

SHRINKING PATTERNS OF GELS

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The pattern formation process in shrinking gels is studied using a confocal laser scanning microscope. The distribution and its time evolution of polymer network in the pattern are observed. The results indicate the non-uniform distribution of the polymer network in the gel during the pattern formation process. From the time evolution of the confocal images, we found that this process occurs much faster than the collective diffusion process of the polymer network.

Key words: gel, volume phase transition, pattern, confocal laser scanning microscope, collective diffusion

1. INTRODUCTION

When a gel is exposed to the condition at which the gel collapses into compact state, beautiful patterns appear in the gel. The shrinking pattern of the gel is characterized by its polymorphism [1]. The pattern formation in the shrinking gel strongly suggests that the distribution of polymer network in the gel changes in time and space creating either dense and dilute regions. Although we expect such dynamics of polymer network during pattern formation process, experimental studies have yet to be made.

One of the recent advances in the optical microscopic technology is the development of confocal laser scanning microscope [2]. By using the confocal laser scanning microscope, the distribution of polymer network in the focal plane can be determined. Here, we use a confocal laser scanning microscope to study the time evolution of density distribution within the gel during pattern formation process in shrinking gel.

2. EXPERIMENTAL

Gels were prepared by the radical copolymerization of acrylamide and the cross-linker at a temperature of 60 °C for 12 hrs. The total concentration of monomer was fixed at 700 mM. Gels were prepared in the micropipetts of known inner diameter (506 μm). The gel thus obtained were taken out of micropipetts. Then the gels were soaked in fluorescein isothiocyanate solution to label the polymer network. The gels were washed in a large amount of water to remove the residual chemicals. Both ends of the gel were fixed on a gel holder and then the gel was collapsed in acetone-water mixture. The pattern formation process was observed using a confocal laser scanning microscope that was equipped with an image processor. The time evolution of the image was also recorded on a video tape. The images thus obtained were analyzed by NIH Image. The confocal laser scanning microscope used in this study was constructed by the inverted microscope (Axiovert S100; Carl Zeiss), the confocal unit (CSU 10;

Yokogawa), and the Ar-ion laser (type 532-50BS/170, 488 nm, 50 mW; Omnicrome) equipped with the fiber optic apparatus. In the present apparatus, the fluorescence image of the sample, which is excited by the light source (Ar-ion laser), is observed by the confocal system. The thickness of the sliced focal plane is determined by the optical setup of the system: in the present case, the thickness is less than 35 μm (objective: $\times 10$, N.A.=0.3). The microscope system was set on an optical table to avoid the external mechanical disturbance. The gel was set in a special cell and the environmental solvent was changed from water to acetone-water mixture of known volume fraction. The time evolution of the confocal image of the gel was monitored using an image processor system (cooled charge-coupled device camera C5985H and ARGUS-20; Hamamatsu) and also recorded by a video recorder.

3. RESULTS and DISCUSSION

Figure 1 shows the typical patterns that appear in the shrinking gels. These patterns are observed when the gels are collapsed in the mixed solvent of water and acetone. The volume fraction of acetone in the mixed solvent is 70 % or 80 %. These phase contrast images clearly indicate that various patterns develop in the shrinking gels. By the phase contrast method, the difference of the refractive index within the sample is enhanced to aid the clear observation. The refractive index of the system depends on both the polarizability and the density of the sample. In the present case, the polarizability and the density of sample is initially constant since the sample used here is poly(acrylamide) gel that prepared at a concentration of 700 mM. These images, therefore, suggest that the non-uniform spatial distribution of the polymer network evolves during the shrinking process of the gel. Although the images are clear, quantitative discussion of the pattern may be difficult only by the phase contrast method.

The confocal images of shrinking pattern are shown in Fig 2. A hollow bubble is formed in this case. The focus is set at the center of the gel throughout the observation. Since the fluorescence

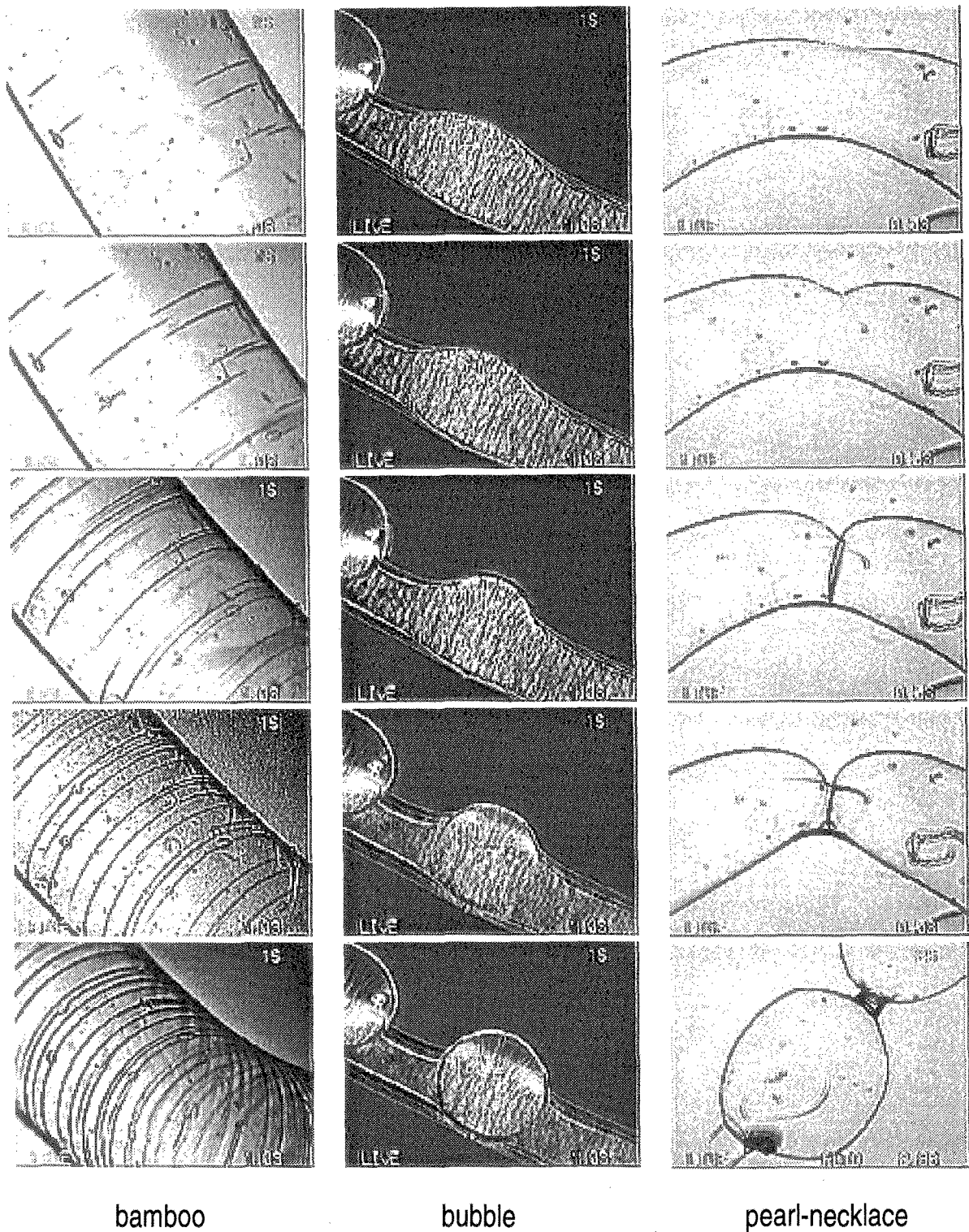


Figure 1 The time evolution of typical patterns that appear in the shrinking gels (from top to bottom). These snap shots are reproduced from the video tape. The images are taken by the phase contrast method. The objective lenses used here are X5 for bamboo and pearl-necklace patterns and X10 for bubble pattern, respectively. The time interval between any two successive snap shots are not the same.

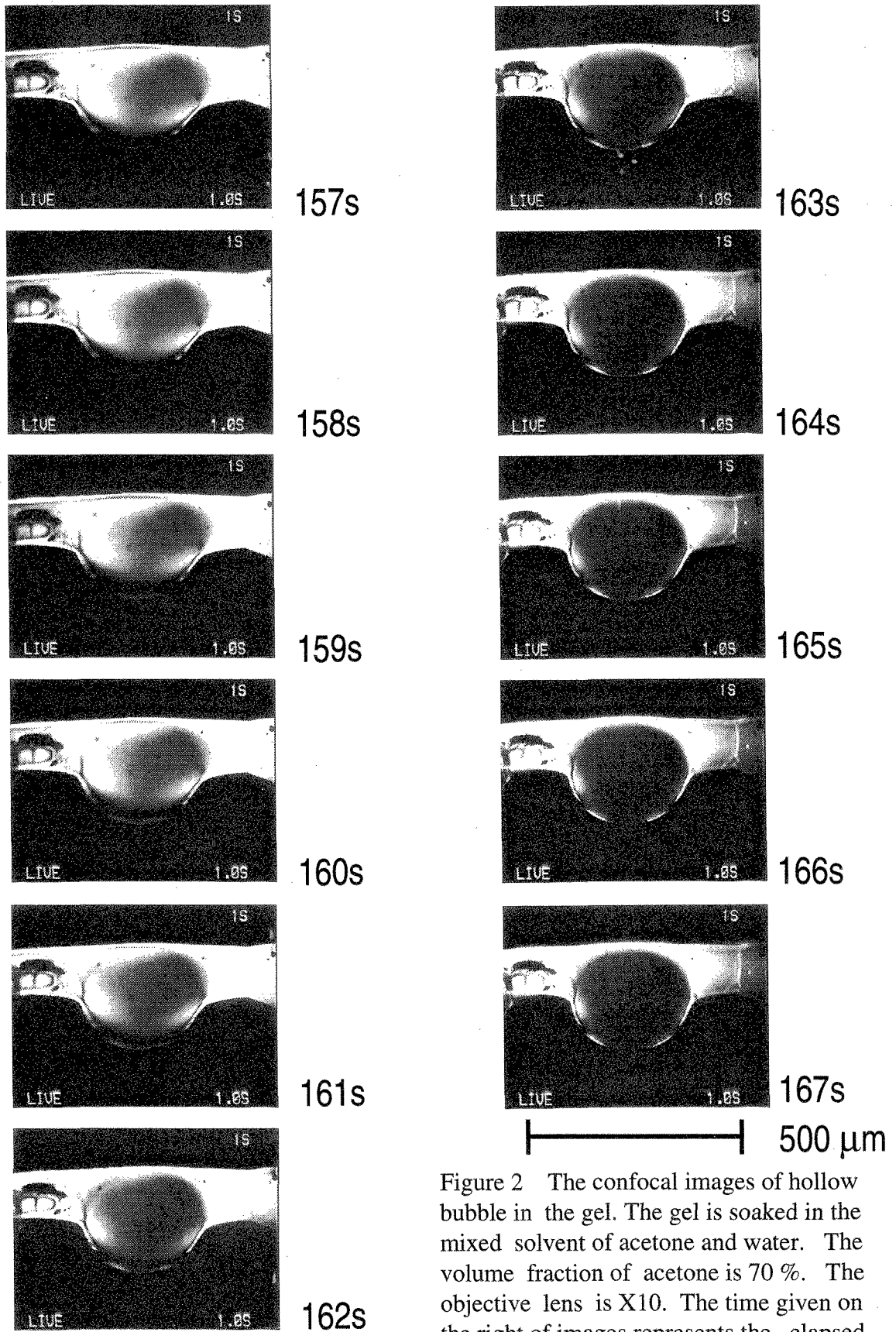


Figure 2 The confocal images of hollow bubble in the gel. The gel is soaked in the mixed solvent of acetone and water. The volume fraction of acetone is 70 %. The objective lens is X10. The time given on the right of images represents the elapsed time after changing the solvent from water to mixed solvent.

dye is labeled to the polymer network, the bright portion of the image corresponds to the portion where the density of polymer network is higher than darker portions. The distribution of the brightness in the gel, therefore, directly represents the spatial distribution of the polymer network in the pattern. It is clear from these snap shots that that the fluorescence are observed within the bubble in the early stage of the pattern formation. The bright portion, however, quickly disappears from inside the bubble. Then the hollow bubble is formed within 10 sec.

It is worth noting that the pattern formation in the shrinking gel is rather fast process than the collective diffusion process of the polymer network. The characteristic time τ of the collective diffusion process of the polymer network is given as follows [3].

$$\tau = r^2 / D_{coop} \quad 1)$$

Here r and D_{coop} are the typical scale of the length and the collective diffusion coefficient of the gel. In the present case, for instance, the polymer network that exists in the hump at 157 s disappears with time as shown in Fig 2. The characteristic time for this process can be estimated using eq 1. The radius of the bubble is of the order of 0.15 mm that corresponds to r . The collective diffusion coefficient of the gel is reasonably assumed to be of the order of 10^{-7} cm²/s [4]. The characteristic time of the collective diffusion of the polymer network in the bubble is, thus, estimated to be $\tau = 2.3 \times 10^3$ s. On the other hand, the confocal images that shown in Fig 2 indicate that the polymer network in the bubble disappears within 10 s. This estimated characteristic time is two orders of magnitude larger than the observed time scale. These results strongly suggest that the pattern formation in the shrinking gel can not be explained in terms of the simple collective diffusion process of the polymer network.

4. CONCLUSIONS

We demonstrate that the confocal laser scanning microscope is useful to study the pattern formation process in the gel. It is shown that the spatial distribution of the polymer network rapidly changes with time when the pattern is formed in the shrinking gel. This process occurs much faster than the collective diffusion process of the polymer network.

The thick membrane is formed on the surface of the shrinking gel. Such a thick membrane prevent the shrinking process of the gel. For instance, the diffusion of solvent may be affected by the membrane [5]. It is also expected that the elastic property and the frictional property of the membrane may change the shrinking process of the gel [6]. The mechanical properties of the membrane, therefore, play essential

roles for the polymorphism of pattern in the shrinking gel. We believe that further studies on the pattern formation process in the shrinking gel will promote the better understanding of the dynamics of polymer network.

5. REFERENCES

1. E.S. Matsuo and T. Tanaka, *Nature*, **358**, 482-485 (1992).
2. M.D. Egger and M. Petran, *Science*, **157**, 305-307 (1967).
3. T. Tanaka and J.D. Fillmore, *J. Chem. Phys.* **70**, 1214-1218 (1979).
4. T. Tanaka, L.O. Hocker, and G. Benedek, *J. Chem. Phys.*, **59**, 5151-5159 (1973).
5. M. Tokita, T. Miyoshi, K. Takegoshi, and K. Hikich, *Phys. Rev.*, **E53**, 1823-1827 (1996).
6. M. Tokita and T. Tanaka, *J. Chem. Phys.*, **95**, 4613-4619 (1991).

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