

## Effect of Organic-Solvent Treatment on Swelling of Poly(acrylamide-co-sodiumacrylate) Gel

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Some hydrogels can adsorb harmful heavy-metal ions, of which the property can be usable for purifying wastewater. One of the difficult problems for such a practical use is a slow rate of swelling process due to slow diffusion of the solvents in the hydrogels. In this circumstance, the authors have observed the swelling behaviors and SAXS profiles of the *poly*(acrylamide-co-sodium acrylate) gels after having soaked in several respective organic solvents for a while; they have found a considerable increase in the swelling rate as well as the swelling ratio in the gels and a definite peak in their SAXS profile.

Key words: gel, inhomogeneity, swelling, organic solvent, small angle X-ray scattering (SAXS)

### 1. INTRODUCTION

It cannot be denied that our modern life is maintained by many industrial products. However, it should be aware of existence of their by-products, wastes, some of which are very toxic and menace our secure life. By an upsurge of the concern about such an environmental problem and with continual efforts for untangling it, the problems on the emission of the hazardous wastes from the industrial facilities have been settled. However, it should be remembered that some persistent wastes which was already discharged from these facilities will remain in the environment for a long term and the contaminated area will extend by diffusion. In such a case, an immediate treatment to recover the hazardous materials should be performed [1-4]. Among such stable hazardous wastes, the authors have been paying attention to heavy metal refuse and have expected that the hydrogel can be available as a kind of heavy-metal recovery material because the gel shows useful properties through the interaction change between network polymer and solvent [5-10].

In these circumstances, the authors have been examining the heavy-metal capturing property of the hydrogels and have found a large ion-capturing potential usable for the environmental purifying application [11-15]. However, also in the previous studies, due to the small diffusion constant of water in the gels, they have observed that the rate of swelling process, which is necessary for capturing the heavy-metals sufficiently, is too slow to use practically on the spot. Because the swelling process should be accelerated in order to adsorb the heavy-metals quickly, the authors have planned to increase the diffusion constant by introducing a porous

structure with internal channels which enable the ambient water to penetrate into the middle of the hydrogel block quickly.

In the previous study [16], as the first attempt along this line, the authors utilized a *poly*(acrylamide/sodium acrylate) (PAAm/SA) gel with prescribing an excessive amount of cross-linker in the preparation process because the hydrogel is known to become turbid above a certain cross-linker concentration ( $C_{cloudy}$ ) due to

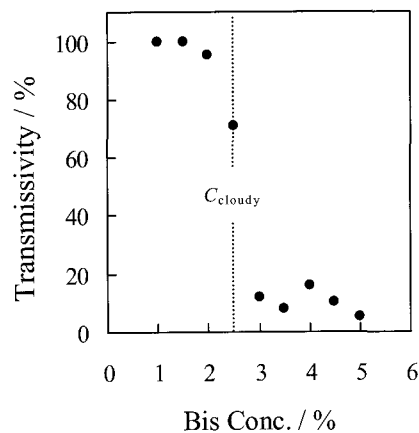


Fig.1 The light transmissivity (at 600 nm) of the PAAm/SA (500mM/200mM) gels with different cross-linker (Bis) concentrations. The dotted line in the figure indicates  $C_{cloudy} = 2.5$  wt% in concentration observed in the previous study [16].

network polymer inhomogeneity with a scale of light wavelength. In the previous study, the cross-linker (*NN*-methylenebisacrylamide, Bis) concentration of the 500mM/200mM PAAm/SA gel where the turbidity occurs was  $C_{\text{cloudy}} \approx 2.5$  wt% (Fig.1), around which there revealed several interesting property change [16]. However, a considerable elasticity increase was also observed around  $C_{\text{cloudy}}$ , which is not favorable for the present usage of the hydrogels because the swelling process will be restrained by the large elasticity. Because of the difficulty of utilizing the inhomogeneity induced by an excessive amount of cross-linker, the authors have attempted another method for increasing in the swelling rate as mentioned below.

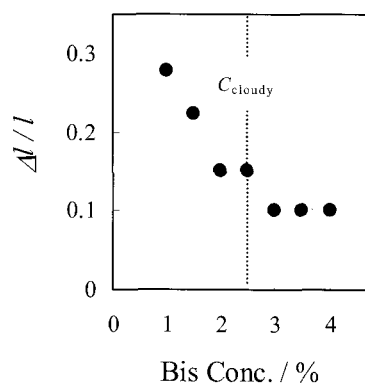


Fig.4 The shrinkage ratios ( $\Delta l/l$ ) of the PAAm/SA (500mM/200mM) gels with different cross-linker concentrations. The dotted line in the figure indicates  $C_{\text{cloudy}} = 2.5$  wt% in concentration observed in the previous study [16].

As described above, by the interaction between the constituents, polymer network and solvent, hydrogels show interesting and useful properties, among which the considerable volume change by a small shift of an environmental condition, namely the volume phase transition [5-9], is the most famous phenomenon. Related to the application of the hydrogels for the environmental purification, the authors have also paid attention to a kind of the volume phase transition caused by a solvent-property change on adding an organic solvent (such as acetone) to the ambient solution: some hydrogels soaked in an acetone-water mixture swell up to 100 times when the acetone concentration is low, on the other hand, they contract less than 1/10 under the high-acetone-concentration condition. Though this phenomenon is well-known, there are almost no reports on the property change of the hydrogel *after* such solvent-substitution treatments.

In these circumstances, in the present study, the authors have investigated the swelling property and internal nano-scale structure of the PAAm/SA gels after soaked in several kinds of organic solvent, and have found a remarkable increase in the swelling rate and also have noticed the emergence of a nano-scale structure by the solvent-substitution treatments.

## 2. EXPERIMENTALS AND RESULTS

### 2.1 Solvent Treatment Effects on Swelling Process

The PAAm/SA gel was obtained by keeping the temperature of an precursor aqueous-solution (500mM of AAm, 200mM of SA, 0.12mM of Bis and 0.024mM of ammonium persulfate (initiator)) at 60°C for 24 hours. After the polymerization process, the gelled dollops were cut into several column-shaped specimens (10mm in length and 5.6mm in diameter). Then, the column-shaped specimens were immersed in pure water for 24hrs in order to wash up unreacted ingredients. After then, two treatments were applied to the washed specimens as described follows:

#### Treatment I

Application of 2-week dehydration of three kinds of specimens prepared by 24-hr immersion in different organic solvents: hexane, ethanol, methanol and benzen.

#### Treatment II

Application of 2-week dehydration before Treatment I.

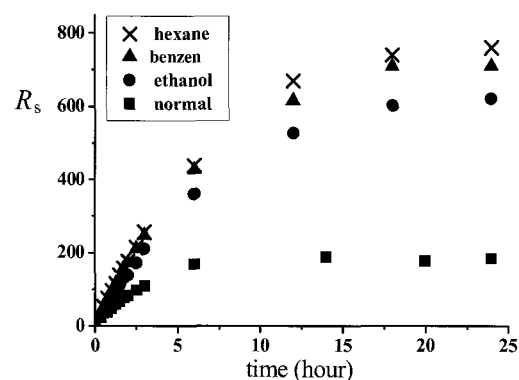


Fig.5 Evolution of the swelling ratios of the several organic-solvent-treated PAAm/SA gels prepared by Treatment I. For comparison, the data of the simply dehydrated specimen without the organic-solvent treatment are also plotted in the figure. (see also text).

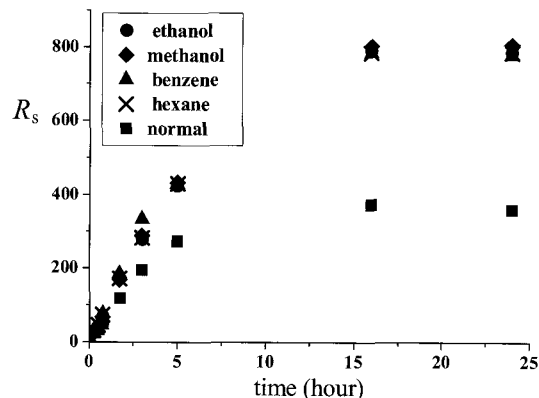


Fig.6 Evolution of the swelling ratios of the several organic-solvent-treated PAAm/SA gels prepared by Treatment II. For comparison, the data of the simply dehydrated specimen without the organic-solvent treatment are also plotted in the figure. (see also text).

A characteristic features during the treatments is briefly described before showing the detailed results of the swelling evolutions. In the organic-solvent treatments, there observed characteristic features: the specimens soaked in the transparent ethanol or methanol became turbid and shrunk considerably, while the other gels immersed in hexane and benzen were almost transparent before and after the treatments showing a small shrinkage.

In order to compare the swelling evolutions of the specimens with different initial weights, the authors calculated and plotted the normalized weight change, hereafter, which will be referred as swelling ratio ( $R_s$ ),

$$R_s = \frac{w - w_0}{w_0}$$

where  $w$  is the weight during swelling process and  $w_0$  is the initial weights of the respective specimens.

The experiments of the swelling evolution were carried out by measuring the time dependence of the weights of the specimens prepared by Treatments I and II after immersing in pure water. Figs. 5 and 6 show the evolution of  $R_s$ 's of the specimens with Treatments I and II. For comparison, the data of the simply dehydrated specimen without the organic-solvent treatments are also plotted in the figures. The weights of the specimens increase rapidly in the initial stage then saturated after a certain time. By comparing the data of the specimens with and without the treatments, it has been clearly demonstrated that the organic-solvent-treatments have remarkable effects on the swelling evolution in both the swelling rate in the initial stage and the value of  $R_s$  in the final stage. Though the mechanism of such effects is not clear now, these phenomena is very interesting and will be useful for the application aiming at in the present study.

## 2.2 SAXS Profile Changes

The Small Angle X-ray Scattering (SAXS) experiments were carried out with a SAXS apparatus (SAXES) installed at BL-10C of Photon Factory in Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. An X-ray beam from a synchrotron orbital radiation (1.3918Å in wave-length) was used as a light source. The observed X-ray intensity was corrected for the cell scattering and absorption, and then normalized with the thickness of the sample and irradiated time. With these correction and normalization, the value of final data straightforwardly corresponds to the scattering efficiency.

For the SAXS experiment, the authors prepared two kinds of specimens,

- the dehydrated specimens prepared by Treatment I,
- the wet specimens prepared by the treatments leaving out the last dehydration process from Treatment I.

In this experiment, the organic-solvent treatments were done with benzen and hexane by the reason of the turbidity of the ethanol- and methanol-treated gels

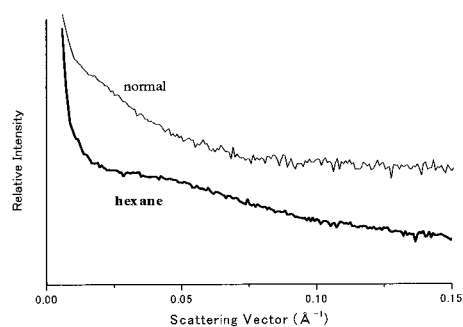


Fig.7 The SAXS profiles of the wet PAAm/SA gels with and without the organic-solvent (hexane) treatments. A peak around  $0.05\text{\AA}^{-1}$  is clearly seen in the profile of the hexane-treated gel. (see also text)

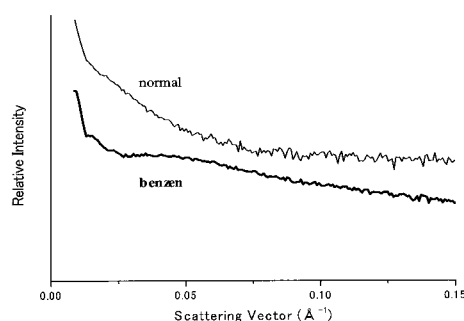


Fig.8 The SAXS profiles of the wet PAAm/SA gels with and without the organic-solvent (benzen) treatments. A peak around  $0.05\text{\AA}^{-1}$  is clearly seen in the profile of the benzen-treated gel. (see also text)

mentioned above. For comparison, the wet and simply dehydrated specimens without the organic-solvent treatments are also prepared.

While the noteworthy aspects were observed in neither of the SAXS profiles of the dehydrated specimens with and without the organic-solvent treatments, the very interesting features were found in those of the wet gels in both the hexane- and benzen-treated PAAm/SA gels. Figures 7 and 8 show the SAXS profiles of the wet PAAm/SA gels with and without the organic-solvent (hexane and benzen) treatments. A peak around  $0.05\text{\AA}^{-1}$  is clearly seen in the profiles of both the hexane- and benzen-treated gels.

## 3. DISCUSSIONS

The effects of the organic-solvent treatments on the properties of the PAAm/SA gel observed in the present study can be summarized as follows:

- The methanol- and ethanol-treated gels becomes shrunk and turbid considerably, while the other gels treated by hexane and benzen did not show large property change in the macroscopic scale.

- (ii) By the organic-solvent treatments, the swelling rates in the initial stage and the swelling ratios in the final stage are considerably improved.
- (iii) By the hexane- and benzen- treatments, there occurs a clear SAXS peak around  $0.05\text{\AA}^{-1}$  in the wet gels, while the dehydrated gels show almost no change in the profile compared with the SAXS profile of the specimen without the treatment.

At first sight, it seems strange that the nonpolar (hydrophobic) organic solvents such as hexane and benzene affect the swelling process so much as observed in the present investigations because the PAAm/SA gel is a hydrogel of which the solvent is water; the organic solvent with less compatibility with water may not infiltrate into the inner part of the PAAm/SA gel and may not affect the macroscopic property so much. However, there is also a systematic change in the affecting feature of the organic solvents with the water compatibility, which is demonstrated by the turbidity emergence and the considerable shrinkage of the ethanol- and methanol-treated PAAm/SA gels, therefore the effects of the organic-solvent treatment seems largely related to a change in the polymer-network structure of the PAAm/SA hydrogel.

For the present, taking into consideration of the SAXS profile changes of the ethanol- and methanol-treated PAAm/SA gels, the authors estimate the mechanism of the large effect of the organic-solvent treatments on the swelling properties of the PAAm/SA gel as follows: Even though the nonpolar solvents are hard to intermix with water, their small amount may get mixed in water and the hydrophobicity of the solvent surrounding the network polymer may increase by small amount. With increasing in the solvent hydrophobicity, some of the hydrophilic network-polymers can aggregate and the small channels in the gel may be formed which may enable the ambient water to permeate into the inner part of the hydrogel. By forming these small channels, the diffusion constant of water in the gel may increase and the swelling process can be promoted as observed in the present experiments. The clear peak observed the SAXS experiments may indicate these aggregated structures.

From the results in the present study, the organic-solvent treatments of the PAAm/SA gel have been found to be considerably effective on promoting the swelling properties, the swelling rate in the initial stage and the swelling ratio in the final stage of the swelling process, even though their mechanisms are not clear thoroughly at the moment. However, the distinct peaks in the SAXS profiles indicate that there occurs some definite structure in the PAAm/SA gel by the organic-solvent treatment. If the more detailed features are clarified, which are now in progress, this technique will be useful in both the industrial and environmental application.

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