

Property Change by Heterogeneity in Gels

Kazuhiro Hara¹, Yusuke Sueyoshi²
Masaaki Sugiyama³ and Takao Tanigawa²

¹Faculty of Engineering, Kyushu University, Fukuoka, Hakozaki 812-8581, Japan
Fax: 81-92-642-3771, e-mail: haratap@mbox.nc.kyushu-u.ac.jp

²Graduate School of Engineering, Kyushu University, Fukuoka, Hakozaki 812-8581, Japan
Fax: 81-92-642-3771, e-mail: haratap@mbox.nc.kyushu-u.ac.jp

³Research Reactor Institute, Kyoto University, Kumatori, Sennan-gun, Osaka 590-0494 Japan
Fax: 81-724-51-2635, e-mail: sugiyama@rri.kyoto-u.ac.jp, tfuku@rri.kyoto-u.ac.jp

Several properties of a PAAm/SA gel were investigated with changing cross-linker concentration including the point at which the gel becomes cloudy. It was observed that the volume changes in swelling in pure water and shrinking in ion-capturing process is considerably suppressed above the cloudy point. By considering the factors governing the gel volume, the authors estimated that the largest change can occur in the network elasticity, which was also confirmed by a simple elasticity experiment. In addition, in order to investigate the influence of such a change on nanostructure, the authors also measured cross-linker fraction dependence of the SAXS profile of the PAAm/SA gel and observed that the SAXS profile of the PAAm/SA gel with the higher cross-linker concentration shows a steeper initial slope, which indicates a larger structure in the PAAm/SA gel with higher cross-linker concentration. Beside, the SAXS profile of dehydrated NIPA/SA gels with different cross-linker concentration was also observed because it is known that the dehydrated NIPA/SA gel shows an environment-sensitive peak in the SAXS profile. In the measurement, the SAXS profiles of the dehydrated NIPA/SA gels with the cross-linker fractions around the cloudy point show a drastic change, of which the behavior can be also explained by the increase in the network elasticity.

Key words: heterogeneity, SAXS, PAAm/SA, NIPA/SA, gel

1. INTRODUCTION

The gels are composed of solvent and network polymers, of which the properties are considerably influenced by their interaction [1,2], and many interesting features are observed in their wet conditions such as the volume phase transition [1] and ion-capturing function [3-5]. Besides, in a dehydrated condition, a distinct micro-phase separated structure very sensitive to environmental conditions has been found in *N*-isopropylacrylamide/sodium acrylate (NIPA/SA) gels [6,7].

In addition to these phenomena, the gels show interesting and general property-changes: with a small increase in cross-linker concentration, there occurs a drastic change in turbidity by a spatial inhomogeneity. Though many studies on such an inhomogeneity have been reported [8-14], the mainly observed property changes are relatively in the weakly turbid state and there seems not to be enough systematic investigations on several properties across the drastic turbidity change cross-linker concentration. Therefore, in the present study, such investigations of polyacrylamide/sodium acrylate (PAAm/SA) gels have been performed putting an emphasis on the

relation between the drastic turbidity increase and property change with adopting the same specimens in all the experiments. In addition, small angle X-ray scattering (SAXS) measurements were performed in order to examine the influence of the turbidity-inducing property change on the nanostructure of the PAAm/SA gel and the micro-phase separated structure in the dehydrated *N*-isopropylacrylamide/sodium acrylate (NIPA/SA) gel, which also revealed drastic changes in their nanostructures as described below. All the experiments were performed at room temperature and in the atmosphere.

2. EXPERIMENTALS AND RESULTS

2.1 Specimens

In order to measure the cross-linker concentration dependence of several properties of PAAm/SA gel, several aqueous solutions containing 500 mM of acrylamide (AAm), 200 mM of sodium acrylate (SA) and different amount of *NN*-methylenebisacrylamide (Bis, cross-linker) in a range from 0.5 wt% to 4.5 wt% were prepared and heated for 24 hours at 60 °C after adding 0.05 wt% of ammonium persulfate to each the solution. Though all the mixture solutions were transparent before heating, the gelled specimens showed different feature

by the cross-linker concentration: the gels with above 2.5 wt% of cross-linker concentration become turbid, while the gels with the concentration below that value remains transparent.

In order to prepare the NIPA/SA gels with different concentration of cross-linker, precursor solutions of 500 mM of *N*-isopropylacrylamide (NIPA), 200 mM of sodium acrylate (SA) and different amount of *NN'*-methylenebisacrylamide (Bis, cross-linker) in a range from 0.5 wt% to 4.5 wt% were prepared and conducted gelation for 24 hours at 5 °C after adding 0.05 wt% of ammonium persulfate and 10 μ L of *N,N,N',N'*-tetramethylethylenediamine (TEMED). After the finishing gelation, the NIPA/SA gels with the cross-linker concentration above 1.5 wt% become cloudy, while the specimens with the concentration below that value remains transparent. From the gelled lumps, disk-shaped samples with a dimension of 10 mm in diameter and 3 mm in thickness were cut out. Then,

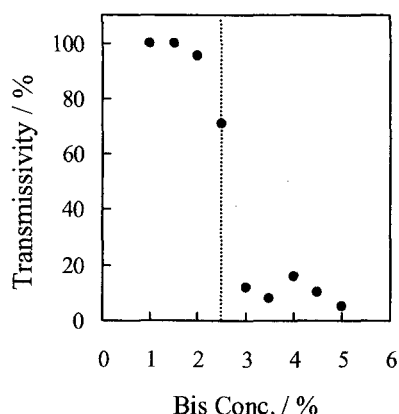


Fig.1 The light transmissivity (at 600 nm) of the PAAm/SA (500mM/200mM) gels with different cross-linker (Bis) concentrations. The dotted line in the figure indicates 2.5 wt% in concentration.

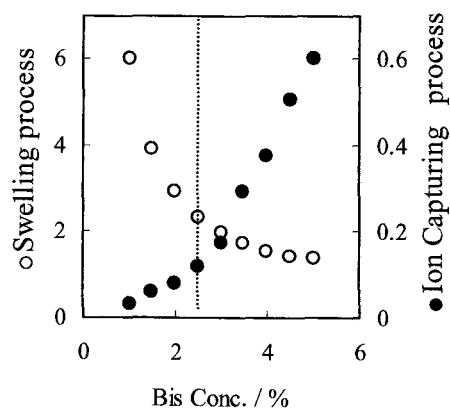


Fig.2 The ratios of the weights after to before swelling (○) in pure water and those of shrinking in the Cu^{2+} -capturing (●) process of the PAAm/SA (500mM /200mM) gels with different cross-linker concentrations. The dotted line in the figure indicates 2.5 wt% in concentration.

the samples were soaked in pure water for 24 hours in order to remove unreacted ingredients. The dehydrated samples were prepared by dehydrating the purified samples for 6 days in a condition around 25 °C in temperature and below 30 % in humidity. The water contents of all the dehydrated gels were below 20 wt%, and the dimensions were reduced to around 5 mm in diameter and 1 mm in thickness.

2.2 Light transmissivity measurement

In order to examine turbidity of the PAAm/SA gels with different cross-linker concentrations, light transmissivity measurements were performed by utilizing a spectrometer (APEL PD-303, grating: 1200 lines/mm, incident light wavelength width: 10 nm, light source: krypton lamp). The dimension of the measured plate-shaped specimens was 10mm \times 10mm \times 1mm. The wave length range of the incident light in the measurements was from 400 nm to 600 nm.

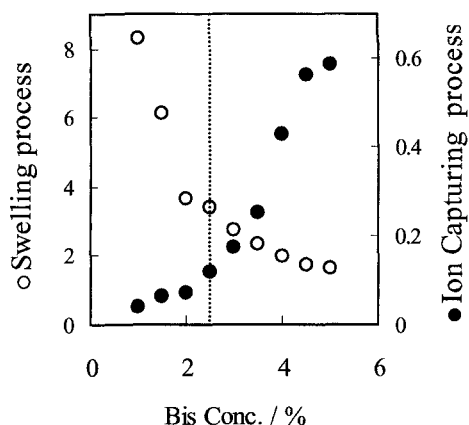


Fig.3 The ratios of the volumes after to before swelling (○) in pure water and those of shrinking in Cu^{2+} -capturing (●) process of the PAAm/SA (500mM /200mM) gels with different cross-linker (Bis) concentration. The dotted line in the figure indicates 2.5 wt% in concentration.

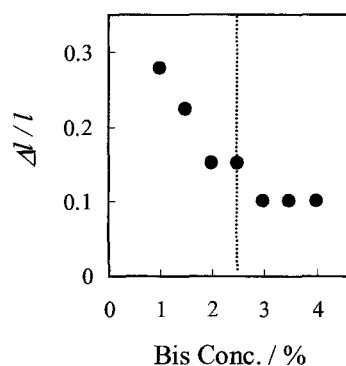


Fig.4 The shrinkage ratios of the PAAm/SA (500mM /200mM) gels with different cross-linker concentrations. The dotted line in the figure indicates 2.5 wt% in concentration.

Figure 1 shows the cross-linker dependence of the light transmissivity observed at 600 nm. As can be easily seen from the figure, the transmissivity decreased drastically around the cross-linker concentration of 2.5 wt% (C_{cloudy}). The light transmissivity observed at other wavelengths showed the similar crosslinker dependence and the deviation of the characteristic cross-linker concentration was within 0.2 wt%.

2.3 Weight and volume measurements in swelling and ion-capturing process

The cross-linker concentration dependences of weight and volume of the PAAm/SA gel in swelling and ion-capturing process were observed by utilizing an electric balance and a micrometer. The PAAm/SA gels with different cross-linker concentration without the washing treatment were cut out into column-shaped samples with a dimension of 5 mm in diameter and 10 mm in height. The first measurements of weight and volume were performed at this stage. After the measurements, the samples were soaked in pure for 24 hours until the completion of swelling process. The second weight and volume measurements were carried out after that period.

After then, the swollen samples were put in the cells containing 10 mM and 15 g of aqueous CuCl_2 solution for 24 hours again until the finish of Cu^{2+} -capturing process. The weight and volume were again measured at this stage.

Figures 2 and 3 show cross-linker concentration dependences of the ratios of the weights after to before swelling (\circ) in pure water, and shrinking in the Cu^{2+} -capturing (\bullet) process of the PAAm/SA (500mM /200mM) gels. As can be seen from the figures, both the weight and volume show similar behavior which indicates that the polymer network can expand and shrink in both the process. Besides, by taking the changing features of the data around C_{cloudy} into consideration, it can be said that the expand and shrinking features seems to be related to the occurrence of the turbidity in the PAAm/SA gel: the expanding degree in the swelling process becomes much smaller above C_{cloudy} , and so does the shrinking degree in the Cu^{2+} -capturing process as well.

2.4 Simple elasticity measurement

In order to observe the influence of cross-linker concentration on the elasticity of the PAAm/SA gel, simple compress measurements were performed by putting a weight on the gels. For the experiments, the authors adopted column-shaped (5 mm in diameter and 10 mm in height) PAAm/SA (500mM/200mM) gels without washing process. The sample lengths were measured with a micrometer before and after putting a weight (15.95 g) on them, and strains were estimated from the measured lengths.

Figure 4 depicts the cross-linker concentration dependence of the strain, which clearly reveals a drastic change in the cross-linker concentration

dependence of the elastic property around C_{cloudy} .

2.5 Small angle X-ray scattering measurements

The disk-shaped specimens with a dimension of 5 mm in diameter and 1 mm in thickness were adopted for the SAXS measurements of wet PAAm/SA gels; the specimens were measured without the washing process in order to observe the raw structures formed in the gelation process. On the other hand, the specimens of the dehydrated NIPA/SA gel were prepared after the washing process as mentioned in section 2.1: the dehydrated specimens were also disk-shape with the same dimension mentioned above.

The SAXS experiments were carried out with a SAXS apparatus (SAXES) installed at BL10C 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.

Figure 5 shows the SAXS profiles of the wet PAAm/SA gels prepared in the condition below and above C_{cloudy} . A remarkable change can be observed in the SAXS profiles' initial slopes

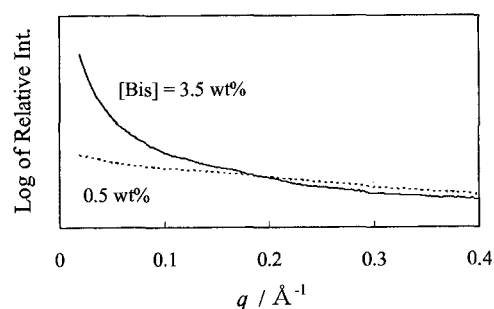


Fig.5 The SAXS profiles of the wet PAAm/SA (500mM /200mM) gels with cross-linker concentrations below and above $C_{\text{turbid}}=2.5\text{wt}\%$.

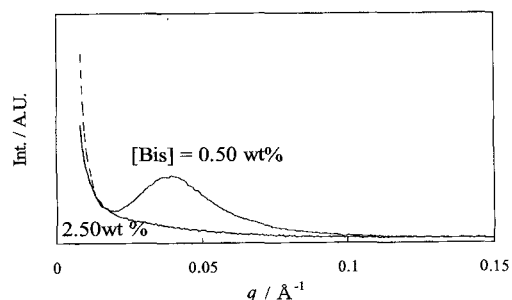


Fig.6 The SAXS profiles of the dehydrated NIPA/SA (500mM /200mM) gels with cross-linker concentrations below and above $C_{\text{turbid}}=1.5\text{wt}\%$.

which are related to the cluster sizes in the specimens, which are estimated by the Guinier Plot as 21 Å in the specimen with cross-linker concentration of 0.5 wt% and 87 Å at 3.5 wt%.

Figure 6 shows the SAXS profiles of the dehydrated NIPA/SA gels prepared from the wet gels with the cross-linker concentration below and above C_{cloudy} . In the case of the NIPA/SA gel, C_{cloudy} is 1.5 wt% as mentioned in section 2.1. A remarkable change was also observed in the SAXS profile of the dehydrated NIPA/SA gel: disappearance of the low- q peak which indicates the destruction of the micro-phase separated structure.

3. DISCUSSION

In the present study, it has been observed how the heterogeneity caused by cross-linker concentration increase influences the properties of the PAAm/SA gel. The feature of the property change is drastic and very interesting.

However, one should notice that one cannot derive the structure in the gel from the light scattering features in the turbid state because the multiple scattering of an incident light occurs so much in this state [15]. In other words, the strong turbid feature is a measure of the multiple light scattering by a close arrangement of strong light scatterer in a range of the coherence length of the incident light, which is also an important property of the material. Therefore, in the turbid state, the scatterers with a large light scattering power should be located with spacings around the coherence length of the order of μm because the light source in the present study is a krypton lamp in the spectrometer. (If a laser light is used as a light source, the coherence length becomes above few meters, namely, usually larger than sample's dimension.) Besides, because the light scattering power becomes large with the dimension of the scatterer, there can exist a thicker network in turbid gels than that in the transparent gels. Therefore, it can be said that a μm -spacing arrangement of a thick network induces the drastic property change observed in the present study.

Such a consequence is supported by the consideration of basic interactions which govern the size of the gel [1,2]: because the change occurs with small increase in the cross-linker fraction, chemical properties such as the affinity between network and solvent and the electrostatic interaction between ionized groups in the side chains and small ions in the solvent may not change so much. Therefore, the elasticity increase of polymer network can take a principal role for the drastic property changes observed in the present study. The SAXS results of the PAAm/SA gels also support such a feature with increase in the gyration radius with increasing cross-linker concentration.

The SAXS results of the dehydrated NIPA/SA

gels are very interesting. The micro-phase separation in the dehydrated NIPA/SA gel can be established by a delicate balance of related ingredients' interactions, which is known to be easily destroyed with increase in only 0.2% of water content [6]. The drastic coagulation of polymer network which causes the turbidity may destroy the delicate interaction balance and result in the disappearance of the micro-phase separated structure in the dehydrated NIPA/SA gel with cross-linker fraction beyond C_{turbid} .

REFERENCES

- [1] T. Tanaka: *Sci. Am.* 244, 124 (1981).
- [2] P. G. de Gennes, "Scaling Concepts in Polymer Physics," (Cornell University Press, Ithaca, NY, 1979).
- [3] K. Hara, M. Sugiyama and M. Annaka, *Trans. Mater. Res. Soc. Jpn.*, 28, 1017 (2003).
- [4] K. Hara, M. Iida, K. Yano and T. Nishida, *Colloids and Surfaces B*, 38, 227 (2004).
- [5] K. HARA, M. Yoshigai and T. Nishida, *Trans. Mater. Res. Soc. Jpn.*, 30, 823 (2005).
- [6] M. Sugiyama, S. Kuwajima, Y. Soejima, A. Nakamura, N. Hiramatsu, T. Kikukawa, A. Suzuki and K. Hara, *Jpn. J. Appl. Phys.*, 38, L1360 (1999).
- [7] M. Sugiyama, M. Annaka, K. Hara, M. E. Vigild, G. D. Wignall, *J. Phys. Chem.*, 107, 6300 (2003).
- [8] S. Mallam, F. Horkay, A.-M. Hecht and E. Geissler, *Macromolecules*, 22, 3356 (1989).
- [9] L. Benguigui and F. Boué, *Eur. Phys. J. B* 11, 439 (1999).
- [10] S. Durmaz, O. Okay, *Polym. Bull.*, 46, 409 (2001).
- [11] M. Y. Kizilay and O. Okay, *Macromolecules*, 36, 6856 (2003).
- [12] H. Cerid, O. Okay, *Eur. Polym. J.*, 40, 579 (2004).
- [13] I. Yazici, O. Okay, *Polymer*, 46, 2595 (2005).
- [14] A. Ozdogan, O. Okay, *Polym. Bull.*, 54, 435 (2005).
- [15] K. Hara, K. Kuboyama, H. Okabe and K. Matsushige, *Jpn. J. Appl. Phys.*, 32, 996, (1993).

(Received January 31, 2006; Accepted June 2, 2006)