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Stripe Pattern Formation in K-carrageenan Gel

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The rod shape gel with the liquid crystalline layers periodically frozen is firstly obtained. The rod gel is prepared when the potassium ion is diffusing into the κ-carrageenan solution from the one end of the glass capillary that contains the κ-carrageenan solution. Both of the distance between two adjacent liquid crystalline layers (spacing, Δx_m) and the thickness of liquid crystalline layers (width, w_m) linearly depend on the distance from the diffusing end of the potassium ion. Furthermore, the spacing coefficient p and width coefficient α is inversely proportional to the concentration of potassium ion. These results are in good agreement with the Liesegang pattern.

Key word: Gelation, K-carrageenan, Liesegang pattern, Liquid Crystalline, Diffusion

Introduction

The spatial pattern in the chemical and biological systems is currently interested phenomena in the chemistry and the physics [1,2]. One of the familiar spatial pattern that appears in the gel is Liesegang pattern. Liesegang pattern is formed by product that result from the reaction of diffusing metal ions in the gel [3-9]. The gel only works as a supporting medium of the spatial patterns in the system. In this study, we introduce a new spatial pattern of liquid crystal layers in gel. The pattern is formed as a result of the coupling of the ion diffusion and the gelation.

The system studied here consists of κ-carrageenan and potassium chloride. The repeating unit of κ-carrageenan consists of →3)-β-D-Gal*p* 4-sulfate-(1.4)-3,6-anhydro-α-D-Gal*p*-(1→, as shown in Fig. 1. K-carrageenan in water transforms into gel and then into liquid crystal under the presence of group I cations [10,11]. K-carrageenan aq. solution gels at lower concentration regions of the gel promoting cations. In contrast, the liquid crystalline gels are obtained at higher concentration regions of the gel promoting cataions [12,13]. In the following sections, we describe what rules govern its pattern and discuss the results in terms of the Liesegang phenomenon.

Experiment

K-carrageenan and potassium chloride (reagent grade) were purchased from Wako Pure Chemical Co. Ltd. and used without further purification. K-carrageenan was dissolved into water at a concentration of 1 wt % at 50°C. The solution was then transferred into a glass capillary. The inner diameter and the length of the capillary were 1.9 mm and 40 mm, respectively. One ends of the capillary were sealed with the cellulose membrane whose pore size is 2.5nm (Japan Medical, Science, Japan). The one end sealed with the cellulose membrane was kept in contact with the potassium chloride solutions for 1day at a temperature of 50°C. The concentrations of potassium chloride solution were changed from 0.1 to 4.0 M. The gels obtained were taken out of the capillary and observed under polarized microscope. The polarized microscope images of the gels were captured the digital camera. The intensity profile of the images was obtained by using the image analyzing software.

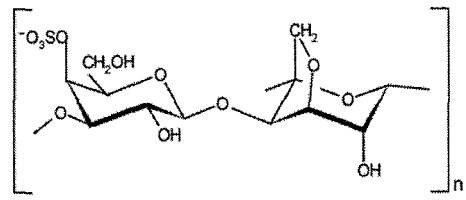

Figure 1. Chemical structures of repeating unit of κ-carrageenan.

Results

The rod gels obtained are almost transparent under the

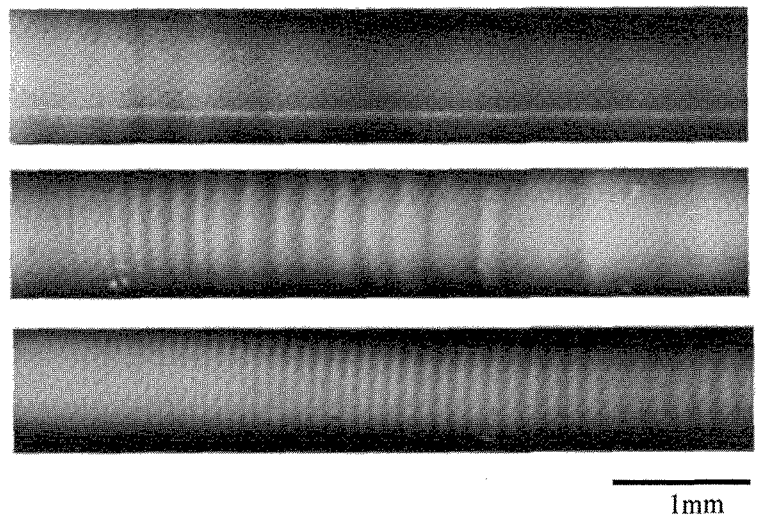

Figure 2. The polarized microscope images of κ-carrageenan gel. The potassium chloride concentrations are 0.2M, 0.5M, and 3.0 M from top to bottom.

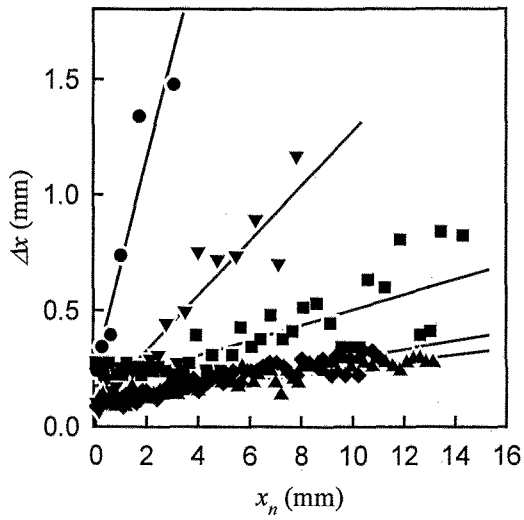

Figure 3. The relationship between the spacing Δx_n and the distance form the diffusing end x_n. The potassium chloride concentrations are, 0.2M; ●, 0.5M; ▼, 2.0M;■, 3M; ◆, and 4M; ▲, respectively. The lines are the least-squares fit to the results.

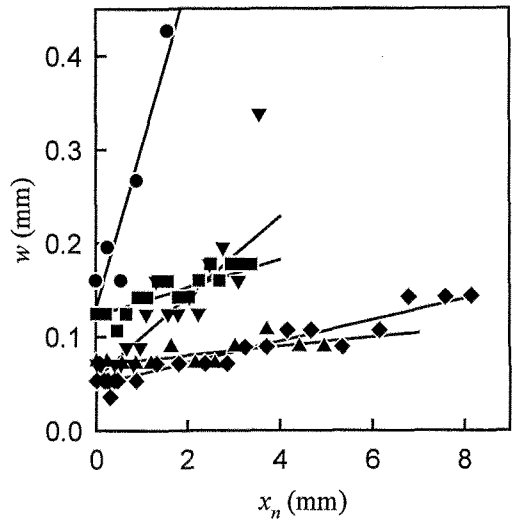

Figure 4. The relationship between the width w_n and the distance form the diffusion end x_n. The symbols are the same with that of Fig. 3. The lines are the least-squares fit to the results.

natural light. The gels exhibit, however, strong polarized light under the cross-nicoles as shown in Fig. 2. Figure 2 also show the samples obtained under various concentrations of the potassium chloride. The periodical stripe pattern whose width are about 80~500μm is created within the gel. The rotating gel on the stage of polarized microscope changes the intensity of the polarized light. It strongly suggests that the brighter regions consist of the liquid crystal whose domains are oriented to the same direction. The distance between adjacent liquid crystalline layers " Δx_n " and the thickness of the liquid crystalline layers " w_n " varies according to the distance from a diffusing end of the potassium ion" x_n " as shown in Fig.2. The dependence of the x_n on Δx_n is show in Fig.3 The Δx_n linearly increases with x_n. This linear relation can be written as,

$$\Delta x_n = p\, x_n + const. \qquad (1)$$

The coefficient p is called as the spacing coefficient. On the other hand, Fig. 4 shows the dependence of x_n on w_n. This figure demonstrates that w_n also, linearly increases with the x_n. Hence, w_n are, as same as formation of Δx_n, expressed by.

$$w_n = \alpha x_n + const. \qquad (2)$$

The coefficient α is called as the width coefficient. Furthermore, Fig. 3 and Fig. 4 indicate that the spacing coefficients p and the width coefficient α strongly depend on the concentration of the solution of potassium chloride. In Fig. 5, the spacing coefficients p and the width coefficients α are plotted as a function of the concentration of the solution of potassium chloride in a double logarithmic manner. This figure clearly indicates that both p and α are inversely proportional to the concentration of the solution of potassium chloride.

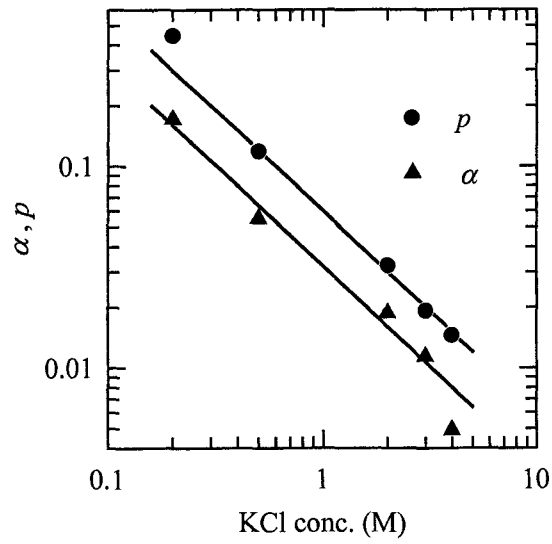

Figure 5. Double logarithmic plot of the spacing coefficient p,●, and the width coefficient α,▲, as a function of the concentration of potassium chloride. The slop of the lines are −1.

Discussion

The spatial pattern obtained here looks quite similar to Liesegang pattern [3-9]. In Liesegang pattern, both of Δx and w linearly increase with distance from the diffusing end x_n as eq. (1) and eq.(2) [5-8]. Moreover, the spacing coefficient, p, in the Liesegang pattern is well described by the following equation in experimentally [9] and theoretically. [6]

$$p = F(C_{B0}) + G(C_{B0})/C_{A0} \qquad (3)$$

Here, C_{A0} is the initial concentration of the salt A that diffuses into the gel and C_{B0} is the initial concentration of the salt B that presence in the gel (hereafter, A and B are called as the diffusant and the reactant for the sake of simplicity). The coefficients F and G are functions of the concentration of the reactant, C_{B0}. The substances A and B correspond to potassium chloride and κ-carrageenan in the present system. In this experiment, we only take into account the initial concentration of the salt A ,C_{A0}, as variable, hence C_{B0}=*const.* Therefore, the spacing coefficient in eq. 3 depends on the concentration of diffusant inversely.

On the other hand, the dependence of diffusant to w_n also needs to characterize in terms of the Liesegang pattern. However, the dependence of diffusant concentration to width coefficient, α is not well has yet to be clarified in detail in experimentally, though it already has been discussed theoretically [8]. Here we will consider the dependence of diffusant to width coefficient α. The distance between adjacent liquid crystalline layers is expressed by Δx_n. The concentration of κ-carrageenan before pattern formation is C_{B0}, which is uniform in space. After pattern is formed, the region Δx_n separates into two regions. One region consists of the liquid crystalline gel whose width is w_n with the average concentration of C_{LC}. The other is the amorphous gel, its width is $(\Delta x_n - w_n)$, with average concentration C_{AG}. Both the amorphous and the liquid crystalline regions of the patterned gel solely consist of κ-carrageenan in the present case. The decrease of the concentration of polymer network in the amorphous gel is, hence, compensated by the increase of the concentration of liquid crystalline gel in the layer. The conservation of mass yields following relationship.

$$C_{B0}\,\Delta x_n = (\Delta x_n - w_n)\, C_{AG} + w_n C_{LC} \qquad (4)$$

The width of the pattern can be written as follows.

$$w_n = \frac{C_{B0} - C_{AG}}{C_{LC} - C_{AG}} \Delta x_n \qquad (5)$$

Substitution of eq. 1 into above equation yields following equation.

$$w_n = \frac{C_{B0} - C_{AG}}{C_{LC} - C_{AG}}\, p x_n \qquad (6)$$

By comparing eq. 6 with eq. 2, the width coefficient α is simply expressed by the spacing coefficient p as follows.

$$\alpha = \frac{C_{B0} - C_{AG}}{C_{LC} - C_{AG}}\, p \qquad (7)$$

The front factor of the spacing coefficient in eq. 7 is only

a function of the concentration of the reactant. The width coefficient, hence, depend on the concentration of the diffusant in the same manner. Hence, the dependence of diffusant concentration to width coefficient expressed as $p \sim \alpha \sim C_{B0}^{-1}$.

Because the presented pattern can be regarded as one of the Liesegang pattern, the κ-carrageenan should behaves as a supporting medium of the pattern as well as a pattern forming substance. The liquid crystal state in gel would be the result of alignment of the double helical zones of κ-carrageenan [10,11]. The creation of the liquid crystal, dense phase of the polymer network also indicates the creation of the dilute phase of polymer network according to the conservation of mass. Both phases are spontaneously fixed in space because the formation of liquid crystal and the growth process occur in the gel state. Once the liquid crystal layer is formed in space, it triggers the formation of layers along the direction of diffusion. These may be the origin of the stripe pattern in the present system.

Conclusion

We found out that the rod gel with periodic liquid crystalline layers can be arranged using simple method by which potassium chloride diffuse into the solution of κ-carrageenan. The spacing and width of the liquid crystalline layers linearly increase with the distance from the diffusing end. Both of the spacing coefficient p and the width coefficient α depend on the concentration of potassium ion inversely. The pattern obtained from this method agrees well with Liesegang phenomenon. In this system, the κ-carrageenan, hence, behaves as a supporting medium of the spatial pattern as well as the pattern forming substance. The pattern should be spontaneously frozen into the polymer network of the gel because the formation of the liquid crystalline gel occurs in the gel state.

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