Anomalous Aggregation Pattern Observed on Gels in Mixed Solvent

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Introduction. Permanent gels swell extensively in good solvent and shrink into a compact form in poor solvent. If the quality of solvent is somehow changed from good to poor, a phase separation takes place. So far, however, studies of phase separation of gels have been quite scarce as compared with extensive studies on polymer blends. We know only a few previous studies[1-3] on the phase separation of permanent gels, most of which have been made by light scattering measurement under the shallow quench condition.

We note that the phase separation of gels has a notable feature as compared with that of polymer blends or solutions. It is frequently observed that the phase separation creates a stable heterogeneous structure within gels, and the process stops at some intermediate stage. In other words, the phase separation of gels often fails to go to completion on a macroscopic scale. Usually gels in the incompletely phase-separated state are opaque, so that it has been deduced that the structure consists of alternating polymer-rich and solvent-rich regions with spacing on the order of the wavelength of light. The term "microsyneresis" has often been used[4] to represent this heterogeneity in gels. Although microsyneresis has long been known to occur in various gels, the structure of a gel network trapped in this state has not been studied in detail.

In the course of studying the inhomogeneity of phase-separated gels, we have recently met with a very peculiar aggregation pattern. The pattern is formed in the bulk of gel in the course of phase separation and, thus, is quite different from the pattern appearing on the surface of swelling gels reported previously.[5] The present paper is a preliminary report of this new finding. The pattern was observed on poly(*N*-isopropylacrylamide) (NIPA) gels in water–ethanol mixtures when the composition of the solvent was changed abruptly. Qualitatively the same results were observed also with water–methanol and water–*n*-propanol mixtures.

Neutral NIPA gel in a water–ethanol mixture has been known to show a reentrant-type behavior between the swollen and the shrunken phases as a function of solvent composition.[6,7] Figure 1 shows the equilibrium swelling ratio α of NIPA gel as a function of solvent composition x (the volume fraction of ethanol) at a few temperatures. We define the swelling ratio α by $\alpha = (V/V_0)^{1/3} = (\phi_0/\phi)^{1/3}$ where V is the volume and ϕ is the concentration of the gel. The subscript 0 means the value of the relaxed network. It is to be noted that the gel swells extensively in pure water as wel as in pure ethanol, whereas it collapses in the intermediate composition region. The transition between the swollen and the shrunken phases is discontinuous in the water-rich region, whereas it is continuous in the alcohol-rich region.

Sample Preparation. In the present experiment, the phase separation of gels was induced by changing abruptly the composition of the outer solvent at a constant temperature (~20 °C), and the change of state of the gel was observed with an optical microscope. Because the gel became opaque on phase separation, it was crucial to use very thin films as samples in order to observe the structure of gels by transmitting light. In the present experiments, gel films with 10–50 μm thicknesses (at the preparation) were used.

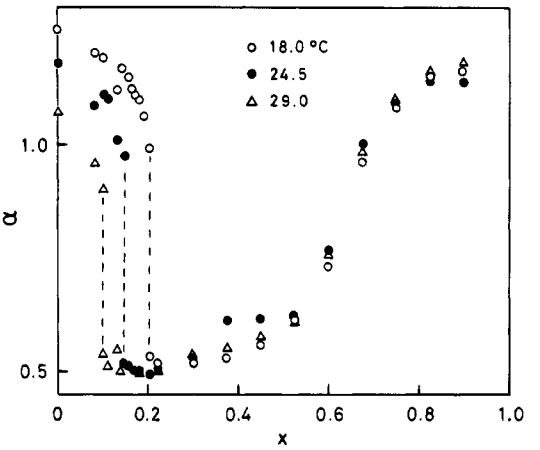

Figure 1. Equilibrium swelling ratio α of NIPA gels in water–ethanol mixtures as a function of ethanol concentration x. Dashed lines indicate a discontinuous collapse.

NIPA gels were prepared as in the previous studies.[2,6] The pregel solution contained 700 mM NIPA monomer and 8.6 mM *N,N'*-methylenebisacrylamide (cross-linker). The mold to prepare the gel films was made of two parallel glass plates separated by spacers of polyethylene films, the thickness of which was 10–50 μm. After the gelation reaction was completed, the gel films were carefully removed from the mold and put into a large amount of distilled water to realize swelling equilibrium. After a few days, the films were taken out, cut into rectangular pieces with a side of several millimeters, and used in the following experiments.

Gels Swollen in Water: Cell Pattern. In the first experiment, the gel films swollen to equilibrium in pure water were put into water–ethanol mixtures with various concentrations. It turned out that the change of gel depends strongly on the composition of the solvent x into which the gel was put. When x was smaller than ~0.20, no recognizable change occurred except a slight shrinkage of the film area. However, when the solvent with x larger than ~0.20 was used, a dramatic change occurred. After the gel was immersed in the mixed solvent, numerous fine fibers appeared at the edges and grew along the film surface (Figure 2a). As fibers grew, branching occurred and neighboring fibers intersected with each other, forming cell patterns (Figure 2b). Meanwhile, fibers extending from different edges met with each other in a central portion of the film (Figure 2c), and, eventually, the whole surface was covered with the cell pattern (Figure 2d).

The rate of evolution of the pattern depended strongly both on the composition of the solvent and on temperature. For example, at 20 °C and with $x = 0.25$, it took a few minutes for the pattern to develop over the whole sample, but it took only a few seconds with the solvent with $x = 0.35$. In the present paper, however, we will not go into the kinetics.

Gels Swollen in Ethanol: Dot Pattern. In the next experiment, contrary to the first one, we started from gels swollen in pure ethanol and put them into mixed

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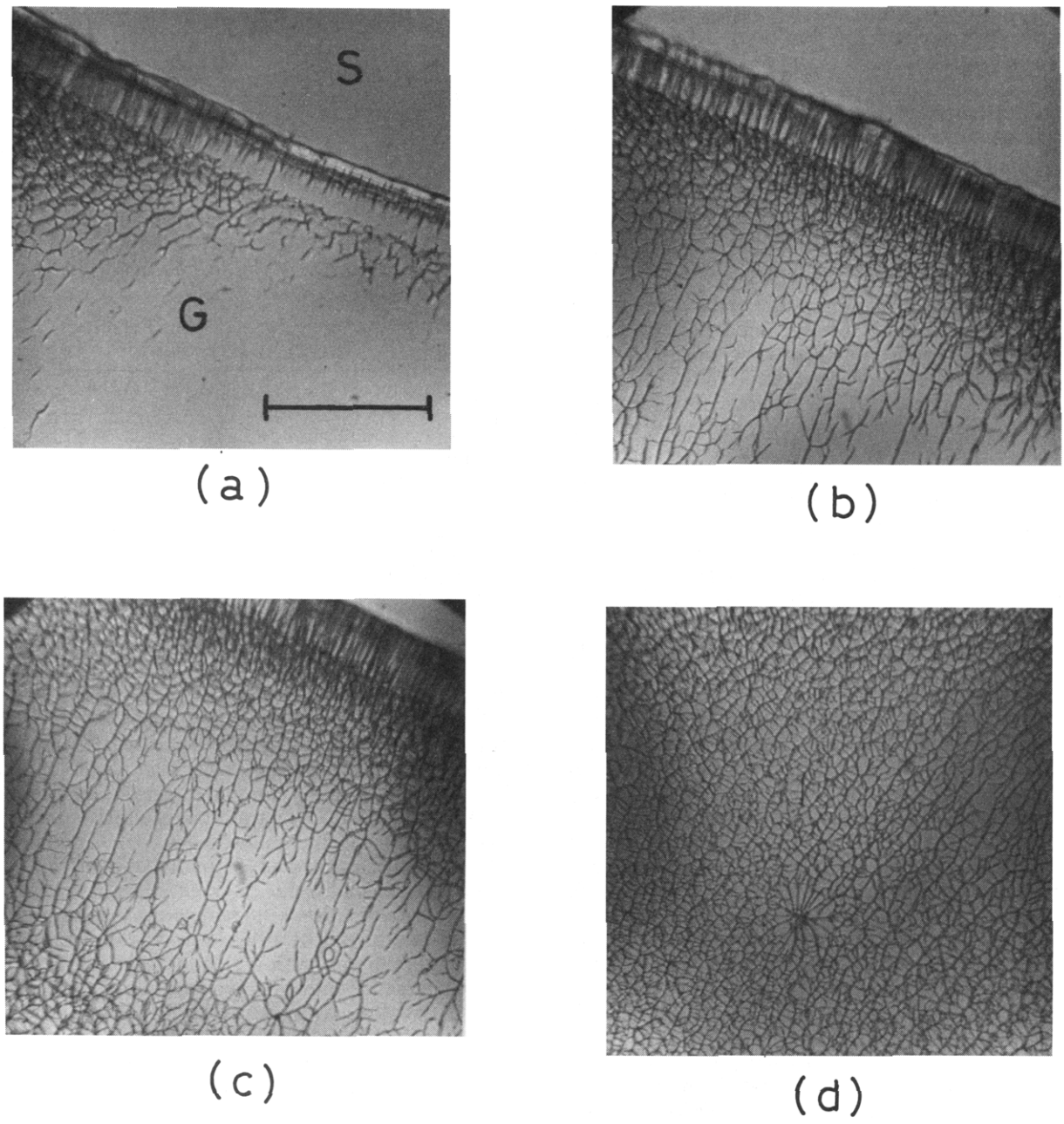

Figure 2. Phase-contrast image of the cell pattern formed when a NIPA gel film swollen in water was put into an ethanol–water mixture (x = 0.25) at 20 °C, observed perpendicularly to the film surface. Letters S and G indicate solvent and gel, respectively. The bar represents 500 μm. Times (in seconds) after the solvent was changed are (a) 10, (b) 20, (c) 40, and (d) 120.

solvents with various concentrations. The result of this observation was rather unexpected, because the resulting pattern was composed of numerous fine dots as shown in Figure 3, which is completely different from the cell pattern. The size of the single dot was less than 1 μm. The number of dots continued to increase with time, and finally the gel became perfectly opaque. From these results, we can deduce that the conformation of chains (or that of chain–solvent complex) is different between NIPA gels swollen in water and those swollen in ethanol.

The dot patterns such as those shown in Figure 3 have frequently been observed in various gels and polymer solutions on phase separation and may result from random aggregation of polymer chains. In contrast, the cell pattern such as that shown in Figure 2 has not previously been observed. Thus, it is of particular interest to investigate the mechanism of formation of such an anomalous pattern.

Features of the Cell Pattern. We will describe below some more details on the cell pattern. First, the cell pattern was completely reversible. When the gel was brought back into the initial solvent, the pattern soon disappeared.

Second, the pattern was not permanent, and its duration depended on the composition of the solvent. When the composition corresponded to the shrunken state, i.e., $0.25 < x < 0.4$, the pattern lasted for a few days. Otherwise, the pattern disappeared in minutes to hours, and the gel returned transparent.

Third, as is shown in Figure 4, the fibers constituting the cell pattern are birefringent. To be more specific, the fibers were invisible when they were parallel to the direction of either a polarizer or an analyzer but appeared bright when they lay in other directions. On rotating the microscope stage, the brightness of the fibers changed periodically with a period of 90°. This shows that these fibers have a crystalline order; i.e.,

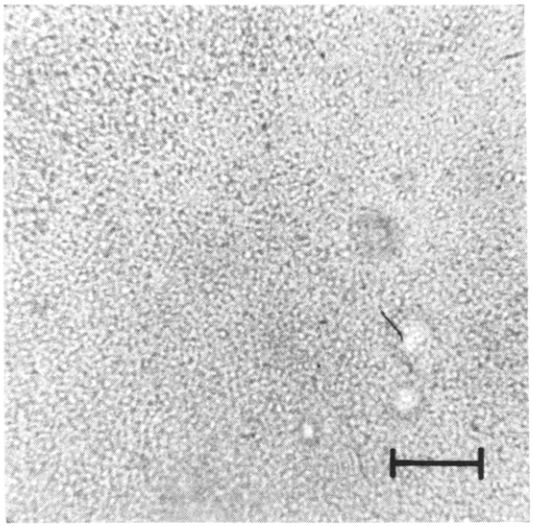

Figure 3. Phase contrast image of the dot pattern observed when a NIPA gel film swollen in ethanol was put into an ethanol–water mixture ($x = 0.25$) at 20 °C. The bar represents 10 μm.

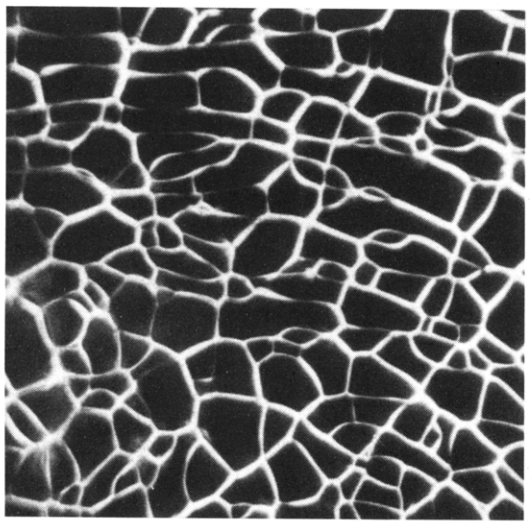

Figure 4. Cell pattern observed between crossed polars. The polarization directions are nearly parallel to the edges of the photograph. Dark portions are isotropic, transparent gel, whereas the bright fibers are optically anisotropic aggragates. Note that the fibers parallel to the polarization directions appear faint and thin, whereas others are bright and apparently thick. The field width is 500 μm.

they are bundles of polymer chains which are parallel with each other.

Fourth, the pattern is not on the surface but in the bulk of the gel. Moreover, the formation of the pattern always started from the edges of the film but never from sites on the upper or lower surfaces. This seems to be curious considering that the whole sample was soaked in the solvent and suggests that the initial stage of the fiber formation can occur only at breakages of the network. Because the sample was cut out from large films with a glass razor, each edge of the sample constitutes breakages of the network. On the contrary, the surfaces of the film contain no breakage because they were formed at the time of gelation in contact with the glass plates.

Fifth, as is clearly seen in Figure 2a–c, the pattern is different in a region within ~200 μm of the edges of the film. In this region only fibers perpendicular to the edge are present. This will be related to the mechanical stability of the pattern, though the reason for this phenomenon is not clear.

Discussion. Now, let us consider the mechanism of the formation of the cell pattern. In general, aggregation of polymer chains depends on the stiffness of the chain. Flexible chains aggregate into spherical globules, whereas stiff chains aggregate into bundles of fibers. A dot pattern shown in Figure 3 will correspond to the former case, and fibers seen in Figure 2 will correspond to the latter case.

It is well-known that many proteins and polysaccharides form fibers in biological bodies. Collagen, actin, and (glycosamino)glycans are typical examples. These fiber-forming macromolecules invariably have characteristic secondary structures such as helices, which make these chains quite stiff and straight. The secondary structures are stabilized by intra- as well as intermolecular interactions such as hydrogen bonding or hydrophobic interaction. It is not unreasonable to suppose that NIPA chains swollen in water have some kind of secondary structures, because C=O and N–H groups easily form hydrogen bonds with water molecules as well as among themselves. The stiffness of the chain will be an important factor inducing the volume phase transition.

The most interesting feature of the cell pattern shown in Figure 2 is that the fibers are produced not randomly but in a fairly regular way. Nearly homogeneous (on a macroscopic scale) distribution of the permanent crosslinkings will be responsible for this ordered structure. In this context, it is interesting to note that Sekimoto[7] has obtained a pattern resembling that shown in Figure 2 by a computer simulation on phase-separating gels. Although it is not certain at present how well the model he used represents our experimental situation, it will be interesting to perform the simulation by incorporating the chain stiffness.

References and Notes

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