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Dissipative Structure in the Course of Drying Suspensions and Solutions

*Tsuneo Okubo**

Summary: Convectional, sedimentation and drying dissipative patterns during the course of dryness of suspensions and solutions are reviewed. The whole processes of convection were analyzed in the seven steps: irregular circulation accompanied with the upward heat transportation, global convectional flow from the central area toward outside edge at the surface layers of liquid, cooperative formation of distorted Benard cells, reversal of global flow of convection, growing of the spoke lines from the outside edge toward central area at the liquid surface layers, cluster and further bundle formation of the spoke lines, and the convectional flow by the pinning effect. The sedimentary colloidal particles were suspended above the substrate by the electric double layers and moved by the balancing of the external force fields including convectional flow and sedimentation. Principal macroscopic drying patterns are broad rings and spoke lines. Microscopic patterns such as star, needle, street road, string and cross-like are formed. The stratified structures form from micro to macro scales. Information on the *size*, *shape*, *conformation* and/or *flexibility* of particles or polymers is transferred cooperatively, and further accompanied with the *amplification* and *selection* processes during the course of dryness.

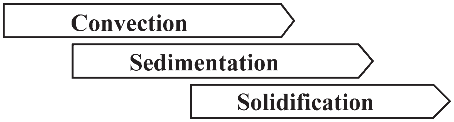
Keywords: colloidal suspension; convection; dissipative structure; dryness; polymer solution; sedimentation

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. In order to know 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 during the course of drying colloidal suspensions and solutions of simple and polymer solutes as systematically as possible, though the three kinds of patterns are correlated strongly and overlapped to each other as is shown in Scheme 1. Furthermore, the sedimentation patterns are not formed in general for the suspensions of very small particles and for solutions.

Most famous *convectional* patterns is the *hexagonal circulating* one, *Benard cell*, and has been observed when liquids contain plate-like colloidal particles as monitors and are heated homogeneously in a plain pan.[1–3] Another typical convectional dissipative pattern is the spoke-like lines, which were observed in the whole area at the liquid surface 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] Thus, the authors like to name the spoke-like pattern as *Terada*

Institute for Colloidal Organization, Hatoyama 3-1-112, Uji, Kyoto 611-0012, Japan, and Graduate School of Science and Technology, Yamagata University, Johnan 4-3-16, Yonezawa, Yamagata 992-8510, Japan
Fax: (+81) 0774-32-8270;
E-mail: Okubotsu@ybb.ne.jp



Scheme 1.
Overlapping of Convectional, sedimentation and solidification processes during the course of dryness of suspensions and solutions.

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,[10] coffee,[11] black tea,[12] and colloidal crystals of poly (methyl methacrylate) (PMMA) spheres on a cover glass and a watch glass.[13,14] Distorted Benard cells were often observed for miso-soup, coffee and black tea. For the 100% ethanol suspensions of colloidal silica spheres, Terada-cell type convectional flow was observed clearly with the naked eyes, and the convectional patterns changed dynamically with time.

Deegan et al.[15,16] have reported the traces of spoke-like patterns in the suspensions of polystyrene spheres (1 μm in diameter) under a microscope. They introduced the capillary flow theory accompanied with the pinning effect of the contact line of the drying drop. From our series of drying experiments of suspensions and solutions, however, the pinning effect was not supported except experiments at high concentrations and for small colloidal particles. Generally speaking, at high solute concentrations, the broad ring-like drying patterns were always formed irrespective of the substrates used, but they moved toward the central area as their size increased and/or their concentration decreased.[8,17–22] Broad ring size decrease until the solute-solute repulsive or attractive interactions become strong enough to form the inter-solute structures such as colloidal crystal formation,[13,14] helix or sheet structures of biopolymers,[22] or micelles.[23,24] For typical anisotropic shaped particles, furthermore, broad rings at the outside edge disappeared and round hill appeared instead.[25] Calchile et al.[26,27] reported that the droplets of completely wetting liquids deposited on a thoroughly smooth and wetting surface for which no contact line anchoring occurs. The author believes that the convectional flow of solvent and solutes is essentially important for all the convectional, sedimentation and drying pattern formation. Furthermore, the pinning effect was not supported in a glass dish, where drying frontier starts from the central area of the substrate and developed toward outside.[28,29] In conclusion, the broad rings were formed at the outside area in many cases. However, the broad rings became small when the solute concentration decreased. It should be mentioned further that theoretical and experimental studied for the convectional patterns have been made hitherto, but these are not always successful yet.[13,15,16,30–37] It should be noted further that information on the *size*, *shape*, *conformation*, and/or *flexibility* of particles or polymers is *transferred* cooperatively and further accompanied with the *amplification* and *selection* processes toward the succeeding sedimentation and drying patterns during the course of dryness of solutions and suspensions.[23,24,38,39]

Recently, the whole growing processes of the *convectional* patterns were summarized in seven steps.[10–14] Firstly, at the initial stage of convection, appearance and disappearance of the circulating lines (irregular circulations) are formed at random in their direction accompanied with the gravitational upward transportation of heat. Secondary, global flow of the convection takes place at the surface layers from the center toward outward edge of the liquid. Thirdly, the cooperated distorted Benard cells form at the liquid surface. Fourthly, the reversed global flow of convection from the outside edge to the central area is observed at the liquid surface at the middle stage of convection. The reversal takes place mainly by the Marangoni convection. Fifthly, growing of the spoke-lines from the outside edge to the central area takes place at the liquid surface layers. Sixthly, the clusters and further bundles of the spoke lines are formed at the final stage of convection. The bundles are also considered to be the sedimentation patterns in many cases and are further transformed to the drying patterns with fine structure. Growing of the broad-ring sedimentation and drying patterns are formed in the middle and/or final stage of convection. Seventhly, the convectional flow by the pinning effect proposed by Deegan et al.[15,16] is sometimes important at the final stage of convection.

Sedimentation dissipative patterns in the course of drying suspensions of colloidal silica spheres (183 nm to 1.2 mm in diameter),[19,21,40–43] size-fractionated bentonite particles,[25] and green tea (Ocha)[44] 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 by the electrical double layers and always moved by the balancing of the external force fields including convectional flow and sedimentation. Sharpness of the broad rings was sensitive to the time gradients in room temperature and/or humidity.[42] The main cause for the broad ring formation is the convectional flow of water and solutes along the cell wall at the lower layers of liquid at the different rates where the rate of the latter is slower than that of the former. Quite recently, it was clarified that the dynamic bundle-like sedimentation patterns formed cooperatively from the distorted spoke line-like convectional structures of colloidal particles of coffee,[11] colloidal crystal suspensions of PMMA spheres,[13,14] and black tea.[12]

Drying dissipative patterns have been studied for suspensions and solutions of many kinds of colloidal particles,[8–14,17–21,25–57] linear-type synthetic and bio-polyelectrolytes,[22,58] water-soluble and non-soluble neutral polymers,[59,60] ionic and non-ionic detergents,[61–63] gels,[64] and dyes.[65] The macroscopic broad ring patterns of the hill accumulated with the solutes in the outside edge formed on a cover glass, a watch glass and a glass dish when the solute concentration was high. Size of the broad rings decreased when solute concentration and/or solute size decreased. For the non-spherical particles, the round hill was formed in the central area in addition to the broad ring.[25] Macroscopic spoke-like cracks or fine hills, including flickering spoke-like ones, were also observed for many solutes. Furthermore, beautiful microscopic fractal patterns such as earth worm-, branch-, arc-, block-, star-, cross-, and string-like ones were observed. These microscopic drying patterns were often 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 sedimentation patterns were formed already in the liquid phase before dryness, and they grew toward fine structures in the process of solidification.[25]

Convectional Patterns

The growing processes of the convectional patterns were mainly studied from the macroscopic and microscopic pattern observation of 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,[10] coffee,[11] black tea,[12] and colloidal crystals of poly (methyl methacrylate) (PMMA) spheres on a cover glass and a watch glass.[13,14] The convectional processes were analyzed in seven steps. (1) At the initial stage of convection appearance and disappearance of the circulating lines (*irregular circulations*) took place at random in their directions accompanied with the gravitational upward heat transportation. (2) Total flow of convection at the surface layers at the initial stage was observed with the naked eyes in the direction from the center toward outside edge, especially in the coffee with cream[11] and black tea with cream.[12] (3) The distorted Benard cells were formed at the liquid surface. Figure 1 shows the distorted Benard cell formation clearly in the Miso-soup in a cup.[10] (4) Meanwhile, total flow of convection was reversed from outside edge to the central area at the liquid surface layers, and the outward flow remained until solidification started. This inward flow was observed in the initial course of drying Chinese black ink in a glass dish,[8] coffee,[11] and black tea.[12] The reversal takes place mainly by the Marangoni convection. (5) At the same time, few and short spoke lines grew at the outside edge. Then, number of spoke lines increased. Figure 2 shows the extended pictures of the outside area of coffee with cream in a watch glass.[11] It is clearly seen that around 20 min after setting, few and short spoke lines appeared at the outside edge. Then the number of the spoke lines increased. (6) The spoke lines further grew toward central area accompanied with the dynamical fusion and separation between the neighboring spoke lines and clusters at the final stage of convection as is shown in Figure 2. The clusters are further bound dynamically to the bundles (see also Figure 2). The bundles are considered to be the sedimentation patterns and are further transformed to the drying patterns with fine structures. (7) The convectional flow by the pinning effect proposed by Deegan et al.[15,16] comes important at the final stage of convection in a few cases. It should be mentioned here that growing of the broad ring-like sedimentation and drying patterns are formed in the middle and/or final stage of convection.

The convectional patterns observed hitherto are compiled in Table 1. It should be noted that the convectional patterns have been observed only for colloidal suspensions, and not for solutions. Anisotropic-shape colloidal particles suspended work as an optically good indicator of the liquid flow by the *flow birefringence* effect. However, we should note that the quite the similar convections as those of colloidal suspensions should exist even in solution systems such as polymer and simple solutions.

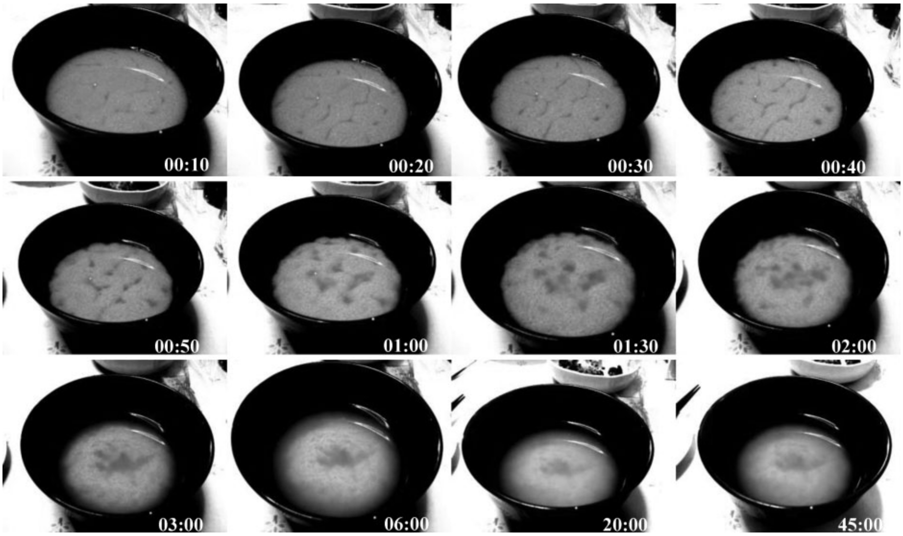


Figure 1.
Convectional patterns of type I miso-soup in a bowl from approximately 60 °C to 30 °C. [Miso-I] = 0.06 g/ml, 180 ml, time [minute: second].

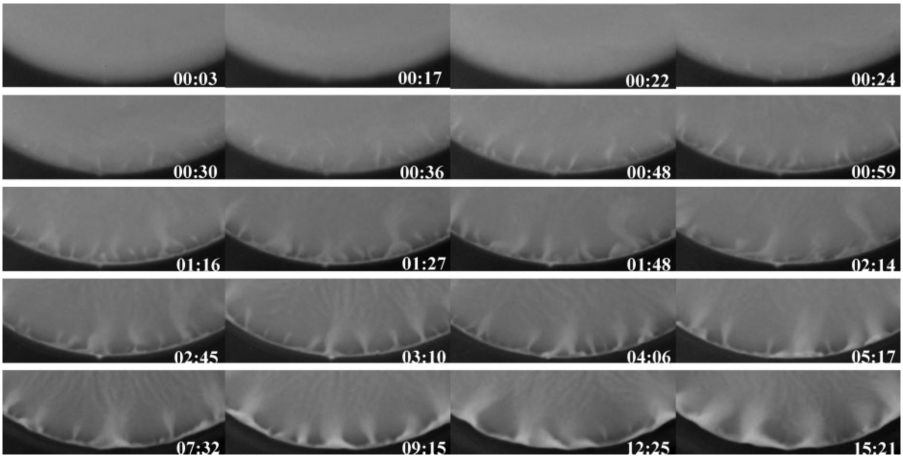


Figure 2.
Convectional patterns of coffee with cream in a watch glass. Lower outside areas od patterns were extended. $w = 2.3$ wt%, 40 ml, liquid temperature goes down from 70 °C to 20 °C, time shows [hour: minute].

Sedimentation Patterns

In most Japanese hotels, a guest will find in his or her room a set of green tea (*Ocha* in Japanese), which is composed of green tea granules in a paper filtering bag, a tea cup (*Ochawan*) and hot water. The tea is prepared conveniently by shaking the tea bag dipped into a hot water in an Ochawan. The author was excited to find that the broad ring always formed within several tens of minutes when green tea in a cup stood still on a desk.[44] Figure 3 shows the pictures of the broad ring patterns of the green tea in the hotels of Yonezawa (a), Supporo (b), Kumamoto (c) and Ishigaki cities (e). Pictures d and f are the side views of the cups in Yonezawa and Kumamoto. The broad ring, which is the circular hill accumulated with green tea colloids, was formed on the inclined inner wall of the cup and not in the deepest central area. The author clarified that the broad ring structures were formed by the balancing of the upward convectional flow of the colloidal particles and downward gravitational gravitation. The broad ring patterns were named as *sedimentation* structures and so often formed unexpectedly fast in the suspension state irrespective of the particles and also cells used. The sedimentation patterns have been studied for many colloidal suspensions in the author's laboratory.[11–14,19,21,25,40–43] The broad rings of the sedimentation patterns became sharp with time in many cases. Sharpness of the

Table 1.
Typical convectional patterns of colloidal suspensions.

	Macroscopic patterns	
Spoke lines (*Terada cell*)		Chinese ink,[8] PMMA,[13,14] Coffee,[11] Black tea[12]
Hexagonal circulating cells (*Benard cell*)	*Normal*	Liquid with metal flakes[2]
	Distorted	Miso-soup,[10] Coffee[11]
Circulating cells		Chinese black ink,[8] Coffee
Smoke like		Chinese black ink[8]
Cooperative circulation		Silica spheres in ethanol[9]
	Microscopic patterns	
Cell convection (*Terada cell*)		Chinese black ink[8]

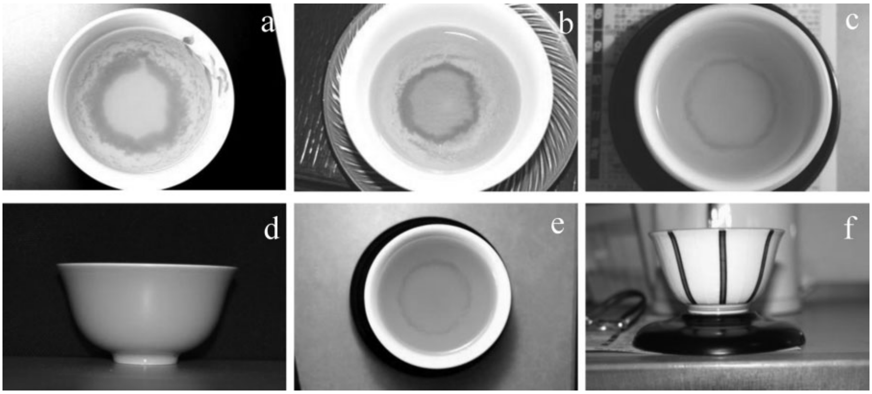


Figure 3.
Sedimentation patterns of green tea in a tea cup at 24 °C. **a** From a hotel in Yonezawa, **b** in Sapporo, **c** in Kumamoto, **d** side view of tea cup in Yonezawa, **e** in Ishigaki, **f** side view of a tea cup in Kumamoto.

broad rings was sensitive to the change in room temperature and/or humidity.[42]

The sedimentation and drying patterns were also formed during the course of drying binary and ternary colloidal crystal mixtures among colloidal silica spheres of 183 nm, 305 nm and 1.205 μm in diameter in aqueous suspension on a watch glass, a glass dish and a cover glass.[19,20] The broad ring-like sedimentation patterns were formed within several hours in suspension state for all the substrates used. Colorful macroscopic broad-ring-like drying patterns appeared on the basis of the sedimentation structures. In a watch glass, for example, macroscopic sedimentation and then drying patterns were composed of the outer and inner layers of small and large spheres, respectively, for the binary mixtures.[19]

Most of the sedimentation patterns observed was the broad ring-like macroscopic ones. However, vague but wrinkled microscopic sedimentation patterns were observed even in the suspension phase for bentonites.[25] These patterns became clearer and finer in the course of solidification. Clearly, the drying patterns are formed on the basis of the sedimentation patterns, which are also formed from the convectional structures in suspension state.

The sedimentation patterns observed in the author's laboratory are compiled in Table 2.

Drying Patterns of Colloidal Suspensions

Figure 4 shows the typical patterns of colloidal silica spheres, their diameters ranging from 29 nm to 1.09 mm.[21] The broad rings and the spoke-like cracks were observed. There appeared holes, where there were quite few spheres, in the central area, whereas broad ring region was occupied with many spheres. The

Table 2.
Typical sedimentation patterns of colloidal suspensions.

Macroscopic patterns	
Broad ring	Colloidal silica spheres,[19–21,40–43] PMMA,[13,14] Green tea,[44] Coffee,[11] Black tea[12]
Flame-like	Coffee,[11] Black tea,[12] Silica spheres in ethanol[9]
Microscopic patterns	
Vague wrinkled pattern	Bentonite[25]

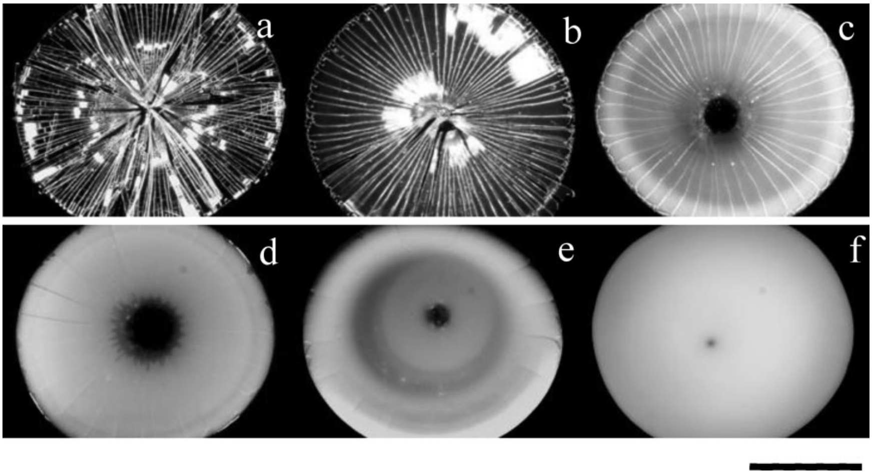


Figure 4.

Drying patterns of colloidal crystals of silica spheres on a cover glass at 25 °C. **a** CS22p(29 nm in diameter), **b** CS45 (56.3 nm), **c** CS82 (103 nm), **d** CS161 (183 nm), **e** CS301 (311 nm), **f** CS1001 (1090 nm), in water, $\phi = 0.0333$, 0.1 ml, length of the bar is 5 mm.

cracks were clearly formed in the process of shrinking of the wetted films. Interestingly, the cracks were introduced in the final stage of drying the colloidal suspensions along the outer edges first, where the dryness proceeds in advance. The cracks curved and then developed straight toward the center of the film. It is impressive that the new cracks developed successively keeping the same angle with the adjacent elder cracks.[53] Film is transparent and so many cracks are observed for small spheres. When sphere size increases, film becomes whitey and the number of the cracks decreases sharply. Increase in size will result in increase in the rigidity of the film and then decrease in the crack number. It should be noted here that so many potential cracks are formed already in the suspension state by the Terada cells with cell convections. The spoke-like cracks and the broad rings were observed for most suspensions and solutions examined so far.

A main cause for the broad ring is also due to the convectional flow of solvent and colloidal spheres from the central area toward outside edge in the lower layers of the liquid drop, which was observed directly from the movement of the temporary aggregates of the particles of Chinese black ink.[8] The convectional flow is enhanced by the evaporation of water at the liquid surface, resulting in lowering of the bulk temperature at the surface layers of the liquid. When the spheres reach the edge of the drying frontier, a part of the spheres will turn upward and go back to the central area. However, the movement of most spheres may stop at the frontier region, because of the disappearance of water. These processes must be followed by the broad ring-like accumulation of the spheres near the round edge. Importance of the convectional flow of colloidal spheres in the ring formation has been often reported in the processes of film formation.[48] It should be noted here again that the pinning effect is not supported to be valid in general in the drying processes.[15,16]

In a glass dish and a watch glass, the broad rings formed at the outside edge of the dried film within the inner wall of the substrate. The size of the broad ring decreased as the initial sphere concentration decreased (see Figure 5a in a glass dish, for example). The cooperative microscopic drying pattern was observed for colloidal silica suspensions with sodium chloride,

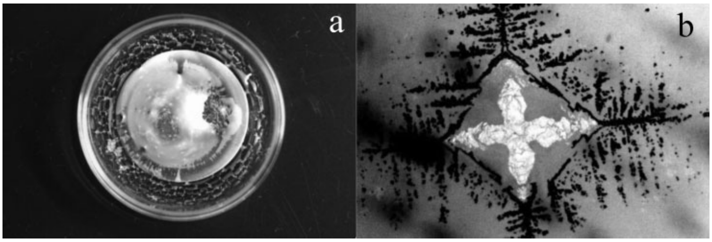


Figure 5.
a Macroscopic drying pattern of colloidal silica spheres (CS300, 305 nm in diameter, 0.00038 in volume fraction) in a glass dish at 27 °C, **b** Microscopic drying pattern of silica spheres (1.205 μm, 0.00129, [NaCl] = 0.001 M)in a glass dish at 24 °C.

where the cross-like structure of sodium chloride is surrounded with the dendritic silica spheres as is shown in Figure 5b in a glass dish.[41]

Drying patterns of the binary mixtures of colloidal silica spheres in a watch glass were composed of the outer broad ring of small spheres and the inner ring of large spheres, and the width ratio of the rings changed in proportion to the mixing ratio.[19] On a cover glass the width of the broad rings of small spheres at the outside edge increased as the mixing ratio of small spheres increased.[19] Recently, the drying structures of the ternary mixtures of spheres were studied, and the size segregation was observed.[20]

Drying Patterns of Solutions

Drying patterns of poly (allylamine hydrochloride), one of the cationic polyelectrolytes, were studied on a cover glass.[58] The fractal patterns of 1.2 to 1.6 in dimension were observed as is shown in Figure 6. Surprisingly, shape of the crystal structures changed from cross-like to coil-like via dendritic, as polymer concentration increased from 1×10^{-7} monoM to 0.001 monoM. Furthermore, crystal size increased with increasing concentration. It should be recalled that the conformation of the polyelectrolytes changes from rod to coil as polymer concentration increases. Thus, it is highly plausible that the shape information of the polymer in solution state was transferred to the drying patterns.

Drying patterns of a series of poly (*N*-alkylpyridinium halide) were studied.[66] The patterns were influenced substantially with the hydrophobicities of the polyelectrolytes. Drying patterns of biological polyelectrolytes, sodium poly (α, *L*-glutamate) (PGA) and poly (*L*-lysine hydrobromide) (PLL) were studied on a cover glass.[22] Macroscopic broad rings and spoke-like cracks were observed. Size of the broad rings increased with concentration transitionally above the critical concentration of structure formation such as a-helix and sheet structures. Microscopic patterns such as cross-, rod-, block- and further city road-like ones appeared.

Quite recently, the crystal structures of *spherulites* and *hedrites* were observed for one of the anionic polyelectrolytes, sodium poly (methyl acrylate) on a cover glass, a watch glass and glass dish.[67] The coupled structures of *spherulite* with *lamellae* originated from the fine broad ring were observed for poly (ethylene glycol) (PEG) on a watch glass.[68]

Drying dissipative patterns of thermosensitive gels of poly (*N*-isopropyl acrylamide) were studied on a cover glass.[64] As the suspension temperature rose, the small size of drying area extended transitionally at the critical temperature at ca. 35 °C. The patterns at 25 °C were the single or multiple broad rings. At 50 °C, on the other hand, the flickering spoke-like patterns appeared at the inner area of the broad ring. These observations support that the extended gel spheres at low temperatures apt to associate weakly to each other, whereas the gels

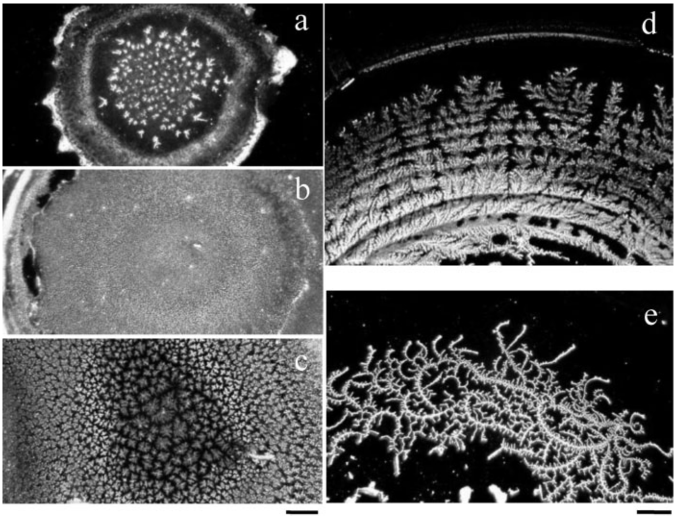


Figure 6.

Drying patterns of poly (allylamine hydrochloride) on a cover glass at 25 °C. **a** 1×10^{-7} monoM, **b** 1×10^{-6} monoM, **c** 1×10^{-5} monoM, **d** 1×10^{-4} monoM, **e** 0.001 monoM, length of the bar is 200 μm.

Table 3.

Typical drying patterns of colloidal suspensions and solutions.

		Macroscopic patterns
Broad ring	*Normal*	Silica spheres,[9,17,19–21,28,40–43,53,55,57] Polystyrene,[18] PMMA,[13,14,29] Green tea,[44] Bentonite,[25] Chinese ink,[8] Gel sphere,[64] PAL,[38] DTAC,[39] n-Alkyl sulfate,[23] POERE,[63] PEG,[60,68] PGA,[22] PLL,[22] Dyes in ethanol[65]
	Notched	Silica + NaCl,[17] Polystyrene + NaCl,[18] Dyes[65]
	Inner & outer	Silica,[55,57] Palygolskite,[70] Tungstic acid,[70] Coffee,[11] Black tea,[12] PGA,[22] PLL[22]
	Multiple	Chinese ink,[8] PMMA,[13,14,29] Green tea,[44] Gel sphere,[64] PAL,[38] n-Alkylsulfate,[23] PEG,[60,68] PGA[22]
Broad band along cell wall		Silica in a d.c. electric field[54]
Spoke-line	*Crack*	Silica,[9,17,21,53,55,57] Polystyrene,[18] PMMA,[13,14,29] PGA,[22] PLL[22]
	Hill	Chinese ink,[8] Gel sphere[64]
	Flame-like	Coffee,[11] Black tea,[12] Silica in ethanol[9] Chinese ink,[8] Gel[64]
Ring-like		Polystyrene,[18] Silica,[17] PEG[60,68]
Wave-like		Silica,[21,42,43] PEG[60,68]
Column-like		Silica in a d.c. electric field[54]
Central round hill		Bentonite + NaCl,[25] Gel sphere,[64] POERE,[63] PEG[60,68]
		Microscopic patterns
Fine spoke lines		PMMA,[13] Silica,[9,17,18,42,53,55] Gel sphere[64]
Fine rings		Gel sphere,[64] Silica[9,42]
Branch-like		Bentonite,[25] Silica[17,21]
Earthworm-like		Polystyrene[18]
String-like		Silica,[40] PAL,[38] n-Alkyl sulfate,[23] POERE[63]
Dendritic		Silica[41–43]
Star-like		Silica,[41–43] Bentonite,[25] PAL,[38] PLL,[22] Dyes[65]
Street road-like		PAL,[38] PLL,[22] Dyes[65]
Flower-like		Gel sphere,[64] PAL,[38] DTAC,[39] PGA,[22] Dyes[65]
Block-like		Bentonite,[25] Green tea,[44] Gel sphere,[64] Chinese ink,[8] PGA,[22] n-Alkyl sulfate,[23] POERE[63]
Cross-like		PGA,[22] PEG,[60,68] DTAC[39]
Rod-like		PGA,[22] PEG,[60,68] DTAC[39]
Arc-like		PGA,[22] DTAC,[39]
Needle-like		Dyes[65]
Wrinkled		Bentonite,[25] PEG[60,68]
Chapped		Bentonite,[25] PEG[60,68]
Netting		Silica[21]

at high temperatures shrink and move rather freely with the convectional flow of water, though the very weak inter-gel attractions still remain.

The microscopic patterns of cationic surfactant, *n*-dodecyltrimethylammonium chloride (DTAC) were observed.[51] Basic structures were cross-like. However, crystal size increased and the clustered blocks appeared at the central region. Film surfaces of polyoxyethylene alkyl ethers (POERE) changed from the smooth to rough as the HLB (hydrophile-liophile balance) values of the surfactants increased.[63] It was clarified that size and shape of surfactant molecules and their micelles influence the drying patterns. Drying patterns of fluorescent dyes[65] and simple electrolytes[69] such as KCl, NaCl, $CaCl_2$ and $LaCl_3$ were studied. The patterns changed greatly in the process of the solidification, i.e., crystallization. Many kinds of macroscopic and microscopic drying patterns observed mainly in our group are compiled in Table 3.

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