

## Characteristics of the Hydrophilic Clusters in Dehydrated Ionized NIPA Gel

Shuichiro KUWAJIMA, Yuji SOEJIMA, Masaaki SUGIYAMA<sup>1</sup>, Kazuhiro HARA<sup>2</sup>,  
Atsushi NAKAMURA<sup>3</sup>, Nobuyasu HIRAMATSU<sup>3</sup>, Masahiko ANNAKA<sup>4</sup>,  
Takashi KIKUKAWA<sup>2</sup> and Atsushi SUZUKI<sup>5</sup>

Division of Fundamental Physics, Graduate School of Science, Kyushu University, Fukuoka 812-8581, Japan

Fax: 81-92-642-2553, e-mail: syu6scp@mbox.nc.kyushu-u.ac.jp

<sup>1</sup>Division of Chemistry and Physics of Condensed Matter, Graduate School of Science, Kyushu University,  
Fukuoka 812-8581, Japan

<sup>2</sup>Institute of Environmental Systems, Graduate School of Engineering, Kyushu University,  
Fukuoka 812-8581, Japan

<sup>3</sup>Department of Applied Physics, Faculty of Science, Fukuoka University, Fukuoka 814-0180, Japan

<sup>4</sup>Department of Materials Technology, Chiba University, Chiba 263-8522, Japan

<sup>5</sup>Department of Materials Science, Yokohama National University, Yokohama 240-8501, Japan

The small angle X-ray scattering (SAXS) measurements have been made for dehydrated *N*-isopropylacrylamide/sodium acrylate (NIPA/SA) gel with various concentrations of SA and water. It is found that the intensity of a prominent peak observed in the SAXS profile increases with increase in SA concentration while that decreases with water content. It is also found that the peak position shifts to lower momentum region with increase in both SA and water content. The results indicate that the appearance of the peak is attributed to an inhomogeneous density contrast due to the clustering of SA in the gel network. On the basis of the present experimental results, discussions on the clustering are given and a model of the self-organizing structure in the gel is proposed.

Key Words: NIPA gel, Dehydration, water content, SAXS, microphase separation

### 1. INTRODUCTION

Since a gel consists of three-dimensional polymer network and solvent, the properties of the gel depend strongly on the interaction of these two components. By dehydration, one of the components, namely the solvent, is reduced; therefore it is expected that the gel demonstrates interesting properties with drastic change in the interaction between the ingredients. The report on the dehydration of the hydrogel was given by Takushi *et al.*<sup>1)</sup> for heat-treated egg-white gel; they found successive two stages of time-dependent mass reduction which are characterized by different mechanism of the dehydration process. The first stage is attributed to the reduction due to the evaporation of weak-bound water (free water),

and the second one is that of strong-bound water (bound water). In addition, characteristic behavior of non-crystalline polymer were observed by the thermal measurements<sup>2)-5)</sup>, experiments in elasticity<sup>5),6)</sup> and low frequency Raman scattering measurements<sup>4), 7), 8)</sup>. The characteristics indicate that the dehydrated gel is in a glass state. However, a difference between the dehydrated gel and the simple polymer glass is pointed out by the observation of the low-lying Raman peak: the dehydrated gel is composed of clusters with different nature. This reveals an inhomogeneous feature in the dehydrated gel. In order to elucidate the inhomogeneity, Sugiyama *et al.*<sup>9)</sup> investigated the mesoscopic structure of the dehydrated *N*-

isopropylacrylamide/sodium acrylate (NIPA/SA) gel by the small angle X-ray scattering (SAXS) measurement. The gel contains conflicting hydrophobic (NIPA) and hydrophilic (SA) groups in the gel network, therefore, an enhancement of the inhomogeneity is expected by the dehydration. They found a prominent peak in the SAXS profile probably attributed to the microphase separation during the dehydration.

However, only the previous experiment for the specimen with fixed SA/NIPA ratio: namely single-component-ratio experiment, the origin of the peak has been still ambiguous whether it reflected the size of the SA clusters or the inter-distance of them. In order to manage the problem, a multi-component-ratio experiment, the measurements as a function of SA/NIPA ratio, should be indispensable. Therefore, in the present study, the SAXS measurements are made for dehydrated NIPA/SA gels with various ratio of NIPA and SA and those with various water concentrations, aiming to specify the microphase separation.

## 2. EXPERIMENTAL

NIPA/SA gels were synthesized by a free radical copolymerization of *N*-isopropylacrylamide (NIPA), constituent and sodium acrylate (SA) in water solvent under nitrogen atmosphere. The concentration ratio of NIPA (640-500 mM) to SA (60-200 mM) was varied in the condition that the total concentration was fixed at 700 mM. Respectively, as crosslinker, accelerator and initiator, *N,N'*-methylenebisacrylamide (BIS, 8.6 mM), *N,N,N',N'*-tetramethylethylenediamine (TEMED, 240  $\mu$ l) and ammonium persulfate (APS, 40 mg) were put into the 100 mg deionized and distilled water. The gelation was carried out for 24 hours at 0 °C. After the gelation, these jelled samples were immersed in pure water for a week to wash away the residual chemicals. The purified gels cut into some portions in disk shape ( $\phi 20 \times t 5$  mm). Some of them with 500:200 NIPA/SA ratio were washed in hydrochloric acid to prepare the specimen without sodium. After gently dehydrated in the atmosphere for 6 days, the specimens are obtained in the shape of small disk ( $\phi 5 \times t 1$  mm). Hereafter, we refer to the former and the latter specimens as "specimen- $\alpha$ " and "- $\beta$ ", respectively. For the measurements of the gel with various water contents ( $w=0.3-1.6$ ), the specimens were prepared by adding water to the 500:200 dehydrated gel, referred as "specimen- $\gamma$ ".

The SAXS measurements have been made at BL-10C synchrotron facility in Photon Factory, KEK, Tsukuba. Incident synchrotron beams are monochromatized with 111 diffraction of Si double crystal monochromator and the beam is converged by the bent cylindrical type of mirror. The relative energy resolution  $\Delta E/E$  of the incident beam is  $3.3 \times 10^{-4}$ . The incident beam impinges into the specimen through an ionization chamber for the monitoring the intensity of the beam. One-dimensional position sensitive proportional counter (PSPC) detects the small-angle scattering through the evacuated tube 2 m in length. As standard for the calibration of the channels of PSPC to the scattering angle, the measurement of collagen (spacing, 653 Å) was made. All measurements were made at room temperature. The wavelength of incident beam was fixed at 1.488 Å. The measuring angles corresponded to a range from 0.01 to 0.15 Å<sup>-1</sup> in reciprocal spacing. The observed profile was corrected for the absorption, and then normalized to units of the specimen thickness and irradiation time. After the correction and the normalization, SAXS profiles straightforwardly correspond to the scattering efficiency.

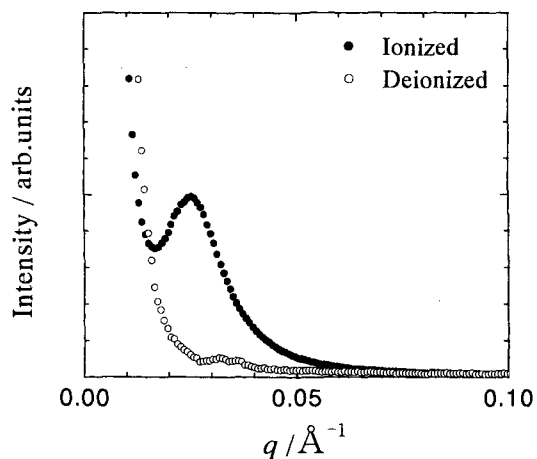


Fig.1 SAXS profiles of ionized (closed circle) and deionized (open circle) dehydrated NIPA/SA gel.

## 3. RESULTS

In Fig.1, SAXS profiles are shown for the specimens- $\alpha$ (500:200) and - $\beta$ . A prominent peak is observed at 0.026 Å<sup>-1</sup> in specimen- $\alpha$ , while there is no remarkable peak in the case of specimen- $\beta$ . Taking the results reported by Sugiyama *et al.*<sup>9)</sup> into account, the present results indicate a fact that SA

takes an important role for the appearance of the peak. Fig.2 shows SAXS profiles of the specimen- $\alpha$  for various NIPA/SA ratio; the intensity of the peak is stronger with the concentration of SA. This supports the fact mentioned above: the peak originates in a kind of inhomogeneous density distribution that mainly consists of SA part. Moreover, we note that the position of the peak shifts toward smaller  $q$  region with increasing SA concentration. By adding water into the dehydrated gel, the specimen- $\gamma$ , the peak becomes weak and then vanishes at  $w \approx 1.3$ , as shown in Fig.3. In contrast with the results shown in Fig.2, the position of the peak shifts to smaller  $q$  region with decreasing in its intensity. The discussions will be given in the following section.

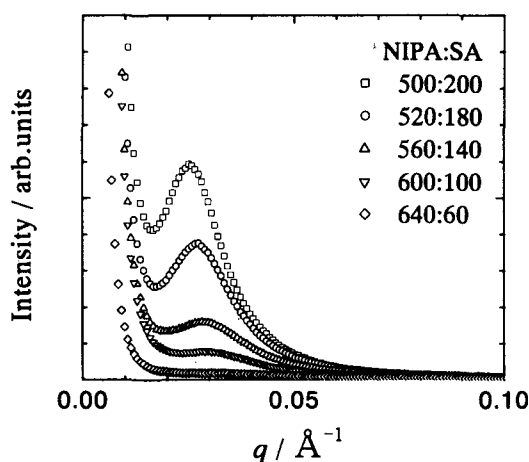


Fig.2 SAXS profiles of dehydrated NIPA/SA gels with various ratio of constituent monomers.

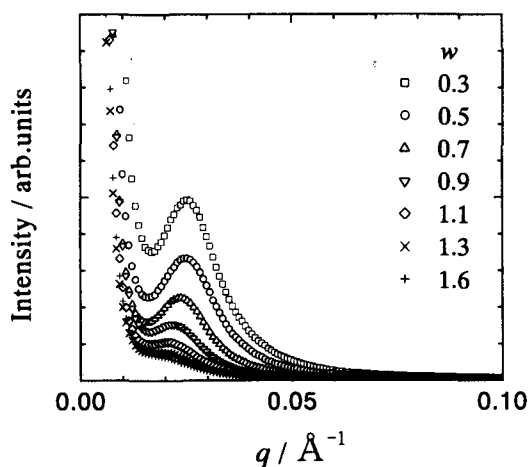


Fig.3 SAXS profiles of the NIPA/SA gels with various water contents.

#### 4. DISCUSSIONS

As discussed by Sugiyama *et al.*<sup>9)</sup>, the peak observed in SAXS profile is probably attributed to the formation of the clustering of SA parts during the dehydration process. The present results strongly supports the hypotheses as mentioned in the previous section. According to the present results, here we propose a model for the clustering. The dehydration of the gel induces a shrinking of the volume which results in a closed packing of the gel molecules, and therefore it is reasonably expected that the chemical interactions of hydrophilic-to-hydrophilic bases and hydrophobic-to-hydrophobic bases become stronger. In the case of hydrophilic SA bases, their connection consists of not only the hydrophilic-to-hydrophilic interaction but also the interaction of hydrophilic-to-water. As a result, at the end stage of the dehydration, SA parts can form clusters which envelope the free water in microscopic scale. This results in the microphase separation of density in the dehydrated gel, and the inhomogeneity of the density distribution contributes to the scattering contrast in the SAXS profile. In fact, the SAXS profile shown in Fig.1 is well represented by the structure function for the spherical clusters dispersed in the system without interaction between them, assuming Gaussian type of distribution of the cluster radius.

In Fig.4, plots of peak intensity and the cluster size determined from the results shown in Fig.2 are given versus SA concentrations. As mentioned in the previous section, the contrast of the inhomogeneous density distribution and the size of the cluster becomes larger with SA concentration. The model is well consistent with the results: *i.e.* in the case that SA concentration is higher in the gel, the model requires higher density of SA and larger radius of the cluster. The former results in more intense peak and the latter causes the peak shift toward smaller  $q$  region in accordance with the results shown in Figs.2 and 4. The mean size of the cluster is 200 Å in radius, in roughly speaking. The same plots versus weight concentration of water determined from the results in Fig.3 are given in Fig.5. In contrast with those shown in Fig.4, the size of the cluster becomes larger while the intensity is with water content. This is well explained as follows: the added water expands the hydrophilic SA clusters by accumulating within them, which leads to low contrast. It is note that the intensity is extremely weak for the case that the cluster is larger than 250

Å in radius. The drastic decrease in the intensity with gentle increasing in radius of the cluster must be attributed not only to the reduction of the contrast but also to a breaking of the cluster. The details in quantitative discussion will be given elsewhere.

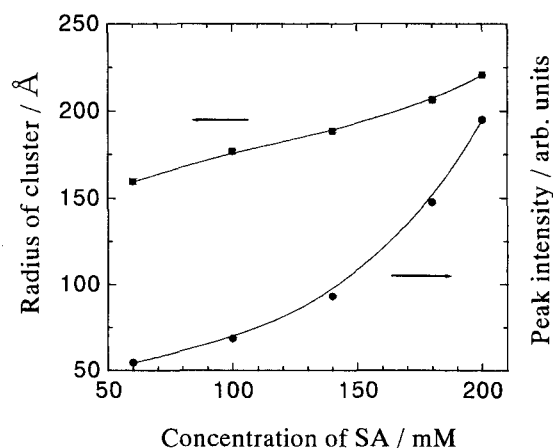


Fig.4 Radius of cluster and peak intensity versus concentration of SA.

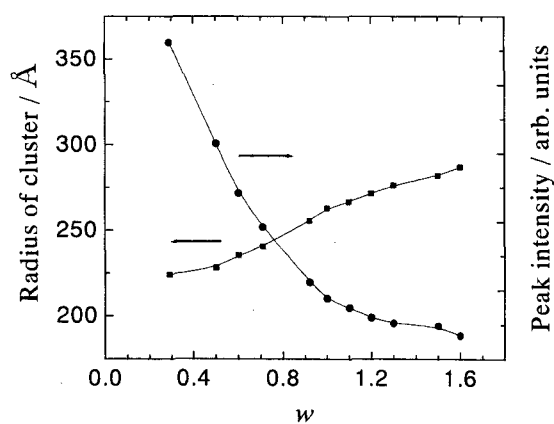


Fig.5 Radius of cluster and peak intensity versus water content.

It is worth to be considered that the size and density of the microphase separation is strongly influenced by the frustration due to two opposite characteristics: namely the chemical property of hydrophilic interaction with water and the physical limitation of stereoscopic conformation of bridging polymer molecules. We thus suppose the "self-organizing structure" of the SA clustering in the dehydrated gel. It is to be hoped that the model will

be discussed in connection with the self-organizing structure, which solves the mechanism and dynamics of the clustering in dehydration process.

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