Nano-structural Analyses of Copper-ion-adsorbed PAAm/SA Gels after UV-light Irradiation

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The cupric-ion adsorption effects on the nano-scale structures of the ultraviolet (UV) light irradiated *poly*(acrylamide/sodium acrylate) gels have been investigated by the small angle X-ray scattering (SAXS) measurements. It has been revealed that, without the cupric ion adsorption, the UV-light irradiated PAAm/SA gels do not show any characteristic structures in the SAXS profiles while a distinct peak has been observed in each of the SAXS profiles of the Cu-adsorbed gels; the SAXS peak position and width become smaller with the UV-light irradiation period indicating the development of the chelating aggregation of the network polymers of which the interconnections are progressively cut off with the UV-light dosage.

Key words: hydrogel, chelation, UV, SAXS

1. INTRODUCTION

Gel is formed by a combination of nano-scale three-dimensional network and solvent; by its characteristic structure, some gels exhibit interesting and useful properties due to the intercomponent interactions between the ingredients, namely the network and solvent [1]. Among the gels' interesting properties, the volume phase transition can be the most famous phenomenon in which remarkable volume change occurs with minor variation of ambient conditions such as temperature, electric field, pH, ingredient compatibility, etc. When the hydrogel's network contains ionized side-groups, the transition features are profoundly affected: the volume change in the transition becomes very large and discontinuous [1-5]. Besides, if the solvent contains multivalent ions such as heavy-metal and/or rare-metal ions, the ionized hydrogels exhibit other valuable functionalities in which the authors have been interested: the adsorption of multivalent ions. The first practical application of the multivalent-ion capturing property of the ionized hydrogel was made for developing the heavy-metal ion detector [6], however, the functionality of the detector utilizing the gel's multivalent-ion capturing property was only to indicate the ion species in the solvent by means of the difference in the volume phase transition temperature; there had not been the applications paying the attention to the multivalent-ion capturing amount. Under these circumstances, the authors have been investigating both of the adsorption and desorption properties of some hydrogels for the heavy- and/or rare-metal cations and anions aiming at the utilization for the environmental purification and the resource recycling [7-20].

In addition to these application studies, the authors have considered that the fundamental researches on the multivalent ion capturing effects on the structures and properties of the ionized hydrogels are indispensable for developing the more effective functional materials. Along this line, in the previous study, the authors investigated the effects of the cupric-ion adsorption on the macroscopic and semi-macroscopic properties of the *poly*(acrylamide/sodium acrylate) (PAAm/SA) gels after the UV-light irradiation for different periods as described below [21]. First, observed were the changes in the macroscopic surface properties of the wet and dehydrated PAAm/SA gels by irradiating UV-light; in spite that the exposed area to the UV-light turns turbid, there was almost no remarkable change in shape even with a large amount of the UV-ray dosage (UV-irradiation for 10 hrs with utilizing a high pressure mercury lamp with 170 mW/cm^2 of output intensity, of which the effective UV wave-lengths are 318 and 365 nm). On the other hand, the wet gels demonstrated very sensitive properties to the UV-light: the wet PAAm/SA gel ([AAm]:[SA]=500 mM:200 mM) readily disintegrated taking on the surface erosion in the UV-light irradiated area only in a few minutes. After 1 hr UV-light irradiation, the digging depth of the channel on the UV-irradiated area of the wet gel's surface became up to 12 mm. Secondly, the authors observed the optical property change of the surface of the UV-light irradiated PAAm/SA gel on the adsorption of cupric ion. As shown in Fig. 1(b), the UV-irradiated area became turbid immediately after dropping a small amount of aqueous Cu^{2+} ion solution on the surface whereas the unirradiated surface region did not show such a feature. The turbid area was still observed after the striped PAAm/SA gel had been dipped in the cupric ion solution for 24 hrs (Fig. 1(c)). Besides, it had been revealed that there were characteristic corrugated patterns in the unirradiated region while such a structure was not observed in the UV-ray irradiated area, as shown in Fig. 2, on the observation of the phase contrast microscope images across the boundary of the UV-ray irradiated and unirradiated areas of the PAAm/SA gel's surface shown in Fig. 1(c).

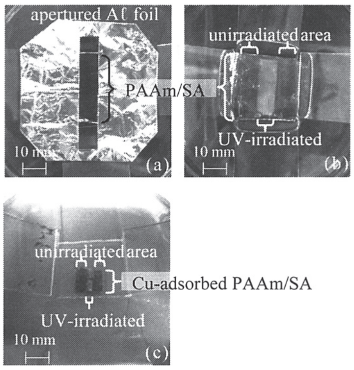

Fig. 1
The property changes of a UV-light irradiated PAAm/SA gel on adsorbing cupric ion [21].
(a) An Aℓ foil with an aperture was put on the gel before UV-ray irradiation. (b) The area having been UV-irradiated for 15 min became turbid immediately after dropping a small amount of aqueous $\mathrm{CuC}\ell_2$ solution on the gel's surface. (c) The turbid area was still observed after the gel shown in (b) having been dipped in aqueous $\mathrm{CuC}\ell_2$ solution for 24 hrs.

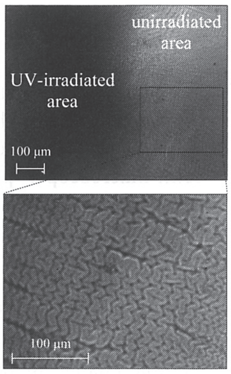

Fig. 2
The phase contrast microscope images of the PAAm/SA gel surface shown in Fig. 1(c) across the boundary of UV-ray irradiated and unirradiated areas observed after immersed in $\mathrm{CuC}\ell_2$ aqueous solution for 24 hrs [21]. Clear corrugated patterns were observed in the unirradiated area.

2. EXPERIMENTALS AND RESULTS

The aqueous solution containing 200 mM of SA, 500 mM of AAm and 12.3 mM of *N,N'*-methylenebis-acrylamide (BIS, cross linker) was prepared as the pregel solution by desolving these reagents in 50 g of water. Then the pregel solution had been left intact for 24 hrs at 60 °C after adding 2.4 mM of ammonium persulfate (polymerization initiator). After the period, several tiled portions with a dimension of $\sim 15 \times 15 \times 4\ \mathrm{mm}^3$ were cut out from the lump of the PAAm/SA gel. Then the small gel pieces were put in pure water in order to wash out unreacted ingredients; in these process, the volume of the gel slips increased ~40 times to the extent of $\sim 50 \times 50 \times 15\ \mathrm{mm}^3$ in dimension.

For the irradiation of UV-light, a high pressure mercury lamp with output of 100 W (HANDY CURERUB Handy 100, SEN LIGHTS Co.,Ltd.) was utilized as a light source of which the intensity was 170 $\mathrm{mW/cm}^2$ and the effective UV wave-lengths were 318 and 365 nm.

After the rinsing procedure, the fully swollen gel specimens had been exposed to UV-light at a distance of 200 mm from the light source for different periods in a range of 0~15 min. Then, some of the UV-ray irradiated specimens had been put in the respective $\mathrm{CuC}\ell_2$ aqueous (100mℓ, 100mM) solutions for 24 hrs, while the others were used without further treatments. After then, the UV-irradiated gel specimens with and without the cupric ion adsorption treatment were cut into disk-shaped specimens with 5 mm in diameter and 1 mm in thickness for the small angle X-ray scattering (SAXS) measurements.

The SAXS experiments were performed with an apparatus (SAXES) installed at BL-10C of Photon Factory in Institute of Materials Structure Science, KEK, Tsukuba, Japan. An X-ray beam of 1.488 Å in wavelength was used as a light source. The scattered X-ray intensity from each of the specimens had been measured by a one-dimesional PSPC for 7200 seconds at room temperature (~25 °C). The observed X-ray intensity was corrected for the cell scattering and absorption, and then normalized with the thickness of the sample and measurement time.

Figure 3 shows the SAXS profiles (in a range of 0~0.15 Å^{-1} in the magnitude of the scattering-vector) of the PAAm/SA gels after the UV-light irradiation for different periods in a range from 0 to 15 min. As can be easily seen from the profiles, their shapes are similar and there are no special features. In the left-hand figure of Fig. 4, described are the SAXS profiles of the UV-light irradiated PAAm/SA gels after the cupric-ion capturing treatment in the same q-range with Fig. 3. As can be easily seen from Fig. 4, a distinct peak emerges in all of the SAXS profiles of the UV-irradiated and cupric-ion adsorbed PAAm/SA gels. The right-hand figure of Fig. 4 descibes the SAXS profiles with the enlarged q-range, 0~0.05 Å^{-1} for helping the more detailed examination of the SAXS profiles; it can be recognized from the figure that the SAXS peak position varies with the UV-light irradiation periods.

3. DISCUSSIONS

In the present nano-scale structural investigations, it has been revealed the UV-light irradiated PAAm/SA gels show the interesting features in the SAXS profiles by capturing the cupric ion. The authors estimate that the premonitory modification of the PAAm/SA gel surface had been already come about before the cupric ion adsorption; and that, however, the scattered X-ray intensities from the PAAm/SA gels were too small to detect by the SAXS systems because of the small X-ray scattering cross sections and the low concentrations of the ingredient elements in the form of the swollen gels.

Such a latent change has been thought to have been elicited by the previous macroscopic measurements [21], in which observed was a large decrease in the transmitted light intensity through the Cu^{2+}-adsorbed PAAm/SA gels with increasing the UV-irradiation periods: in spite the shapes of the light-transmissivity spectra are not affected so much [21]. In addition, a collateral features indicating the surface modification by the UV-light irradiation were also revealed by the phase-contrast microscope investigations of the UV-light irradiated PAAm/SA gel surface after the cupricion-capturing treatments versus that of the unirradiated surfaces adsorbing Cu: in the latter, recognized are the characteristic crinkled patterns (Fig. 2) often emerged in the volume phase transition of the ionized hydrogels; on the other hand, in the former, there are not such a surface structure [1-3,21].

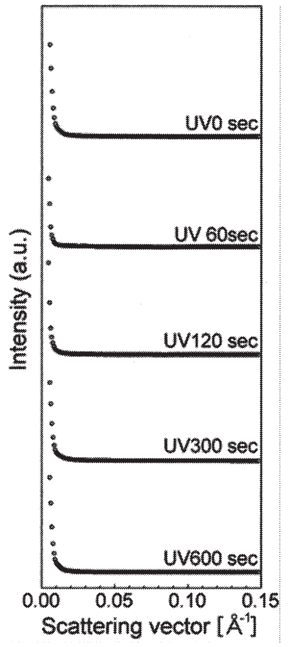

Fig. 3
The SAXS profiles of the UV-light irradiated (for the periods in a range from 0 to 600 s) PAAm/SA gel without the Cu-adsorption treatments. See also text.

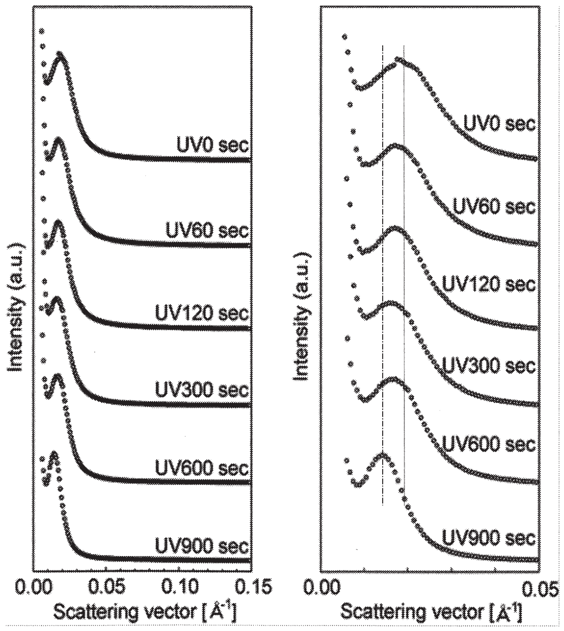

Fig. 4
The SAXS profiles of the UV-light irradiated (for the periods in a range from 0 to 600 s) PAAm/SA gel after the Cu-adsorption treatments. See also text.

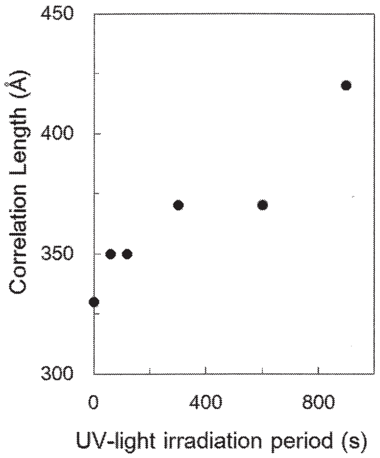

Fig. 5
The UV-light irradiation period dependence of the correlation length derived from the SAXS peak position in Fig. 4. See also text.

Though, at present, the nano-structural changes before the Cu^{2+}-adsorption have not been able to be detected yet, the influence of the UV-light irradiation to the surfaces of the PAAm/SA gels may be inferable from the difference in the SAXS profiles of the PAAm/SA gels capturing cupric ion after the different-period UV-light irradiation; not to mention that the nano-scale structural changes by capturing cupric ion themself have been very interesting and have been very important.

As mentioned above, after the adsorption treatment of the cupric ion, a distinct peak has emerged in each of the SAXS profiles of the UV-irradiated PAAm/SA gels. The noticeable changes in the SAXS profiles related to the SAXS peak appearance can be examined from the two viewpoints (Fig. 4): one is on the SAXS peak position corresponding to the correlation length of the well-defined nano-structure; and the other, the peak width related to the regularity and/or singularity of the nano-structures. As for the SAXS peak position, it can be recognized from the right-hand figure in Fig. 4 that the position of the SAXS peak moves toward the lower q-region with increasing the UV-irradiation period. This profile change indicates that the observed nano-scale structure becomes larger with increasing the dosage of the UV-light (Fig. 5). In addition to the remarkable change in the SAXS peak position, there is perceivable change in the SAXS peak width: apparently, the peak becomes narrower with the increses of the UV-light irradiation period; though the origin of the broadening of the SAXS peak has not been cleared yet, it can be said that the UV-light irradiation makes the emerged nano-structure more regulated. The authors have also considered that there might be a possibility of the superposed peaks in the SAXS profiles from the shapes and their changes with increasing the UV-light irradiation dosage.

The authors have estimated an after-mentioned mechanism in order to explain these characteristic features in the SAXS profiles obsevred in the present study. Some of the weakly charged polyelectrolytes are well-known to have a distict nano-structures caused by the so-called microphase separation which appears by delicate balances of the ingredient interactions between the network polymers and also those between the network polymers and ions in the solvent [22,23]. In this situation, one will expect some characteristic structures, such as a distinct peak in the SAXS profile. However, the observations of such structures by the SAXS experiments are very difficult when the differences of the X-ray scattering cross-sections between the network polymers and the solvent is very small as in the case of the swollen PAAm/SA gel. Therefore, in the hydrogels with low network polymer concentrations, the microphase-separated structures have been often observed by the small angle neutron scattering (SANS) experiments [24,25]. In spite of this situation, the authors have been still able to investigate the hydrogels' microphase-separated structures by the SAXS experiments by dehydrating them, namely in the condition the hydrogels are shrunk by the surface tensions caused by the remnant water in the hydrogels [26-29]. In these authors' SAXS experiments, the effective X-ray scattering occurs by the difference in the scattering cross sections between the network polymers and the counter ion elements of the ionized side chain; and it has been successfully observed that the SAXS peak positions and intensities differ with the counter-ion elements indicating change in the interaction strength [28].

Even in the relatively wet hydrogels, the similar structural situation will happen when the ionized hydrogels shrink due to the formation of the interconnection between the ionized side-chains and the counter ions caused by the chelation mechanism. At this point, one should remind that the conditions of the phase-separated structure are also much influenced by the elastic properties of the network polymer. As in the case of the present study, when the UV-light is irradiated to the hydrogel, some of the network polymers in the hydrogel can be cut off, which will make smaller the elasticity of the hydrogel segments and will make narrower the connection range of the network polymer in the hydrogels. Because the network polymer degradation degree will become higher with approaching the surface of the hydrogel, the elasticity of the surface area becomes very small and the decoupled segments on the surface can easily connect to each other by the adhesive force cause by the chelation between the ionized polymers through the cupric ion. Such a mechanism is thought to have been demonstrated in the abovementioned macro- and semi-macroscopic property changes oberved in the previous study (Figs. 1 and 2 [21]): the turbidity emerging on the surface of the UV-light irradiated PAAm/SA gel by applying a drop of cupric ion solution can be ascribed to the gathering of the small segments up to the size of the light wavelength; and the disappearance of the coagurated patterns is estimated to be caused by decreasing the surface elasticity due to the lost of the long range connection of the network polymer. The similar property change can occur in the internal area of the hydrogels; even though such UV-light irradiation effects become smaller there. The shift of the SAXS peak to the lower q-region can be related to increase in the size of the accumulated clusters composed of the disintegrated segments or in their intercluster distance. The examination for figuring out the origin of the observed changes in the SAXS profile should be very important and such investigations can be also very important from the viewpoint for controlling the nano-structure to develope new smart materials. The detail investigations are in preparation.

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