

# Dissipative crystallization of sodium salts of poly (d-glutamic acid), poly (l-glutamic acid), and their low molecular weight analogs

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**Abstract** Drying dissipative patterns were observed at room temperature on a cover glass, a watch glass, and a Petri glass dish during the course of dryness of aqueous solution of sodium salts of poly (d-glutamic acid), poly (l-glutamic acid), and their low molecular weight analogs, monosodium d-glutamate, monosodium l-glutamate, and monosodium dl-glutamate. The low molecular weight analogs were hygroscopic and their drying patterns were observed in a dry box coexisted with the bags of desiccant. The broad rings, which are the typical macroscopic drying patterns, were observed for all the samples. Optical isomeric effects on the drying patterns were not recognized. Spherulite (or hedrite) and rod-like crystals from the assemblies of helical main chains of the polymers are formed mainly at the inner area from the broad ring (except central area) and the broad ring area, respectively. Coexistence of sodium chloride enhanced the crystal structures by the cooperative interactions between the polymers and the salts. The typical *dissipative* crystallization such as accumulation, segregation, and orientation effects of crystals were observed in the drying patterns.

**Keywords** Poly (d-glutamic acid) · Poly (l-glutamic acid) · Drying pattern · Dissipative structure · Optical isomer · Convection

## Introduction

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 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 *convectonal*, *sedimentary*, and *drying* dissipative patterns during dryness of colloidal suspensions and solutions, though these three kinds of structures are correlated strongly and overlapped each other [1–3]. Furthermore, studies on the drying patterns of colloidal suspensions and polymer solutions are highly important in the industrial aspects such as painting, printing, and micro-array device fields.

Typical *convectonal* patterns are *Benard cell* [4, 5], the *hexagonal circulating* pattern, and *Terada cell* [6–8], the spoke-lines spreading whole the liquid surface accompanied with the huge number of cell convections in the normal direction of the spoke lines. These convectonal patterns were observed often with the naked eyes in the intermediate and final stages in the convectonal processes [9–17]. Recently, all the processes of the convectonal patterns have been clarified experimentally [11, 13, 14]. Theoretical studies of the convectonal patterns progressed mainly using Navier–Stokes equations [18–23]. However, these are not always successful yet when the theories are compared with the experimental results.

*Sedimentary* dissipative patterns during the course of drying suspensions have been studied in detail on a cover glass, a watch glass, a glass dish, and others, for the first time, in our laboratory [11, 24–31]. The broad ring-like patterns were formed in suspension state. It was clarified that the sedimentary particles were suspended above the substrate by the electrical double layers around the particles

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and always moved by the balancing of the force fields between the convective flow and the gravitational sedimentation. Quite recently, dynamic bundle-like sedimentary patterns formed cooperatively from the spoke-like convective structures of coffee [13] and black tea [14] coexisted with cream. It should be mentioned here that the sedimentary patterns are also formed in polymer solutions, though the patterns are not usually observed with the naked eye.

*Drying* dissipative patterns have been studied by many researchers for many kinds of colloidal particles [9, 10, 13–17, 24–49], linear-type synthetic and bio-polyelectrolytes [50–52], water-soluble neutral polymers [53, 54], ionic and non-ionic detergents [40, 55, 56], gels [57, 58], colloidal polymer complexes [59], and dyes [60]. The macroscopic broad ring patterns of the hill accumulated with the solutes formed. The broad rings moved inward when solute concentration decreased and/or solute size increased. For the non-spherical particles the round hill was formed in the central area in addition to the faint broad ring. Macroscopic spoke-like cracks or fine hills including flickering spoke-like ones were also observed for many solutes. Beautiful fractal patterns such as branch-, arc-, block-, star-, cross-, and string-like ones were observed in the microscopic scale.

One of the important findings in our experiments is that the primitive vague sedimentary patterns were formed already in the concentrated suspensions or solutions before dryness and they grew toward fine structures in the processes of the solidification [1–3]. It has been also clarified that *information* of the suspensions and solutions, shape and size of solute, and atmospheric humidity and temperature, for example, is *transferred* into the drying patterns [1–3]. Furthermore, *dissipative crystallization* of poly (allylamine hydrochloride) [49], poly (ethylene glycol) [61], sodium salt of poly (methacrylic acid) [62], poly-d-lysine and poly-l-lysine hydrobromides [63], hydroxypropyl cellulose [64], sodium salt of deoxyribonucleic acid [65], and sodium dextran sulfate [66] has been studied in detail. Accumulation, uneven distribution, symmetric distribution, ordering of the polymer single crystals, and further coupling of the single crystals with the dissipative broad ring patterns have been clarified.

In this work, drying dissipative patterns are studied at room temperature on a cover glass, a watch glass, and a Petri glass dish during the course of dryness of aqueous solution of sodium salts of poly (d-glutamic acid) (NaPDGA), poly (l-glutamic acid) (NaPLGA), and their low molecular weight analogs. One of the main purposes of this work is to clarify the stereo-specific effects of the biopolymers on the drying patterns. It should be mentioned here that the drying patterns of NaPLGA have been observed on a cover glass by the author's group [51]. The broad ring size decreased transitionally below the critical polymer concentration of  $\alpha$ -helix structure at the air–water interface.

## Experimental

### Materials

*GR*-grade of d-glutamic acid (specific rotation,  $[\alpha]_D^{20} = -29.5 \sim -32.5^\circ$ ), l-glutamic acid ( $[\alpha]_D^{20} = +31.5 \sim +32.5^\circ$ ), and dl-glutamic acid ( $[\alpha]_D^{20} = 0 \pm 1^\circ$ ) were purchased from Wako Pure Chemical Ind., Ltd. (Osaka). These solutions were neutralized with *GR*-grade of NaOH pellet to obtain the corresponding sodium salts of the glutamic acid, i.e., monosodium d-glutamate (NaDGA), monosodium l-glutamate (NaLGA), and monosodium dl-glutamate (NaDLGA). Poly-d-glutamic acid, sodium salt (NaPDGA, Lot no. 086K5100, molecular weight is unknown) was obtained from Sigma Co. Poly-l-glutamic acid (HPLGA1, molecular weight 2,000–15,000, Lot no. 2747F) and sodium salt of poly-l-glutamic acid (NaPLGA2, molecular weight 50,000–100,000, Lot no. 017 K5108) were purchased from MP Biochemicals Inc. (Solon Ohio) and Sigma Co. (St Louis, MO), respectively. Water used for the sample preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA).

### Observation of the dissipative structures

Of the solution, 0.1 mL was dropped carefully and gently on a micro cover glass (30×30 mm, thickness no. 1, 0.12 to 0.17 mm, Matsunami Glass Co., Kishiwada, Osaka) set in a plastic dish (type NH-52, 52 mm in diameter, 8 mm in depth, As One Co., Tokyo). The cover glasses were used without further rinse. The contact angle of the pure water was  $31 \pm 0.5^\circ$  from the drop profiles of water on an unrinsed cover glass. Extrapolation to the zero amount of water was made from the measurements at the several amount of water; 0.7 mL was set on a watch glass (50 mm in diameter, TOS TK-50, Toshinriko Co., Tokyo) and 0.7 mL of the sample was also set into a Petri glass dish (27 mm in inner diameter and 15 mm in height, TOP Co., Tokyo). The watch glass and glass dish were rinsed as thoroughly as possible. Dry box was a lunch box made of PMMA plastics (205×150×53 mm, Asvel Factory Co., Shanghai, China) with a transparent cap, from where the pictures of macroscopic patterns were taken. Four bags of chemisorptions-type desiccant (Nisso Dry-M50, Nisso Jushi Co., Ltd (Tokyo)) were set in the box. The disposable serological pipettes (1.0 ml, code 7077-1N, Corning Lab. Sci. Co.) were used for setting the sample suspensions.

The macroscopic patterns during dryness were observed on a desk covered with a black plastic sheet. A canon EOS-10D digital camera with a macro-lens (EF50 mm, aperture ratio,  $F=2.5$ ) and a life-size converter EF were used for

taking pictures of macroscopic patterns. Microscopic drying patterns were observed with a metallurgical microscope (PME-3, Olympus Co., Tokyo).

## Results and discussion

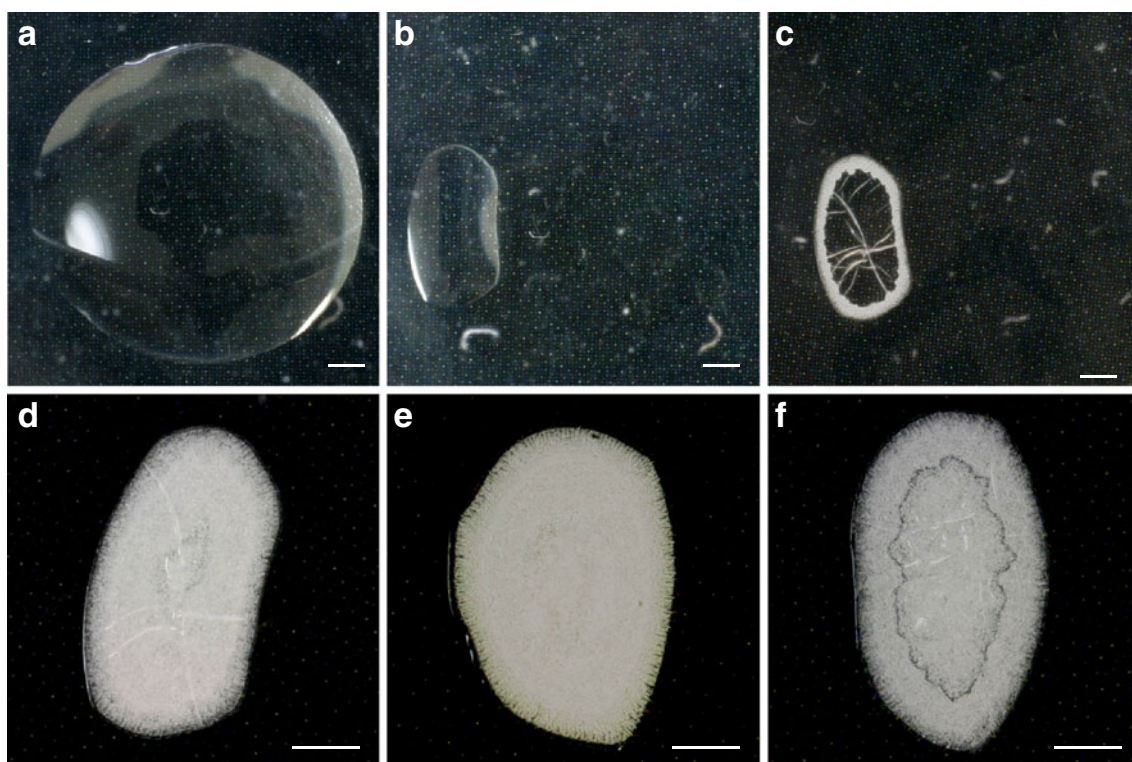
Drying patterns of low molecular weight analogs, NaDGA, NaLGA, and NaDLGA

Three kinds of NaGA were hygroscopic and did not dry up on the substrate in a room. Figure 1a–d shows the macroscopic patterns during the course of dryness of NaDGA on a cover glass in a dry box. After 2 months the broad ring patterns appeared clearly, but dryness of the central area was still incomplete as is shown in Fig. 1c. Pictures d, e, and f are the drying patterns of NaDGA, NaLGA, and NaDLGA 1.5 years after setting the initial solutions. The broad rings originating from the convection appeared clearly at the outside edge irrespective of the samples examined. The spoke lines, which also originated from the convection patterns in the cooperated processes of dryness, i.e., convection, sedimentation, and solidification, were observed especially in the broad ring area [1–3]. The drying patterns NaDGA, NaLGA, and NaDLGA look to be

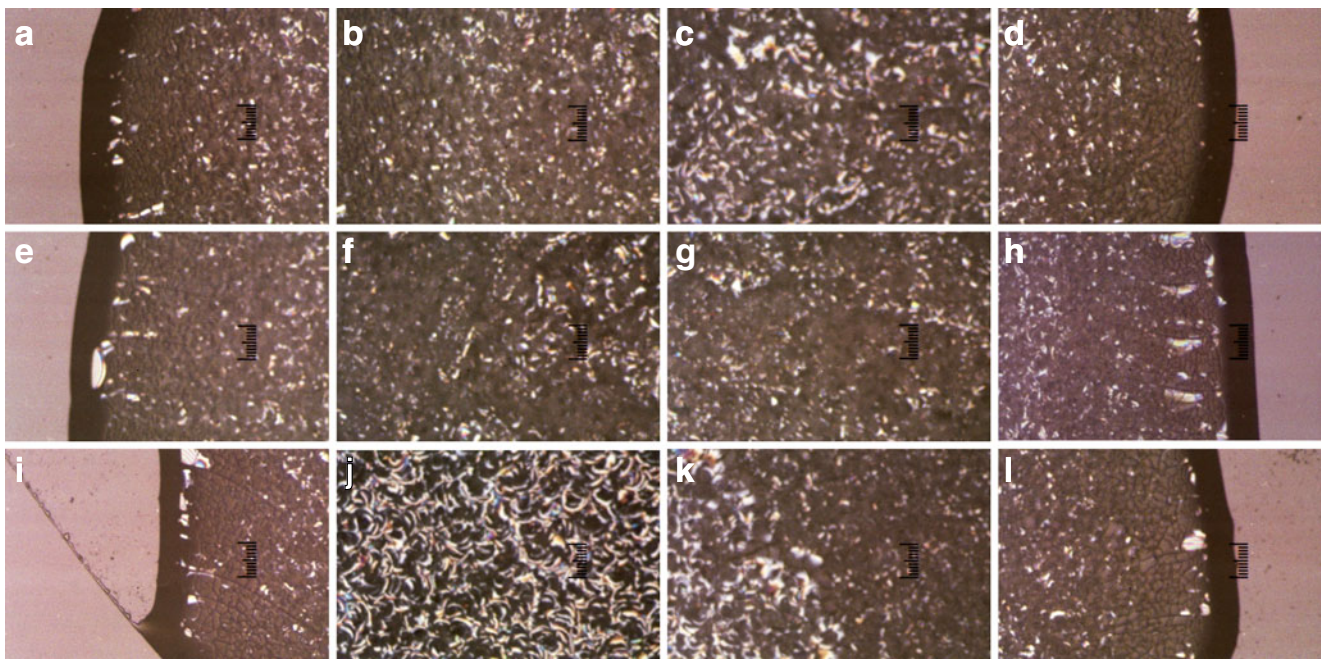
quite similar to each other (see d to f) and insensitive to the optical isomerism (chirality) of the molecules.

Figure 2 shows the microscopic drying patterns of NaDGA, NaLGA, and NaDLGA on a cover glass in a dry box. Single crystals of NaGA are known to be needle-like [67, 68]. However, curved rod-like microstructures are accumulated densely at the outside area near the broad ring and less densely at the central region, respectively. A main cause for the bending of the needles will be due to the irregular super-saturation taking place by the convectional stages followed by the solidification process. It should be mentioned here that the bent rods were not oriented at the central area of the dried film and further any differences in the drying patterns were not recognized among the different optical isomers.

Sizes of the drying broad rings ( $d_f$ ) were very small compared with those of the initial liquid ( $d_i$ ). The ratios  $d_f/d_i$  values are shown in Fig. 3. The  $d_f/d_i$  values are between 0.1 and 0.3 and increased as solute concentration increased and were quite insensitive to the optical isomer. Increase in the broad ring size with the molecular weight has often observed for poly (ethylene glycol) [61], polylysine hydrobromide [63], and hydroxypropyl cellulose [64]. This result is due to the very large excluded volumes of the polymers compared with those of the low molecular weight analogs.



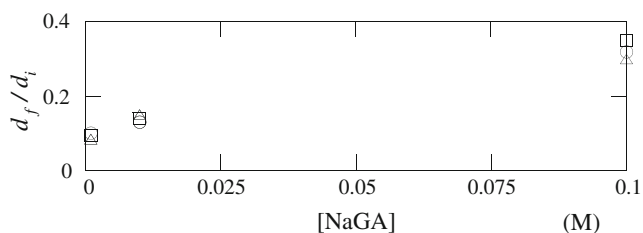
**Fig. 1** Drying patterns during the course of drying aqueous NaDGA (a–d), NaLGA (e), and NaDLGA (f) solution on a cover glass in a dry box at 25 °C. 0.1 ml, 0.1 M, a 45 m after setting, b 23 h and 15 min, c 61 days, and d–f 546 days. Length of the scale bar is 1.0 mm



**Fig. 2** Microscopic drying patterns of aqueous NaDGA, NaLGA, and NaDLGA solutions on a cover glass at 25 °C. 0.1 ml, [NaGA]=0.1 M, **a, e, i to d, h, l** are the pictures from left edge to the right, full scale is 100  $\mu\text{m}$

#### Drying patterns of NaPDGA, NaPLGA, and NaPDGA+NaPLGA

Figure 6 shows the macroscopic drying patterns of NaPDGA (a–d), NaPLGA (e–h), and their mixture NaPDGA+NaPLGA (1:1) (i–l) on a cover glass. Total polymer concentration decrease from the left edge (0.02 monoM) to the right (0.0006 monoM). NaPDGA was slightly hygroscopic in contrast with NaPLGA and the mixture NaPDGA+NaPLGA. The broad rings were observed clearly at the outside edges irrespective of polymer concentration. A secondary faint broad ring also appeared in the inner area of the main broad ring at the outside edge (see pictures h and j, for example). This will be due to the coexistence of the helical and coil-rich conformation of the polymer chain and/or the rather high distribution in the molecular weight of the polymers. It should be recalled here that the size of the broad ring shrank around the central area of the initial solution at the concentrations lower than

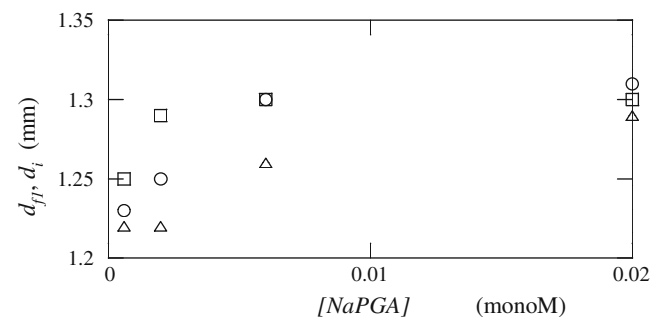


**Fig. 3** Plots of  $d_f/d_i$  of NaDGA (open circle), NaLGA (open triangle), and NaDLGA (open square) solutions on a cover glass as a function of solute concentration

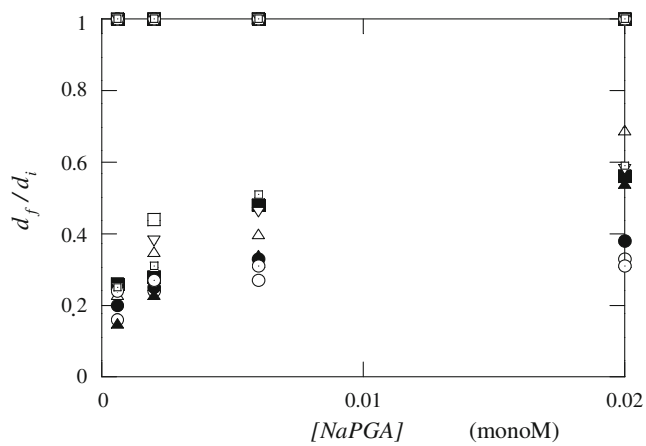
the critical concentration  $m^*$  for NaPLGA [51]. The similar shrinking of the broad rings appeared again in the present work as is shown in Fig. 4, where sizes of the primary broad rings ( $d_f$ ) of NaPDGA (shown by open circles), NaPLGA (triangles), and NaPDGA+NaPLGA (1:1, squares) are shown as a function of polymer concentration. The  $m^*$  values are close to 0.003 monoM being close to the previous work [51, 69].

The  $d_f/d_i$  values are shown in Fig. 5. The symbols being located at unity are the values corresponding to the primary broad rings, and the symbols at the smaller values than unity are the secondary broad rings. All the ratios are insensitive to the optical isomerism of the polymer when the experimental errors are taken into account (Fig. 6).

Figure 7 shows the typical examples of the microscopic drying patterns of NaPLGA on a cover glass (a, b). Pictures

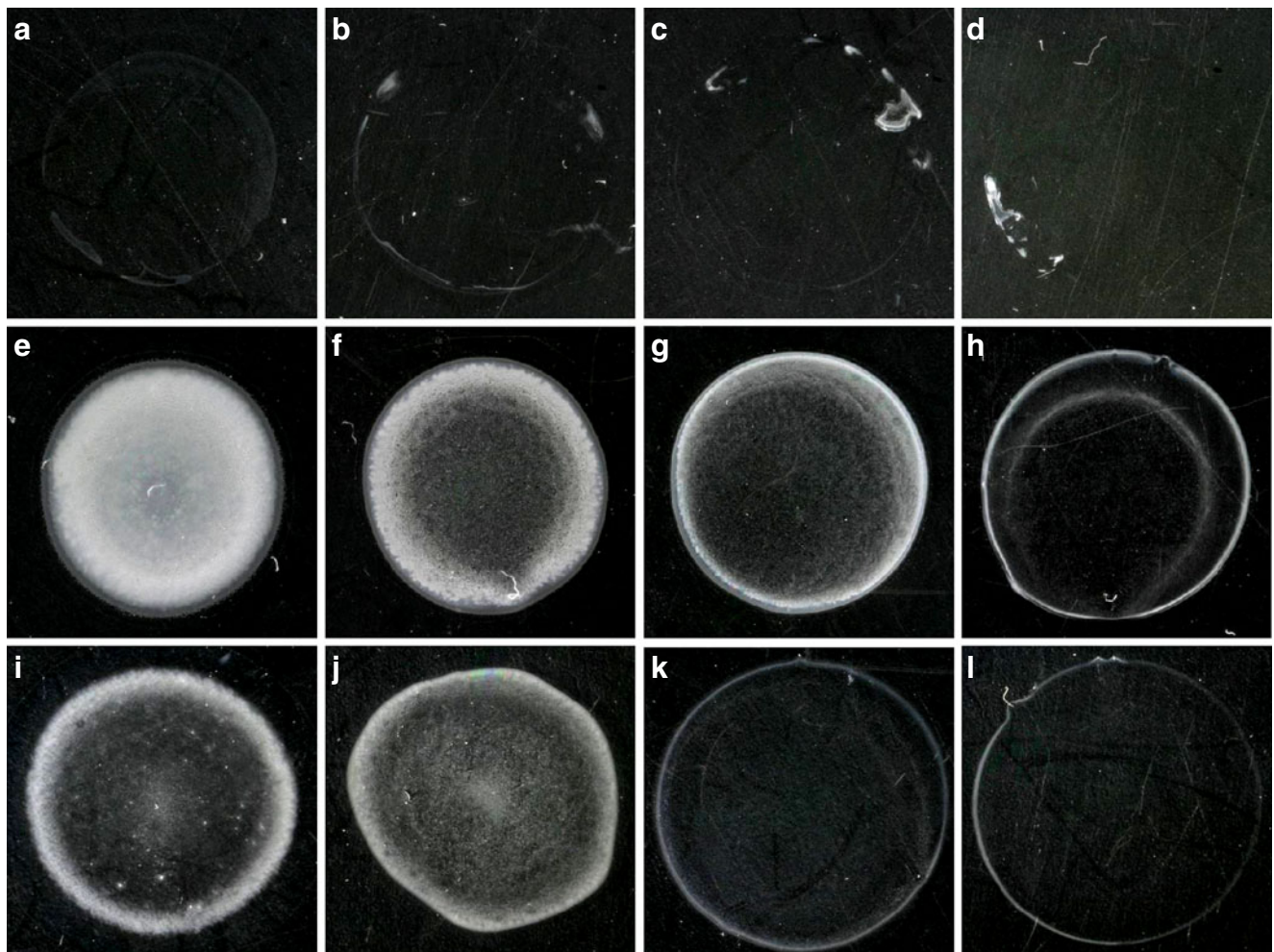


**Fig. 4** Plots of the size of the primary broad rings  $d_f$ , which correspond to those of initial liquids  $d_i$ , of NaPDGA (open circle), NaPLGA2 (open triangle), and NaPDGA+NaPLGA2 (open square) on a cover glass

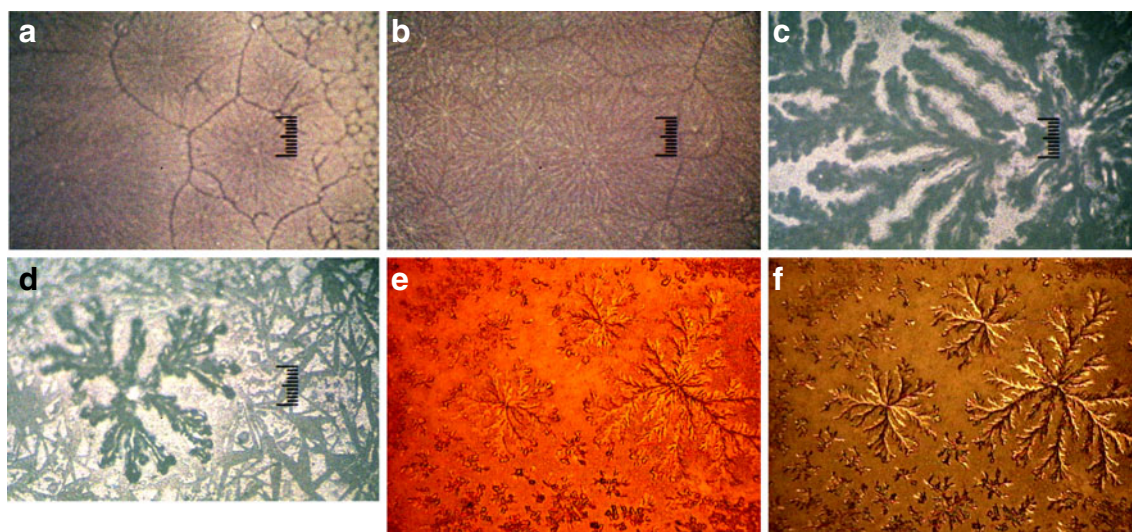


**Fig. 5** Plots of  $d_f/d_i$  of NaPDGA (open circle, open triangle, open square), NaPLGA2 (close circle, close triangle, close square), and NaPDGA+NaPLGA2 (circled dot operator, inverted open triangle, dotted open square) solutions on a cover glass (open circle, close circle, circled dot operator), a watch glass (open triangle, close triangle, inverted open triangle), and glass dish (open square, close square, dotted open square) as a function of polymer concentration

c to f are the patterns of NaPDGA+NaPLGA on a watch glass. Spherulite and hedrite crystal structures are observed clearly a, b, and c to f, respectively. The Maltese crosses, though incomplete, appeared in the pictures e and f from polarizing microscopy. The spherulite and hedrite structures have been observed in the drying patterns of aqueous solutions of poly (ethylene glycol) [61, 70–73] and sodium salt of poly (methacrylic acid) [62]. It should be noted here that the spherulite and hedrite patterns were observed so often at the inner broad ring areas except the central region of the dried film. The rod-like crystal structures formed mainly in the broad ring area (see Fig. 10a below for NaPLGA on a watch glass, for example). Iizuka et al. reported the rod-like liquid crystals for the concentrated aqueous solution of NaPLGA [74]. It should be noted here that the rod-like crystals in this work are similar to the liquid-crystal patterns of hydroxypropyl cellulose [64, 75, 76], sodium salts of deoxyribonucleic acid [77], and polynucleotide complexes [78]. Formation of the microstructures of the spherulite (or hedrite) and the rod-like



**Fig. 6** Macroscopic drying patterns of aqueous NaPDGA (a–d), NaPLGA1 (e–h), and NaPDGA+NaPLGA1 (1:1) (i–l) solutions on a cover glass at 25 °C. a, e, i 0.02 monoM; b, f, j 0.006 monoM; c, g, k 0.002 monoM; d, h, l 0.0006 monoM



**Fig. 7** Optical (a–d) and polarizing (e, f) microscopic drying patterns of aqueous NaPLGA1 (a, b) and NaPDGA+NaPLGA1 (1:1) (c–f) solutions on a cover glass (a, b) and a watch glass (c–f) at 25 °C;

0.1 ml (b, c), 0.7 ml (a, d–f), [NaPLGA1]=0.02 ml, [NaPDGA+NaPLGA1]=0.02 monoM, full scale is 100  $\mu$ m (a–d), length of the picture frame (e, f) is 2.6 $\times$ 3.4 mm

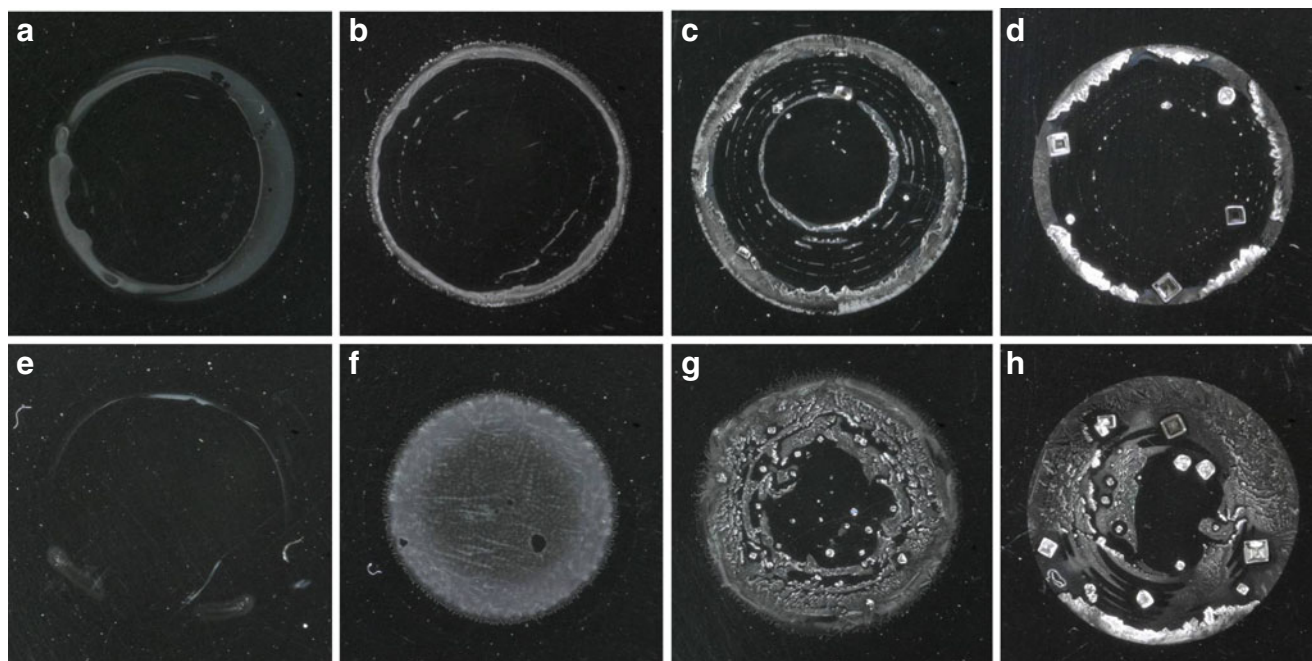
crystals at the different places of the dried film is one of the dissipative effects, which takes place during the course of dryness, especially in the convective processes.

Drying patterns of NaPDGA, NaPLGA, and NaPDGA+NaPLGA with coexistence of sodium chloride

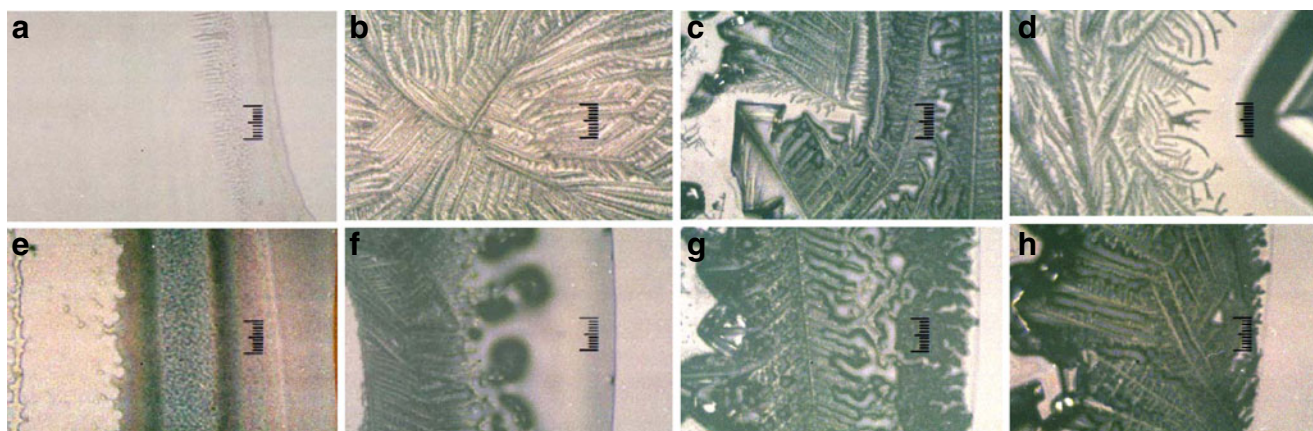
Figure 8 shows the macroscopic drying patterns of aqueous solutions of NaPDGA+NaCl (a to d) and NaPLGA+NaCl (e to h) on a cover glass. The main broad rings remained at

the outside edges irrespective of the salt concentration. However, broadening of the ring took place by the addition of NaCl. Interestingly, secondary broad rings became clear with coexistence of sodium chloride. In the presence of the excess amount of sodium chloride at 0.2 M, cubic single crystals were isolated.

Figures 9 and 10 show the influences of the sodium chloride coexisted upon the microscopic patterns of NaPDGA+NaPLGA on a cover glass and a watch glass, respectively. An important finding is clear from the



**Fig. 8** Macroscopic drying patterns of aqueous NaPDGA+NaCl and NaPLGA+NaCl solutions on a cover glass at 25 °C; 0.1 ml, [NaPDGA]=0.008 monoM (a–d); a [NaCl]=0 M, b 0.004 M, c 0.04 M, d 0.2 M, [NaPLGA2]=0.008 monoM, e 0 M, f 0.004 M, g 0.04 M, h 0.2 M



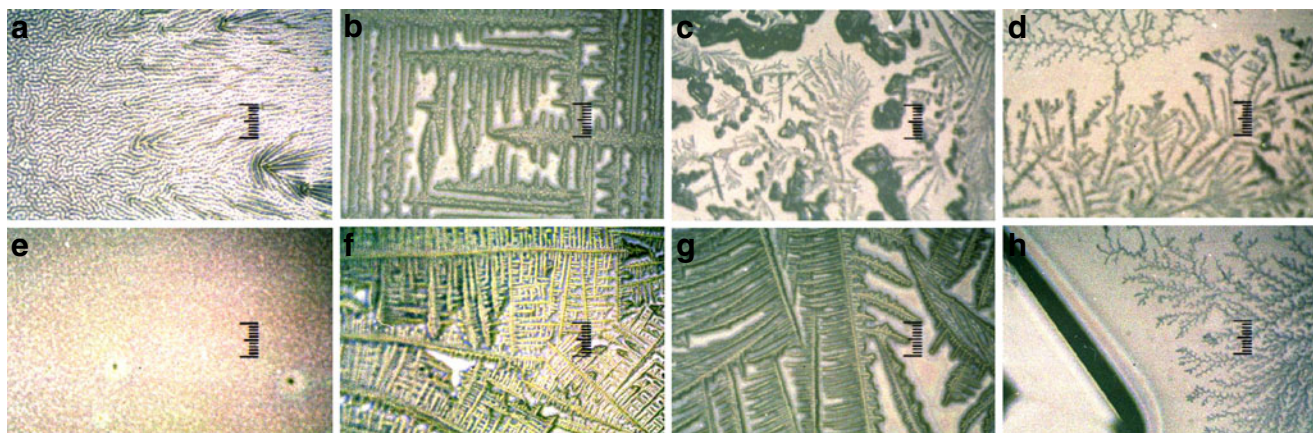
**Fig. 9** Typical microscopic drying patterns of aqueous NaPDGA+NaCl (a–d) and NaPLGA2+NaCl (e–h) solutions on a cover glass at 25 °C; 0.1 ml, [NaPDGA]=[NaPLGA2]=0.008 monoM, [NaCl]=0 M (a, c), 0.004 M (b, f), 0.04 M (c, g), 0.2 M (d, h), full scale is 100  $\mu$ m

pictures, i.e., the microscopic patterns shifted slightly from the microstructures of the rod-like assemblies toward the hedrite structures. This pattern shift will be due to (a) the conformational change from the stretched helical rod to the coil-like main chains. (b) Cooperative interaction between NaPGA polymers and the salt (see, Fig. 9c and g, for example) and the segregation effect between the polymers and the salt (see, Figs. 9d and 10h, for example) are also important.

#### Concluding remarks

In the present work, (a) rod-like liquid-crystal assemblies of the helical-chains, (b) spherulite crystals, and (c) hedrite-type single crystals are observed. Interestingly, these patterns are localized and accumulated at the different places in a dried film. Rod-like crystals formed mainly in the broad ring area, whereas spherulite and hedrite crystals appeared at the inner broad ring areas except the central region of the drying film. Localized accumulation of each

pattern is one of the typical dissipative effects. The main cause is due to the distortional forces upon the polymer molecules raised by the convective flow of solvent and then the polymer themselves during the cooperative drying processes, where convection, sedimentation, and solidification processes coexist. The localized accumulation means that the polymer crystallization does not take place homogeneously on earth. In other words, homogeneous crystallization is almost impossible to take place in the gravity, since the gravitational convection always takes place on earth. Microgravity experiments of the drying dissipative patterns of deionized suspension of colloidal silica spheres were made [79]. It is surprising to note that the broad ring patterns still appeared 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, because the differences in the local solution temperature always takes place by the evaporation of solvent even in microgravity. We should note here that the



**Fig. 10** Typical microscopic drying patterns of aqueous NaPDGA+NaCl (a–d) and NaPLGA2+NaCl (e–h) solutions on a watch glass at 25 °C; 0.7 ml, [NaPDGA]=[NaPLGA2]=0.008 monoM, [NaCl]=0 M (a, c), 0.004 M (b, f), 0.04 M (c, g), 0.2 M (d, h), full scale is 100  $\mu$ m

broad ring patterns are formed already in the processes of convectional flow of water and polymer themselves in solution state. The broad ring-like sedimentation patterns have been observed in many colloidal systems as was described already in **Introduction**. We should further note that the sedimentation process also should exist during the course of drying solution systems, though the direct observation is difficult compared with the suspension systems.

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