

## Surface Structure of Dehydrated Polymer Gels

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We investigated the surface structure of poly(*N*-isopropylacrylamide-co-sodium acrylate) gels in the size range from millimeters to sub-micrometers. The change in the macroscopic surface patterns was observed on a dehydrating process by an optical microscope. It was found that the macroscopic patterns were permanently memorized in the dehydrated surface. The microscopic surface structure of the completely dehydrated gel was examined by an atomic force microscope (AFM). The surface structure characterized by the spongelike domain and its change due to the presence of the copper complex were discussed in terms of the autocorrelation function and the root-mean-square roughness, which were calculated from the AFM topographies.

Key words: poly(*N*-isopropylacrylamide-co-sodium acrylate) gels, copper chelation, dehydration, surface structure, microdomains, AFM

### 1. INTRODUCTION

Polymer gel is one of the soft condensed materials of a random two-phase system; polymer and solvent. In this system, the presence of metal ions in the solvent is well known to strongly affect the swelling behavior of ionized gels [1]. It was reported that the poly(*N*-isopropylacrylamide) gels copolymerized by carboxyl groups could absorb and recover specific molecules through a volume phase transition only by changing the temperature [2]. Since the distance between the ionized groups can be controlled by the degree of swelling, the gel can absorb metal ions and release them in response to the temperature change. It is expected that the carboxyl groups can close each other and form complex with metal ion on shrinking, but this structure will be destroyed by the separation of the network in gel on a swelling process. We found that the poly(*N*-isopropylacrylamide-co-sodium acrylate) (designated here as NIPA-SA) gels can absorb the metal ions in the swollen state [3], which was attributed to the inhomogeneity of polymer networks. Recently, Sugiyama et al. succeeded to observe the mesoscopic structure in the same system of NIPA-SA gels by the small-angle X-ray scattering (SAXS) measurements [4], and found that the randomly dispersed sodium rich clusters with almost the same mesoscopic dimension developed by the hydrophilic groups capturing of the solvent against the dehydration. More recently, Kuwajima et al. confirmed the clustering of SA in the gel network by the SAXS measurements [5], and found that the radius of cluster depends not only on the SA concentration but also on the water content (the degree of the hydration).

In this paper, we investigated the surface structure of NIPA-SA gels in the size range from millimeters to sub-micrometers. The change in the macroscopic surface structure was observed on a dehydrating process by an optical microscope. The microscopic surface structures of the dehydrated NIPA-SA gels were investigated by an

atomic force microscope (AFM). We discuss the microdomain structure, which is affected by the presence of the copper complex.

### 2. EXPERIMENTAL PROCEDURE

Gels were prepared by a free radical copolymerization of NIPA and SA in water under nitrogen atmosphere at the ice temperature [3]. The reagents, 5.885 g of purified NIPA (main constituent, Kohjin) and 1.695 g of SA (ionizable monomer, Aldrich), 0.133 g *N,N'*-Methylenebis-acrylamide (cross linker, Wako), and 240  $\mu$ l of *N,N,N',N'*-tetramethylethylenediamine (accelerator, Wako), were dissolved in 100 g water. After the solution was fully saturated with nitrogen, 40 mg of ammonium persulfate (initiator, Wako) was added to the solution to initiate the polymerization. The pair of two glass plates (slides for an optical microscope) was immediately inserted into the solution. The pregel solution was brought into the thin space by capillary action. The bottom gel surface was chemically adhered onto the slide by Bind Silane (Pharmacia) that was rinsed on the bottom slide before dipping it into the pregel solution. The jellying solution was stored at the ice temperature more than 12 hours. After the gelation the upper slide was carefully removed from the gel, thus forming a clamped disk gel on the other glass plate and then the gel was immersed in a large amount of deionized, distilled water.

The dehydration was conducted in the air at room temperature (25 °C). In order to test the effect of the copper chelation on the surface structure, we dipped the gel for 1 day in an aqueous solution of  $\text{CuCl}_2$  with the concentration of  $10^{-1} \text{ mol l}^{-1}$ .

The macroscopic surface structure of the gel was measured by an optical microscope apparatus equipped with a calibrated CCD (Charge Coupled Device) camera and a video processor, while the microscopic surface structure was observed by the tapping mode of AFM (Digital Instruments, NanoScope III) [6].

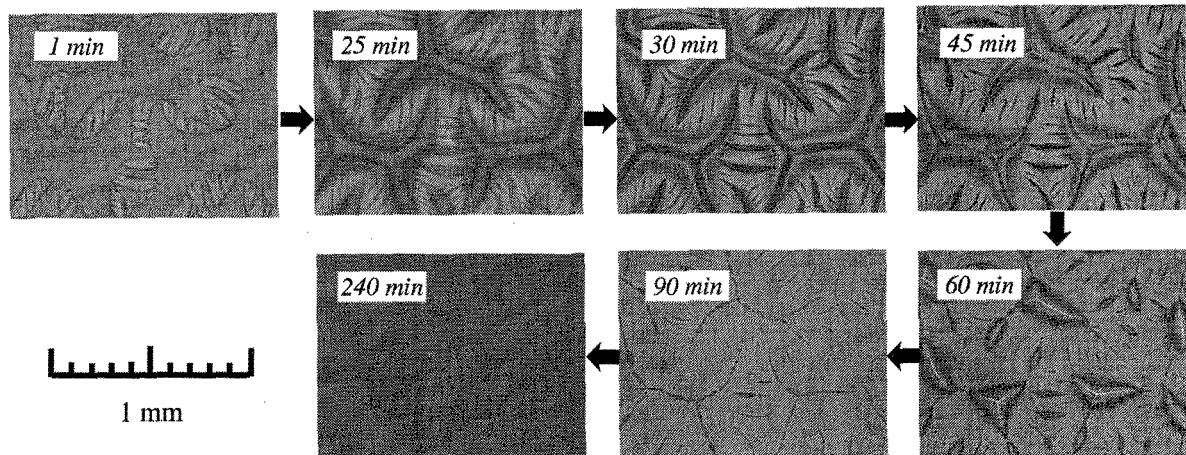


Fig. 1 Time course of the macroscopic surface of the NIPA-SA gel on a dehydrating process.

### 3. RESULTS AND DISCUSSION

#### 3.1 Change in the Macroscopic Surface Structure on a Drying Process

We have first observed the change in the macroscopic surface structure characterized by the surface patterns on a drying process. Figure 1 shows the time course of the surface patterns of a gel with  $160 \mu\text{m}$  thickness. At the beginning of dehydration, the geometrical patterns appeared on the surface, which consists of the polymorphological thick pattern and the linear fine pattern. The unit size of the thick pattern depends on the gel thickness, which is consistent with the literature [7]. At time goes on, the thick pattern became thin, and the linear fine pattern was also getting thin. On the other hand, the unit size of the polymorphological thick pattern did not change, since the gel is chemically adhered on the bottom slide. By adjusting the focus of the optical microscope, we found that the height of the patterns is larger than the flat regions between the patterns, which indicates that the water content is rich at the patterns (the network is much more swollen). After the linear fine pattern became smaller and smaller, and finally started to disappear one by one, the smooth surface developed with time. However, we can identify the permanent pattern (it was the thick pattern at the beginning of the dehydration) on the completely dehydrated surface by the eye (similar to the picture after 240 min in Fig. 1).

*Dipped in the Pure Water    in the  $\text{CuCl}_2$  Aqueous Solution*

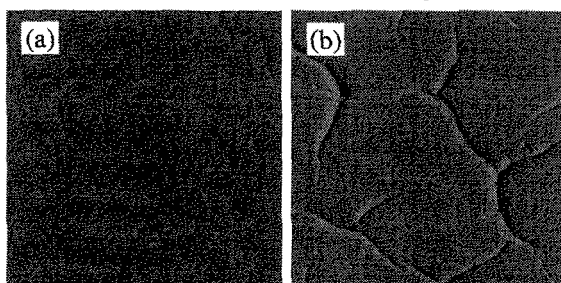


Fig. 2 AFM amplitude (error) images of the dehydrated gel surfaces with  $50 \times 50 \mu\text{m}^2$  size ( $z = 500 \text{ nm}$ ); the gel was dehydrated at  $25^\circ\text{C}$  in the air after dipping in (a) the pure water, and (b) the  $\text{CuCl}_2$  aqueous solution ( $10^{-1} \text{ mol l}^{-1}$ ).

#### 3.2 AFM Images of the Dehydrated Gel

The microscopic surface structure of the completely dehydrated gels was directly visualized at room temperature ( $25^\circ\text{C}$ ) in the air by the tapping mode AFM. Figure 2 presents the amplitude (error) images of the gels with  $80 \mu\text{m}$  thickness dehydrated from the pure water and the  $\text{CuCl}_2$  aqueous solution ( $10^{-1} \text{ mol l}^{-1}$ ). One can see that the permanent thin pattern is memorized on the surface that was dehydrated from the pure water, and the pattern formation is enhanced by the dehydration from the  $\text{CuCl}_2$  aqueous solution. This result could be attributed to the existence of copper ions, especially to the copper chelation with the network polymers. We believe that the chelation can make the excess crosslinks, which increases the network density of the surface. Therefore, the dehydration could be accelerated, which induces the clear surface pattern on the dehydrated surface. It should be noted that the height of the patterns is larger than that of the smooth flat regions, which is consistent with the observation by the optical microscope in Section 3.1.

Figure 3 presents the height images of the completely dehydrated gels with different sizes, which were obtained from the smooth flat regions (not including the pattern). The gels were also dehydrated from the pure water and the  $\text{CuCl}_2$  aqueous solution ( $10^{-1} \text{ mol l}^{-1}$ ). One can see in these figures that the gel consists of the microdomains, which depend on the dipped solvent with or without  $\text{CuCl}_2$ ; when the gel was dipped in the copper aqueous solution before the dehydration, the surface becomes rough, while the size of the microdomain becomes large.

In order to quantitatively identify the images, the autocorrelation function,  $g(r)$  was calculated [8] using the height values obtained from the AFM images. We found that the data points fit well to a Gaussian distribution, and obtained the scaled decay function, defined by  $g(r)/R_{\text{rms}}^2 - g_0 = \exp[-(r/\xi)^2]$ ; in this expression  $g_0$  is a constant and corresponds to the incoherent background noise and  $\xi$  is a correlation length, which is proportional to the dominated domain size in the AFM image. The results calculated using the AFM image ( $1 \times 1 \mu\text{m}^2$  size) of Fig. 3 are shown in Fig. 4. One can see that the root-mean-square roughness,  $R_{\text{rms}}$  ( $= g(0)^{1/2}$ ), increases, while  $\xi$  increases by the copper chelation (the slope decreases).

### 3.3 Effects of Copper Complex on the Surface Structure

There appeared two interesting features that should be noted in the observation of the change in the surface structure by the copper chelation. First, a lot of macroscopic surface patterns can be observed by the optical microscope in the completely dehydrated gel. On a dehydrating process, such patterns can be expected to have larger amount of water than the area of the flat region and they could dehydrate after much delay. Therefore, it is reasonable to assume that the pattern includes a lot of counter ions (cations), which forms the permanent macroscopic pattern on the dehydrated surface. This is reasonable since the pattern was enhanced by the copper chelation (Fig. 2).

Second, the size of the microdomain on the surface can be controlled by the copper chelation. It has been pointed out that in the case of the present kind of polymer gels the crosslink process at gelation itself may produce inhomogeneity [9,10] due to the thermal fluctuation of the pregel solution. The network structure is not homogeneous by nature, but rather consists of

microdomains, resulting in the inhomogeneous strain distribution at the microscopic level. It could be expected in the present system that the ionic groups might not be homogeneously incorporated in the main constituent, but should form a lot of clusters where the density of SA is relatively large. Therefore, even in the swollen state, the carboxyl groups can attract copper ions to form the copper complex [3]. In the presence of copper ions, the present observation clearly shows that the size of microdomains become large (the change in the characteristic length from 25 to 50  $\mu\text{m}$ ), while its total number decreases. It can be expected that the domain has a higher density of the copper chelation, which indicates the existence of a well-defined structure in the dehydrated gel. This is qualitatively inconsistent with the recent report [5] that the radius of cluster (with 5 nm size level) decreases as the SA concentration decreases. We believe that the hierarchical network structure [8,10] or the bicontinuous structure [11,12] should have an important role in determining the surface domains in the present system; a microdomain (the

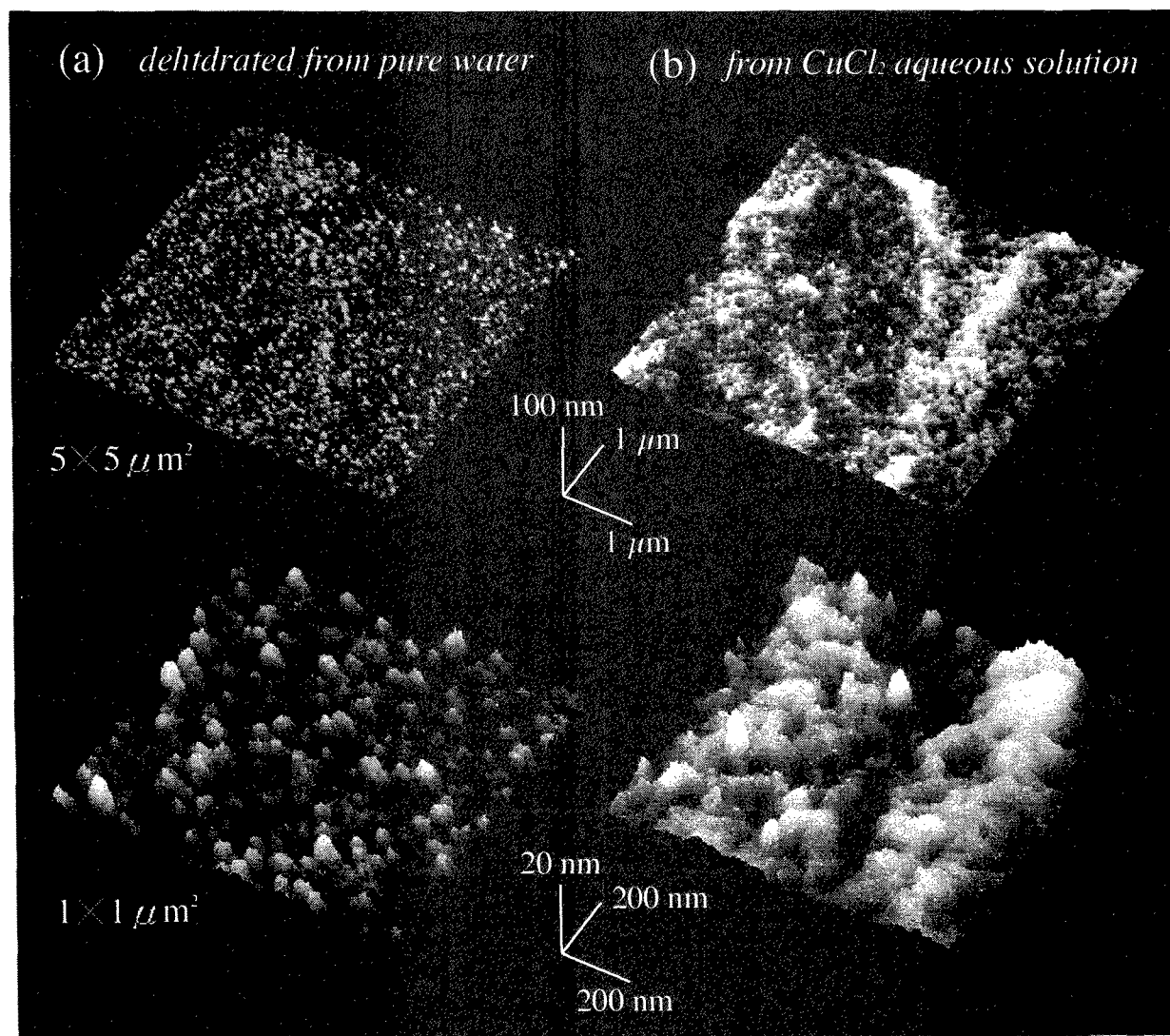


Fig. 3 AFM images of the gel surfaces with 5 X 5  $\mu\text{m}^2$  and 1 X 1  $\mu\text{m}^2$  sizes: the gel was dipped in (a) the pure water, and (b) the  $\text{CuCl}_2$  aqueous solution ( $10^{-1}$  mol  $\text{l}^{-1}$ ). The bottom image is an example of flat smooth region that is obtained by scanning the 1 X 1  $\mu\text{m}^2$  area.

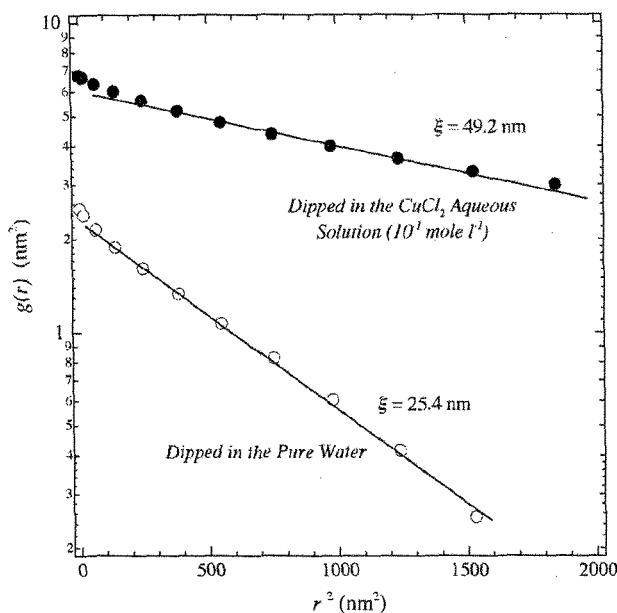


Fig. 4 The autocorrelation function,  $g(r)$ , calculated from the AFM images with  $1 \times 1 \mu\text{m}^2$  size in Fig. 3; the gel was dipped in the pure water (open circles) and the  $\text{CuCl}_2$  aqueous solution of  $10^{-1} \text{ mol l}^{-1}$  (closed circles). Each data can be fitted by a Gaussian except in the small  $r$  range.

characteristic length with 50 nm size level) results from the aggregation of the smaller microdomain (with 25 nm size level), which consists of the clusters with much smaller size level. This speculation can be supported by the observation that  $g(r)$  shown in Fig.4 is not simply expressed by a single Gaussian, but can be deconvoluted by some components in the smaller  $r$  range. Therefore, the present results (the surface roughness and the correlation length can both increase) are not necessarily inconsistent with the reported evidence where the cluster itself becomes smaller by the chelation. Though we do not have a quantitative model to explain the results, the aforementioned network structure, hierarchical and inhomogeneous, should affect the dehydrated surface structure in the microscopic size level.

In order to verify these considerations, it is important to test for the gels dehydrated from the aqueous solution with different  $\text{CuCl}_2$  concentrations and for the gels with the different SA concentrations. These are subjects for future investigations.

#### 4. CONCLUSION

We have studied the surface structure of polymer gels consisting of poly(*N*-isopropylacrylamide) and sodium acrylate. The change in the macroscopic surface patterns on a dehydrating process indicates that the macroscopic patterns due to the mechanical instability were permanently memorized in the dehydrated surface. The microscopic surface structure of the dehydrated gel was characterized by the microdomains, which was observed by an AFM. The shape of microdomains was found to be affected by the copper chelation; when the gel was dehydrated after being dipped in a large amount of aqueous solution of  $\text{CuCl}_2$ , the mesoscopic surface structure was strongly affected.

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