=0.000318, **b** 0.00318, **c** 0.0159, **d** 0.095) and GW6 (**e** ϕ=0.00021, **f** 0.0042, **g** 0.021, **h** 0.063) spheres in a glass dish at 26 and 24 °C, respectively. ***b*** Drying dissipative patterns of GW8 (**a** ϕ=0.000245, **b** 0.0049, **c** 0.0245, **d** 0.0735) and PM1000 spheres (**e** ϕ=0.000266, **f** 0.00266, **g** 0.0133, **h** 0.0797) on a glass dish at 24 and 25 °C, respectively

spheres in a glass dish, respectively. On a cover glass and in a watch glass, the spoke-like convectional patterns (Terada cell) were clearly observed [11, 12]. In a glass dish of this work, however, the clear-cut convectional patterns did not appear. The cyclic patterns look to support the distortion of the colloidal single crystals by the convectional flow of the suspension (see Fig. 1a,b). The reason why the convectional patterns did not appear is not clear yet. However, rather large amount of samples (5 ml) were set in a flat dish in this work, and the strength of the convectional flow of the spheres and solvent may not be so strong to break the colloidal crystals having high elasticity [53–58].

Sedimentation patterns in a glass dish

The broad ring-like sedimentation patterns were observed clearly in the outward region of a glass dish about 20 min to 1 h after the suspensions of GW6, GW8, and PM1000 were set (see Figs. 2b, 3b, and 4a–c, for example). A main cause for the broad ring formation is due to the convectional flow of water and PMMA spheres in the different rates, i.e., the motion of colloidal spheres are slower than that of water molecules. Especially, the flow of the spheres from the central area toward the outside edge in the lower layer of the liquid, which was observed with the naked eyes for suspensions of Chinese black ink [8] in a glass dish and PMMA on a cover glass and a watch glass [11, 12], is important. The convectional flow in a glass dish is enhanced by the evaporation of water at the liquid–air surface, resulting in the lowering of suspension temperature in the upper region of the suspension. When the colloidal spheres reach the outside edge of the liquids, a part of the spheres will turn upward and go back to the central region. However, most of the spheres will be accumulated at the outside edge by the downward flow of the spheres caused by gravitational sedimentation. Thus, the broad rings are formed at the outside edge of a glass dish. The other important reason why the broad rings are formed in a glass dish will be the fact that the inner wall of the dish is wetted with the suspension at a slightly higher level than the air-suspension surface by the surface tension forces between glass wall and suspension. This situation will also introduce the stronger evaporation of water at the outside area than the inner region and quite resembles to the evaporation on a cover glass, where the evaporation of water is much strong at the outside drying frontier. It should be noted that the broad ring-like sedimentation patterns in a glass dish were observed, for the first time, in a previous paper from the author's laboratory [19]. It should be further noted that the sedimentary colloidal spheres, especially in a deionized suspension, are surrounded with the extended electrical double layers and movably keeping apart from the cell wall, which is also surrounded by the double layers.

For the GW1 suspensions, clear-cut sedimentation pattern was not recognized with the naked eyes because of the strong Bragg diffraction of light from the single crystals formed. Sphere size of GW1 is so small (100 nm in diameter), though their density (1.19 g/ml) is rather high compared with that of water (1.00), that sphere sedimentation may not take place so much. However, it is highly plausible that the broad ring-like accumulation of spheres will take place slowly in the outside area by the difference of the rates of convectional flow between small water and large spheres.

It should be mentioned in this paper that the characteristic color changes took place during the course of dryness of the suspensions of GW1, GW6, and GW8 spheres. These changes in colors from the central area to the outward of a glass dish are due to the delicate change in the strength of the Bragg diffraction and the multiple-scattering during the course of concentration and solidification of spheres. It is highly plausible from our experiences that the crystal-like distribution of spheres is stable throughout the course of dryness from liquid to solid [33, 34]. The bluish colors are clearly observed by the Bragg diffraction of light through the crystal-like distribution of spheres. The primary peak wavelength (λ_p) in the reflection spectroscopy of colloidal crystals at the scattering angle of 90° is estimated from the nearest-neighbored inter-sphere distance (D) of the face-centered- and/or body-centered-cubic lattices.

$$\lambda_p = nD/0.6124 \tag{1}$$

Here, the refractive indices of the liquid and dried film (n) are given by Eq. 2.

$$\begin{aligned} n = \phi \times & [\text{refractive index of PMMA sphere}] \\ & + (1-\phi) \\ & \times [\text{refractive index of water (for liquid and wetted film)} \\ & \quad \text{or air(for dried film)}] \end{aligned} \tag{2}$$

Refractive indices of PMMA, water, and air were assumed to be 1.49, 1.33, and 1.00, respectively. For the dried film, ϕ and D are 0.74 and diameter of spheres, respectively. Here, the spheres in the dried film were assumed to be attached to each other and distributed in the closed-packed colloidal crystal structure. The λ_p values of the dried films are estimated to be 220 nm, 430 nm, 650 nm, and 2.2 μm for GW1, GW6, GW8, and PM1000 spheres, respectively. Depending on the scattering angles, color should change, but the color is estimated roughly to be blue (ultraviolet),

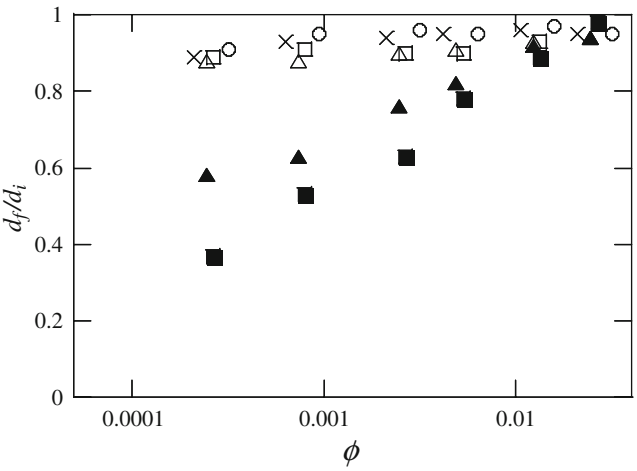

Fig. 6 Plots of df/di of GW1 (*empty circle*), GW6 (*ex symbol*), GW8 (*empty triangle*, *filled triangle*) and PM1000 (*empty square*, *filled square*) in a glass dish as a function of ϕ

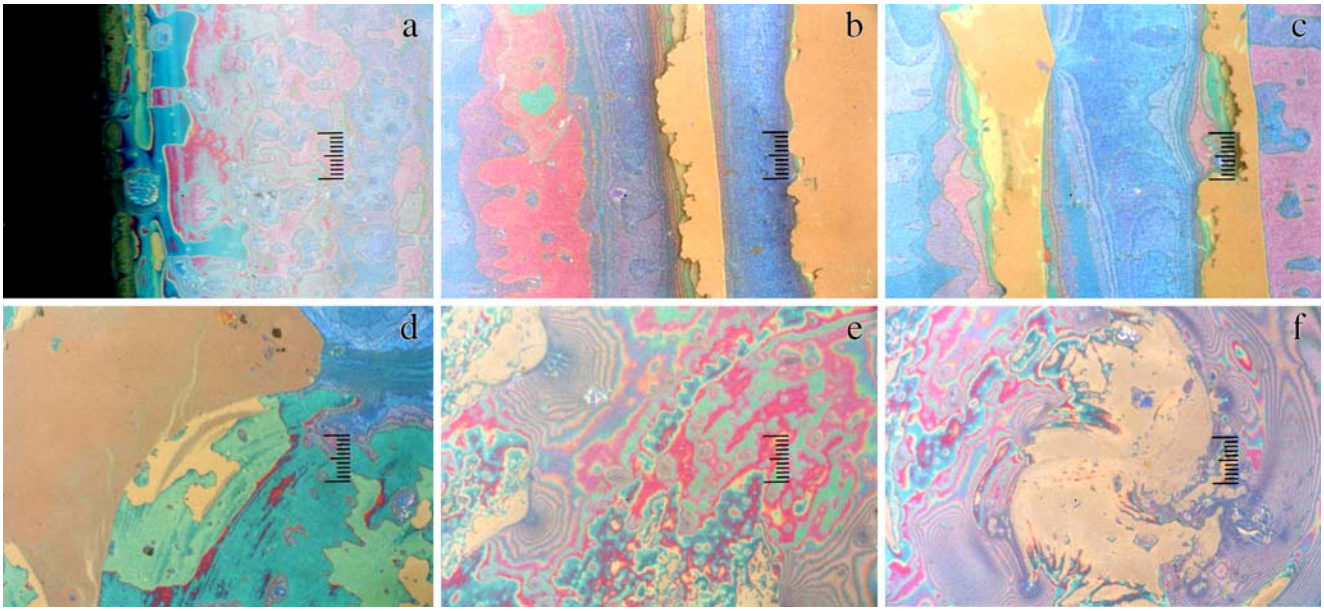

Fig. 7 Drying dissipative patterns of GW6 spheres in a glass dish at 25 °C. ϕ=0.00021, 5 ml, dry, code 481, from left edge (**a**) to center (**f**), full scale=200 μm

green, red, and ultrared (actually purely white by the very strong multiple scattering), respectively. For liquid state of suspensions, the λ_p values should be larger than those of the dried films. Thus, the observed colors of the suspensions of GW1 spheres, for example, at medium and high concentrations and that of the dried film are understood to be green, blue, and whitey blue, respectively.

Drying patterns in a glass dish

The typical drying patterns of colloidal crystals of GW1, GW6, GW8, and PM1000 in a glass dish were compared in Figs. 5a and b. Several important findings are noted. Firstly, colors of the dried films were blue, greenish blue, pink and white for these spheres, respectively. Furthermore, these

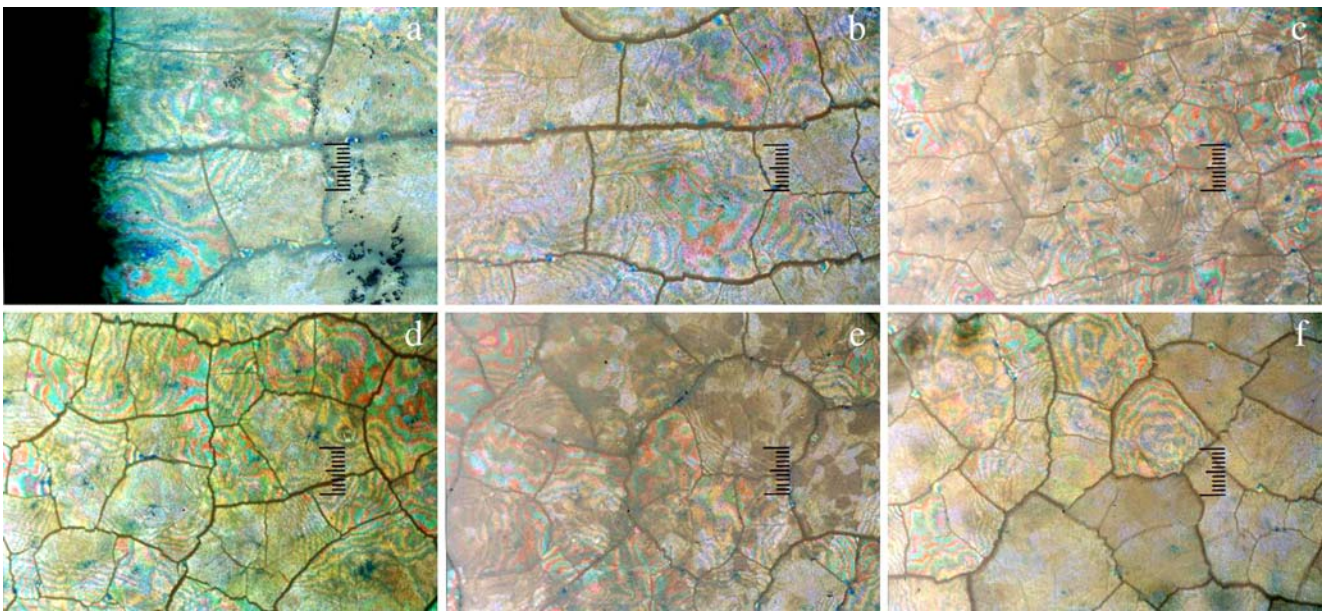

Fig. 8 Drying dissipative patterns of GW6 spheres in a glass dish at 25 °C. ϕ=0.042, 5 ml, dry, code 487, from left edge (**a**) to center (**f**), full scale=200 μm

colors became whitey as initial sphere concentration increased. These findings were already discussed above with Figs. 1, 2, 3, and 4 and the Bragg equation. Secondarily, at the low sphere concentrations, fine multiple rings were formed at the outer regions of the initial liquid areas. Furthermore, the broad ring-like drying patterns extended toward outside edge as initial sphere concentration increased. Clearly, two kind of broad rings were observed at the inner and outer areas of a dish. Both of the inner and outer rings formed at the low initial sphere concentrations, and inner rings disappeared when sphere concentration was high. Figure 6 shows the ratios of the final size of the broad rings in diameter against initial liquid size (inner diameter of the glass dish) plotted against initial sphere concentration. Open and solid symbols show the outer and inner broad rings, respectively. Clearly, both the ratios increased as sphere concentration increased. Furthermore, the outer broad rings are quite insensitive to the sphere size, whereas inner ones are sensitive to sphere size. These results support the fact that the segregation of sphere size takes place in a glass dish just like on a cover glass [11] and a watch glass [12]. Furthermore, these observations do not support the pinning effect, where the drying frontier is pinned on the outside edge of the initial liquid [10, 17]. Thirdly, the macroscopic cracks composed of the spoke lines and rings were observed especially for drying patterns of small GW1 and GW6 spheres at high sphere concentrations. These cracks disappeared when sphere size increased because the rigidity of the dried film increases rapidly as sphere size increases. These observations were also observed for the colloidal crystals of silica spheres [34].

Figures 7 and 8 show the typical microscopic drying patterns of the GW6 spheres on a glass dish at the low and high sphere concentrations. Colors of all the pictures observed with a microscope were very colorful and were a bit different from those of the macroscopic patterns with a close-up camera. At the low sphere concentration, very colorful swirl-like patterns and ring structures were observed around the central and the outer regions, respectively (see, Fig. 7). On the other hand, at the high sphere concentrations, block-like cracks appeared at the central area, and the coupled patterns of the spoke-like and the circle-like cracks were observed, as shown in Fig. 8. These cracks originated from the traces of spheres by the convectional flow at the liquid state. It should be further mentioned that the microscopic patterns changed delicately depending on sphere size and concentration. For large PM1000 spheres, clear-cut microscopic patterns were rather difficult to be observed, though showing the pictures was omitted in this manuscript. This is due to the very strong multiple-scattering of the incident light.

Concluding remarks

The convectional patterns were not observed for the deionized suspensions of PMMA colloidal spheres in a glass dish. It is impressive to observe the very beautiful color changes during the course of dryness. Broad ring-like macroscopic sedimentation and drying patterns were formed. Outer and inner drying broad rings were observed. The size of the outer rings increased as sphere concentration increased but were insensitive to sphere size. The inner rings increased and/or decreased as sphere concentration and/or sphere sizes increased. These observations do not support the pinning effect proposed by Deegan et al. Colorful microscopic drying patterns were also observed.

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). Soken Chemical (Tokyo) is thanked for the kind gifts of PMMA sphere samples. Professor Akira Tsuchida of Gifu University is deeply appreciated for his kind support of the author's experiments and constructive comments.

References

1. Gribbin G (1999) Almost everyone's guide to science. The universe, life and everything. Yale University Press, New Haven
2. Ball P (1999) The self-made tapestry. Pattern formation in nature. Oxford University Press, Oxford
3. Okubo T (2001) Beautiful world of colloids and interfaces. Matsuo Press, Gifu (Japanese)
4. Terada T, Yamamoto R, Watanabe T (1934) Sci Paper Inst Phys Chem Res Jpn 27:173; Proc Imper Acad Tokyo 10:10
5. Terada T, Yamamoto R, Watanabe T (1934) Sci Paper Inst Phys Chem Res Jpn 27:75
6. Terada T, Yamamoto R (1935) Proc Imper Acad Tokyo 11:214
7. Nakaya U (1947) Memoirs of Torahiko Terada. Kobunsya, Tokyo (Japanese)
8. Okubo T, Kimura H, Kimura T, Hayakawa F, Shibata T, Kimura K (2005) Colloid Polym Sci 283:1
9. Okubo T (2006) Colloid Polym Sci 285:225
10. Deegan RD, Bakajin O, Dupont TF, Huber G, Nagel SR, Witten TA (1997) Nature 389:827
11. Okubo T, Okamoto J, Tsuchida A (2008) Colloid Polym Sci 286:1123
12. Okubo T (2008) Colloid Polym Sci 286:1307–1315
13. Palmer HJ (1976) J Fluid Mech 75:487
14. Anderson DM, Davis SH (1995) Phys Fluids 7:248
15. Pouth AF, Russel WB (1998) AIChEJ 44:2088
16. Burelbach JP, Bankoff SG (1998) J Fluid Mech 195:463
17. Deegan RD, Bakajin O, Dupont TF, Huber G, Nagel SR, Witten TA (2000) Phys Rev E 62:756
18. Fischer BJ (2002) Langmuir 18:60
19. Okubo T (2006) Colloid Polym Sci 284:1191
20. Okubo T (2006) Colloid Polym Sci, 284:1395
21. Okubo T, Okamoto J, Tsuchida A (2007) Colloid Polym Sci 285:967
22. Okubo T (2007) Colloid Polym Sci 285:1495

23. Okubo T, Okamoto J, Tsuchida A (2008) Colloid Polym Sci 286:385
24. Okubo T, Okamoto J, Tsuchida A (2008) Colloid Polym Sci 286:941
25. Yamaguchi T, Kimura K, Tsuchida A, Okubo T, Matsumoto M (2005) Colloid Polym Sci 283:1123
26. Okubo T (2006) Colloid Polym Sci 285:331
27. Vanderhoff JW (1973) J Polym Sci Symp 41:155
28. Nicolis G, Prigogine I (1977) Self-organization in non-equilibrium systems. Wiley, New York
29. Ohara PC, Heath JR, Gelbart WM (1997) Angew Chem 109:1120
30. Maenosono S, Dushkin CD, Saita S, Yamaguchi Y (1999) Langmuir 15:957
31. Nikoobakht B, Wang ZL, El-Sayed MA (2000) J Phys Chem 104:8635
32. Ung T, Litz-Marzan LM, Mulvaney P (2001) J Phys Chem B 105:3441
33. Okubo T, Okuda S, Kimura H (2002) Colloid Polym Sci 280:454
34. Okubo T, Kimura K, Kimura H (2002) Colloid Polym Sci 280:1001
35. Okubo T, Kanayama S, Kimura K (2004) Colloid Polym Sci 282:486
36. Okubo T, Yamada T, Kimura K, Tsuchida A (2005) Colloid Polym Sci 283:1007
37. Okubo T (2006) In: Stoylov SP, Stoimenova MV (eds) Molecular and colloidal electro-optics, Taylor & Francis, New York, p 573
38. Okubo T, Nozawa M, Tsuchida A (2007) Colloid Polym Sci 285:827
39. Okubo T, Kimura K, Tsuchida A (2007) Colloids Surf B Biointerf 56:201
40. Okubo T, Nakagawa N, Tsuchida A (2007) Colloid Polym Sci 285:1247
41. Okubo T (2008) In: Nagarajan R, Hatton TA (eds) Nanoparticles: syntheses, stabilization, passivation and functionalization, Chapter 19. ACS, Washington DC
42. Okubo T, Kimura K, Tsuchida A (2008) Colloid Polym Sci 286:621
43. Okubo T (2008) Colloid Polym Sci 286:1411–1423
44. Okubo T, Kanayama S, Ogawa H, Hibino M, Kimura K (2004) Colloid Polym Sci 282:230
45. Okubo T, Onoshima D, Tsuchida A (2007) Colloid Polym Sci 285:999
46. Shimomura M, Sawadaishi T (2001) Curr Opin Coll Interf Sci 6:11
47. Okubo T, Yamada T, Kimura K, Tsuchida A (2006) Colloid Polym Sci 284:396
48. Okubo T, Kanayama S, Kimura K (2004) Colloid Polym Sci 282:486
49. Kimura K, Kanayama S, Tsuchida A, Okubo T (2005) Colloid Polym Sci 283:898
50. Okubo T, Shinoda C, Kimura K, Tsuchida A (2005) Langmuir 21:9889
51. Okubo T, Itoh E, Tsuchida A, Kokufuta E (2006) Colloid Polym Sci 285:339
52. Okubo T, Yokota N, Tsuchida A (2007) Colloid Polym Sci 285:1257
53. Okubo T (1988) Acc Chem Res 21:281
54. Okubo T (1993) Prog Polym Sci 18:481
55. Okubo T (1994) In: Schmitz KS (ed) Macro-ion characterization. From dilute solutions to complex fluids. ACS, Washington DC, p 364
56. Okubo T (2002) In: Hubbard A (ed) Encyclopedia surface and colloid science. Marcel Dekker, New York, p 1300
57. Okubo T (2005) In: Kinoshita S, Yoshioka S (eds) Structural colors in biological systems, Osaka University Press, Osaka, p 267
58. Okubo T (2008) Polymer J 40:1