

Effect of Organic Solvent Substitution on Nano-scopic Structure of Poly(acrylamide-*co*-sodium acrylate) Gel

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Some polymer gels can adsorb heavy-metal ions and can be usable for a wastewater purifying materials. However, a difficult problem for such a practical use occurs due to slow swelling and deswelling rates. In order to overcome this problem, the authors have been trying their property-alterations and, previously, they made a considerable swelling property promotion of the *poly*(acrylamide-*co*-sodium acrylate) gels by once soaking in organic solvents. Because each the swollen gel was also found to shows clear a peak in the Small Angle X-ray Scattering (SAXS) profile, there can be close relation between the nano-structure and the swelling property. Therefore, in the present study, the authors have carried out detailed SAXS-profile examination, in which the SAXS peak shows characteristic behaviors: disappearance by dehydration and different completion periods of the nano-structure formation with the immersed organic solvents.

Key words: poly(acrylamide-*co*-sodium acrylate) gel, swelling, organic solvent, SAXS, nano-structure

1. INTRODUCTION

One should remember that, in the process making almost of all the industrial products which make our life comfortable, produced are their by-products, wastes, some of which are very toxic. By the concern about an environmental problem caused by the hazardous wastes, their emission from the industrial facilities has been strictly regulated by statutes in these days. However, it should be remembered that the accidentally leaked-out wastes will remain in the environment for a long period and the polluted area will extend by diffusion. In that case, a prompt recovery of the hazardous substances is important to intercept outspreading of the polluted area [1-4]. The authors have been paying attention to heavy metal wastes and have developed the hydrogels that can capture the heavy-metals [5-10] by utilizing their useful properties derived from the interaction between network polymer and solvent [11-16]. However, they have also perceived that the rate of volume-change process, namely those of the swelling or deswelling process, is too small for the practical use due to the small diffusion constant of water and ions by friction with the network [5-10].

Because the fast volume-change should be necessary for capturing the heavy-metals promptly, the authors have also made attempts to accelerate the volume-change process by introducing internal channels by forming porous structures with several methods [17-19]. As an initial shot for introducing a porous structure in the hydrogel, the authors adopted *poly*(acrylamide/sodium acrylate) (PAAm/SA) gels which are made with an excessive amount of a cross-linker (*N,N'*-methylene-bisacrylamide, BIS) because they are known to become turbid above a certain cross-linker concentration due to the occurrence of an inhomogeneity of the polymer

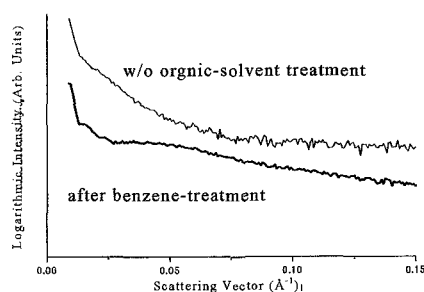


Fig.1 The SAXS profile of the wet PAAm/SA gels and that after the benzene treatment. A peak around 0.05\AA^{-1} is clearly seen in the profile of the benzene-treated gel [19].

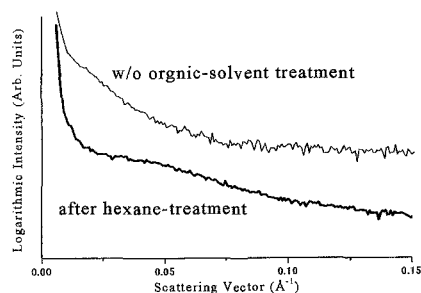


Fig.2 The SAXS profile of the wet PAAm/SA gels and that after the hexane treatment. As in the case of the benzene-treated PAAm/SA wet gel, a peak around 0.05\AA^{-1} is clearly seen in the profile of the hexane-treated gel [19].

network [17]. However, because it was also found that the turbid PAAm/SA gels are highly elastic, they seem unfavorable for the present application: the volume-change process will be hindered by the high elasticity. With this difficulty, the authors have switched to other methods. The second tried method is making the gels with excess amounts of *N,N,N,N*-tetramethylethylenediamine (a polymerization accelerator) above room temperature [18]. By the investigation, it has been revealed that the swelling degree of the PAAm gel in these conditions considerably changes by the polymerization-accelerator concentration and synthesis temperature. The more detailed investigation is currently in progress. In both of the above-mentioned methods, the porous structures are introduced in the gelation process.

The authors have also brought a porous structure into the gels by conducting solvent-substitution treatments after the gel-formation. In the previous study [19], they have investigated the evolution process of the swelling property and nano-scale structure of the PAAm/SA gels after each of them being soaked in one of the several organic solvents. By those investigations, a remarkable increase in the swelling rate has been observed of which the feature can be useful for the above-mentioned purpose. In addition to the considerable effect on the swelling property, they have noticed the emergence of a nano-scale structure characterized by a clear SAXS peak around 0.05\AA^{-1} , as shown in Figs. 1 and 2 [19]. The authors have considered that the SAXS peak can be related to the porous structure which might occur by the solvent treatment. Therefore, in the present study, the more detailed SAXS investigation of the solvent-substituted gels have been performed paying attention to the effect of water content and that of the immersion period in the organic solvent.

2. EXPERIMENTALS AND RESULTS

2.1 Sample Preparation

Specimens were prepared in the same way as the previous study [19]. The PAAm/SA gels were obtained by leaving precursor aqueous-solutions (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 gelation process, several column-shaped specimens (10mm in length and 5.6mm in diameter) were cut out, which were immersed in pure water for 24hrs in order to wash up unreacted ingredients. After the washing, several treatments were applied to the specimens as described below:

Procedure I

Each the specimen was immersed in either of hexane or benzene for 24hrs and, after then, it was submerged in water for 24hrs again. Some of the re-swollen specimens are dehydrated at 5°C for 2 weeks.

Procedure II

Each the specimen was immersed in either of hexane or benzene for a period of 1hr, 3hrs or 24hrs, after then, it was submerged in water for 24hrs again.

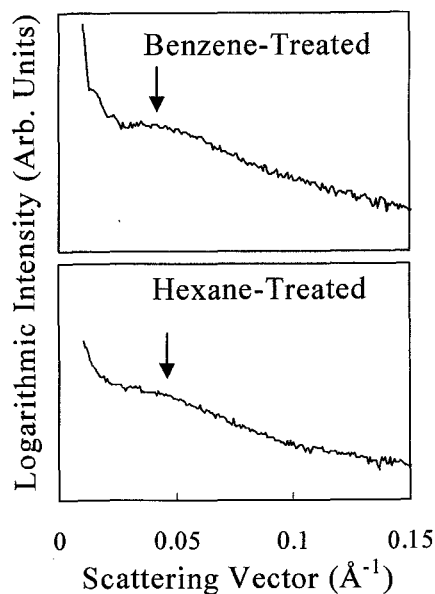


Fig.3 The SAXS profiles of the benzene- and the hexane-treated PAAm/SA wet gels which were prepared by Procedure I. The arrows in the figures indicate occurrence of peaks in the profiles. (see also text)

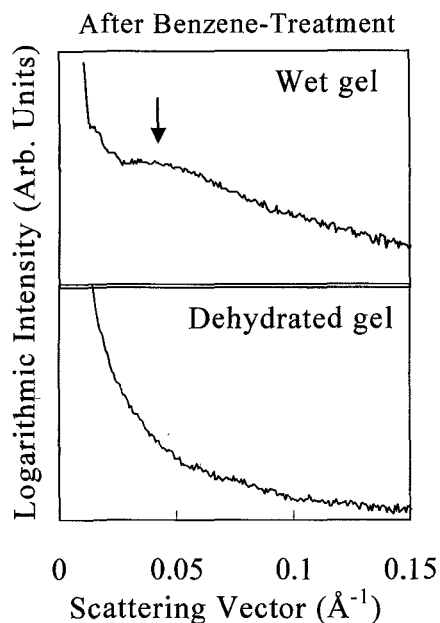


Fig.4 The SAXS profiles of the benzene-treated PAAm/SA wet gel and its dehydrated substance which were prepared by Procedure I. One can notice that the peak in the wet gel (upper part) disappears by dehydration (lower part). The arrows in the figures indicate occurrence of peaks in the profiles. (see also text)

2.2 SAXS Profile Measurement

The Small Angle X-ray Scattering (SAXS) intensity distribution by the specimens was measured 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. A synchrotron light of 1.3918\AA in wave-length was used as an incident X-ray source. In the measurements, the observed scattered-X-ray-intensity data were corrected for the scattering and absorption by the experimental-cell lateral, and then normalized by the sample-thickness and the irradiation time.

Figure 3 shows the SAXS profiles of the benzene- and hexane-treated PAAm/SA gels which were prepared by Procedure I. As is shown in Fig.3, the peak shape of the benzene- and hexane-treated PAAm/SA gels are similar each other with almost the same peak position (around 0.05\AA^{-1}) in the SAXS profiles which indicates the similarity of the nano-structure in both of the benzene- and hexane-treated PAAm/SA gels.

Figure 4 delineates the SAXS profiles of the benzene-treated wet PAAm/SA gel and its dehydrated substance also prepared by Procedure I: the 0.05\AA^{-1} peak observed in the wet PAAm/SA gel disappears by dehydration. The remarkable profile alteration demonstrates considerable nano-structural change by dehydration. Similar difference is also observed between the SAXS profiles of the hexane-treated PAAm/SA wet gel and its dehydrated substance.

Figure 5 depicts the SAXS profiles of the benzene-treated PAAm/SA wet gels by Procedure II. Relatively clear peaks are observed in the SAXS profiles of the 24hr- and 3hr-treated PAAm/SA wet gel, while the peak is barely recognized in that of the 1hr benzene-treated wet gel. Besides, the SAXS peaks in the profiles of the 24hr- and 3hr-treated PAAm/SA wet gels locate around almost the same position (0.05\AA^{-1}), while that of the 1hr benzene-treated wet gel lies far from that location. These features indicate that the nano-structural change can be almost completed at the treatment-period between 1hr and 3hrs.

Figure 6 illustrates the SAXS profiles of the hexane-treated PAAm/SA wet gels by Procedure II. All the profiles of the 24hr-, 3hr- and 1hr-hexane-treated PAAm/SA wet gels seem similar to each other from the standpoint of the clarity and location of the SAXS peaks indicating that the nano-structural change by the hexane-treatment can have almost finished until 1hr, of which the feature is somewhat different from the case of the benzene-treated PAAm/SA wet gels. Beside, it may be necessary to refer to the SAXS profile evolution. One can notice that the skirt-slope of the SAXS profile observed at 3 hrs is steeper than those of other profiles. Because the longitudinal axes are in the logarithmic scale, simple experimental condition differences such as the intensity change in the incident X-ray and difference in the sample thickness cannot affect the SAXS-profile shape, therefore, the increase in the slope may indicate the existence of the very large structure which cannot be measured directly by the present experimental-setup or the diffusive fluctuation.

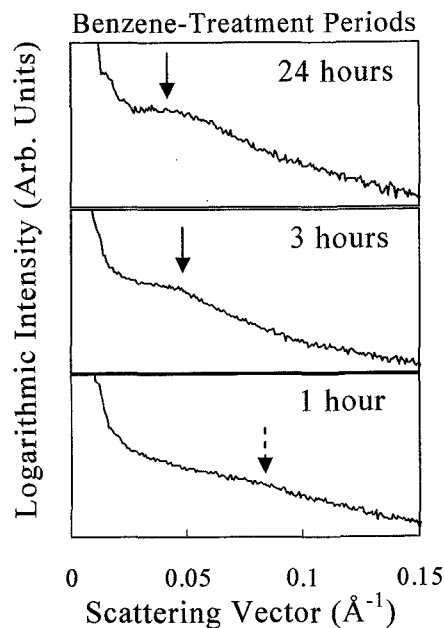


Fig.5 The SAXS profiles of the benzene-treated PAAm/SA wet gels which were prepared by Procedure II. The treatment periods are shown in the upper right side of the figures. The arrows in the figures indicate occurrence of peaks in the profiles. (see also text)

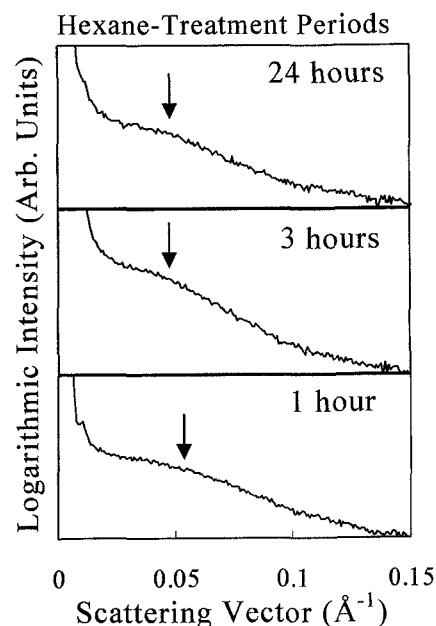


Fig.6 The SAXS profiles of the hexane-treated PAAm/SA wet gels which were prepared by Procedure II. The treatment periods are shown in the upper right side of the figures. The arrows in the figures indicate occurrence of peaks in the profiles. (see also text)

3. DISCUSSIONS

In the previous study, it was revealed that the benzene- and hexane-treatments of the PAAm/SA gel affect its swelling rate and ratio so much [19]. Seemingly, such phenomena may be curious because the PAAm/SA gel is a hydrogel of which the solvent is water being less compatible with the non-polar organic solvents such as benzene and hexane. One may consider that the non-polar solvents can not infiltrate into the inner part of the PAAm/SA gel and can not affect the macroscopic property so much. However, in fact, quite the contrary happened; there is considerable change in the swelling feature by the organic-solvent treatment as demonstrated in the previous study [19]. With these experimental results, by the organic-solvent treatment, the authors have been estimating that there can be occurred a kind of headrace channels through which water outside of the PAAm/SA gel can permeate inside. The authors have been considering that the SAXS peak observed in the previous study can be related to the nano-structure composed of such channels (Figs. 1 and 2 [19]).

In the present study, it has been found that the nano-structures in the benzene- and hexane-treated PAAm/SA gels are similar with each other as shown in Fig. 3 which can come from approximately the same magnitude of the hydrophobicity of benzene and hexane. In addition to this feature, it has been also found that the nano-structure brought by the benzene- and hexane-treatments disappears by dehydration as shown in Fig. 4, which indicates that the estimated headrace channels in the gels can be flexible and easy to collapse by shrinkage of the polymer network by dehydration. This feature convinces the authors that the channels may be hiatus on the gels surface made by heterolytic shrinkage of the polymer network during the hydrophobic-organic-solvent treatment; the weak linkage point in the polymer network can be broken by the shrinkage of the network polymers facing the hydrophobic solvents. The hiatus can be enlarged by the tension on the substantial swelling of the *ionic* PAAm/SA gel in water after the organic-solvent treatment. Such an enlarged channel will allow a large amount of water to flow inside the PAAm/SA gel in a short period and will accelerate the large amount of swelling.

As shown in Figs. 5 and 6, the evolution features of the SAXS peaks has been found to be somewhat different mainly in the completion period of the characteristic nano-structure formation. The authors suppose that this difference can come from the slightly different hydrophobicity between benzene and hexane which can be evaluated by their permittivities, 2.3 (benzene) and 1.9(hexane): the formation completion of the characteristic nano-structure formation of the hexane-treated PAAm/SA gel is sooner than that of the benzene-treated gel, presumably because hexane is more miscible with water than benzene.

The detailed investigations are in progress with more variety of the treatment solvents.

REFERENCES

- [1] Preventative Measures Against Water Pollution, Jinzu River, Toyama Prefecture (in the Home Page of International Center for Environmental Technology Transfer (ICETT)), http://www.icett.or.jp/lpca_jp.nsf/Jinzu%20River,%20Toyama%20Prefecture?OpenView.
- [2] Jun Ui (Ed.), Industrial pollution in Japan (The Japanese Experience Series), United Nations University Press, Tokyo, 1992. (<http://www.unu.edu/unupress/unupbooks/uu35ie/uu35ie00.htm>)
- [3] F. M. D'Itri, in W. P. Cunningham, T. H. Cooper, E. Gorham and M. T. Hepworth (Eds.), Heavy metals and heavy metal poisoning in Environmental Encyclopedia (Second edition), Gale Research, Detroit, 1998, pp.511-513.
- [4] J. S. Thayer, in R. A. Meyers (Ed.), Encyclopedia of Environmental Analysis and Remediation, Vol.4, Wiley, New York, 1998, pp. 2126-2139.
- [5] K. Hara, M. Yoshigai and T. Nishida, Trans. Mater. Res. Soc. Jpn., 30, 823, (2005).
- [6] K. Hara, M. Iida, K. Yano and T. Nishida, Colloids and Surfaces B, 38, 227, (2004).
- [7] K. Hara, M. Yoshigai and T. Nishida, Trans. Mater. Res. Soc. Jpn., 31, 815, (2006).
- [8] K. Hara, M. Yoshigai and T. Nishida, Trans. Mater. Res. Soc. Jpn., 31, 867, (2006).
- [9] K. Hara, M. Yoshigai and T. Nishida, Ferroelectrics, 348, 161, (2007).
- [10] K. Hara, M. Yoshigai and T. Nishida, Trans. Mater. Res. Soc. Jpn., 32, 819, (2007).
- [11] T. Tanaka; Sci. Am. 244, 124 (1981).
- [12] T. Tanaka, Phys. Rev. Lett., 45, 1636 (1980).
- [13] T. Tanaka, Phys. Rev. Lett., 40, 820 (1978).
- [14] S. Hirotsu, Y. Hirokawa, and T. Tanaka, J. Chem. Phys., 87, 1392 (1987).
- [15] S. Hirotsu, Phase Transitions, 47, 183 (1994).
- [16] D.K. Jackson, S.B. Leeb, A. Mitwalli, D. Fusco, C. Wang, and T. Tanaka, J. Intell. Mater. Syst. Struct., 8, 184, (1997).
- [17] K. Hara, Y. Sueyoshi, M. Sugiyama and T. Tanigawa Trans. Mater. Res. Soc. Jpn., 31, 819, (2006).
- [18] K. Hara, K. Yanagihara, T. Tanigawa, A. Nishida and S. Yoshioka Trans. Mater. Res. Soc. Jpn., 32, 831, (2007).
- [19] K. Hara, T. Tanigawa, K. Yanagihara, A. Nishida and S. Yoshioka Trans. Mater. Res. Soc. Jpn., 32, 795, (2007).