

Metal-Ion-Absorption of Environmentally Serviceable NIPA/SA gel – Nano-Structural Study on the Dehydrated Substances –

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By means of small-angle X-ray scattering (SAXS), it has been investigated how metal-ion absorption influences a nanoscopic structure of *N*-isopropylacrylamide/sodium acrylate (NIPA/SA) gel which is known to capture some toxic metal ions and environmentally serviceable. From the SAXS profile variations of the gel dehydrated after the metal ion absorption, some systematic changes in nano-structure dependent both on the radius and valence of the absorbed ion have been revealed, indicating an interaction change in a nanoscopic scale between the constituents through the intermediary of the metal ions.

Key words: SAXS, metal ion, NIPA/SA, gel

I INTRODUCTION

Materials with some structures characterized by nanometer-scale dimensions have attracted a great deal of attention in both the fields of basic science and application technology. In order to realize the nanostructure so far, several methods are adopted according to the dimension of target systems: the lithographic techniques utilized in a scale above ~50nm, self-organization methods in a range from 50nm to few nm's, the molecular manipulation with SPM's in a single-nm range, and so on. Among them, the self-organization methods are thought to be most probable for the mass production technique of the nano-scope scale devices in the future, because it does not require complicated processes to realize the nanostructures.

Even among the self-organizing methods, there may be still many ways in practical manufacturing processes, in one of which the authors have been interested: the self-organizing system realized by compatibility changes of several kinds of constituent polymers; if the system contains fluids, the compatibilities with solvents should be also taken into consideration. Such a system undergoes phase separation with decreasing the compatibilities among the constituents and shows a domain structure of which the morphology is determined by a thermodynamic balance of the entropy of mixing, the surface energy [1]; if there are polyelectrolytes and ions in the system, the electrostatic potential can influence the equilibrium balance. For example, the microphase separation is well-known to occur when the solute is composed of weakly charged polymers, of which the electrified parts are hydrophilic and the electrically neutral parts, hydrophobic; however the mechanism of the microphase separation in this system is a little bit more complicated by the electrostatic interaction effects.

In these circumstances, the author have been inter-

ested in the properties of the heteropolymer gel of which the network polymers are composed of charged (hydrophilic) and hydrophobic parts, with focus on their ion-capture property and their nanoscopic structural change by absorbing the ions through the investigation of the dehydrated substance. In the following sections, the background of our study will be described.

The gels are composed of solvent and network polymers, of which the properties are considerably influenced by their interaction. With elevating the temperature from room temperature, a pure *N*-isopropylacrylamide (NIPA) hydrogel exhibits small and continuous volume reduction at 36°C with a property change in the NIPA-group from hydrophilic to hydrophobic. If the polymer network also has ionized groups inside, the volume change behaviors are considerably affected by an effect of Donan potential [2]: an *N*-isopropylacrylamide/acrylic acid (NIPA/AAC) hydrogel can be a suitable example of such a case because AAC-group can be easily ionized; in fact, the NIPA/AAC gel shows a considerable discrete volume change with a resistance force against shrinking at a higher transition temperature compared with that of the pure NIPA gel [3,4].

This phenomenon is well-known as a volume phase transition [2,5]. As for the structural change in the nano-scale, just below the volume phase transition temperature of a NIPA/AAC gel, emergence of a prominent side peak was observed in small-angle neutron scattering (SANS) experiments [6,7], which indicates an occurrence of the microphase transition induced by interactions between hydrophilic (ionized) AAC-groups and hydrophobic NIPA-groups in the gel.

As for the property changes of the gels composed of constituents with opposite affinities to the solvent as in the case of the NIPA/AAC gel, their dehydration processes can be still interesting as well as the volume phase

transition, because it shrinks by dehydration equally or more than that by the volume phase transition. Besides, by dehydration, several drastic property changes have been also observed which indicate that the dehydrated gel becomes a glass-like substance [8], which has been also confirmed by visco-elastic measurements [9,10], Raman scattering [11] and inelastic neutron scattering experiments [12]. Recently, a distinct nano-structure has been revealed in a dehydrated N-isopropylacrylamide/sodium acrylate (NIPA/SA) gel, a congeneric substance of the NIPA/AAc gel, by a small-angle X-ray scattering (SAXS) study, which demonstrates the occurrence of the micro-phase separation by dehydration (Fig.1) [13].

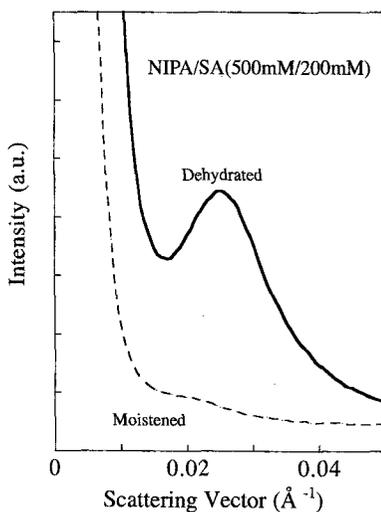


Fig.1 The SAXS profile of a dehydrated NIPA/SA (500mM/200mM) gel and that with absorbing a small amount of water [13].

Moreover, by observations of [SA] dependence of SAXS profile and (heavy-)water-content (w) dependence of SANS profile, some characteristic properties has been revealed on the dehydration-induced micro-phase-separated structure (DIMSS) in the dehydrated NIPA/SA gel: a distinct DIMSS characterized by a clear SAXS or SANS side peak can be realized only in a restricted region of [SA] and w [14], indicating that the DIMSS is formed by a delicate balance of related interactions such as electrostatic forces and hydrophobic interactions among the constituents, surface tension at their interface and so on [15,16]. Conversely, it can be interpreted that there is a sufficient possibility to actualize a nano-scopic structure controlled by macroscopic conditions utilizing DIMSS, which can be an energy-and-material-saving way to manufacture nano-structural devices because essentially the dehydration process requires no special processes and instruments.

Let us discuss on other properties of the heteropolymer gel with the ionized and hydrophobic groups. It is well-known that a polymer network with ionized-groups can capture ions with a counter electric charge to that of the polymer network, and/or by a cooperation of several singly-charged group, chelation of multivalent ions tends to occur. Such mechanisms can be

utilized to detect and/or capture toxic multivalent ions in waste solutions and serviceable to the environmental purification. In fact, Jacson *et al.* invented an ion sensor made of an interpenetrating poly(vinyl alcohol) and NIPA/AAc gel sensitive to metal ions, which can be used to detect the presence and identity of metal ions in a solution [17]. The features indicate that the ion-capture property is valuable and available for the environmental technology. However, except for the authors' ones, there have been almost no investigations from a nano-structural point of view, which should be very important because many of such systems should be stabilized with a balance of the interactions in a nano-scopic scale as in the case of an above-mentioned microphase separated structure in the ionized heteropolymer gels. In these situations, the authors have investigated the nano-structure of the dehydrated NIPA/SA gel by an advantage in a detecting sensitivity of the conflicting interaction compared with that of the moistened ones.

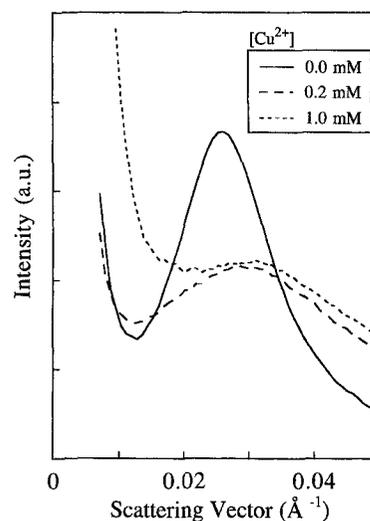


Fig.2 The SAXS profiles of a simply dehydrated NIPA/SA (500mM/200mM) gel and of those dehydrated after absorbing Cu^{2+} ion [18]. Numerals in a square at the upper-right corner are Cu^{2+} concentrations of aqueous solutions in which NIPA/SA gel lumps were immersed before dehydration.

In the previous study, a shift of the above-mentioned SAXS side peak has been observed in a gel dehydrated after absorbing Cu^{2+} ion (Fig.2) [18]. This feature demonstrates a change in nanoscopic-interactions by addition of the copper ions. Besides, by SAXS observations with utilizing an anomalous-dispersion technique, the copper ions are revealed to gather in the sites formed by the dehydration-induced microphase separation which indicates a close correlation between the ion-capture property and the nanostructure in the dehydrated NIPA/SA gel [19]. With these backgrounds on the ion-capture property and the nanostructure in the dehydrated NIPA/SA gel, it should be necessary to carry out more systematic nano-structural investigations on the ion absorption effects with more kinds of ions. Therefore, in the present

study, the authors carried out a systematic examination of the SAXS-profile variation of the dehydrated NIPA/SA gel by adopting several kinds of additive ions.

II EXPERIMENTALS

An aqueous solution of NIPA (400mM), SA (300mM), *N,N'*-methylenebisacrylamide (8.6mM) and *N,N,N',N'*-tetramethylethylenediamine (240 μ L for 100 mL solution) was fully saturated with nitrogen. Then small amount of ammonium persulfate (40 mg for 100 mL solution) was added into the solution in order to initiate gelation, which was carried out at 0°C for 24 hours. After completion of the gelation and subsequent rinse-out of unreacted ingredients, several lumps of wet NIPA/SA gel were cut out; for 12hr's, each gel block was immersed in a 0.2mM aqueous solution of LiCl, NaCl, KCl, RbCl, CsCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂, AlCl₃, FeCl₃, CoCl₃, NiCl₂ and CuSO₄. After the immersion, the gel blocks were dried gently for 6 days in the atmosphere. By dehydration, the wet and soft gel turned into hard and transparent substances, which were used in the SAXS experiments as specimens.

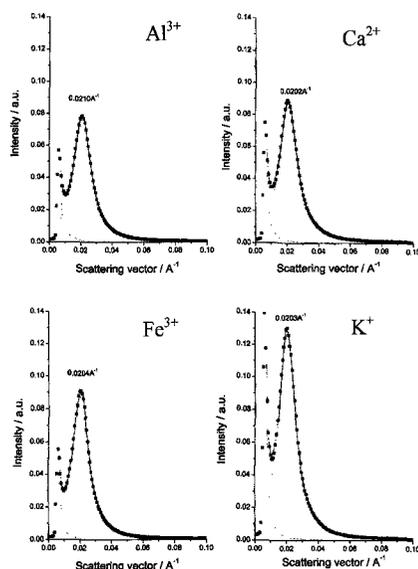


Fig.3 The SAXS profiles of several dehydrated NIPA/SA (400mM/300mM) gels which adsorbed metal ions indicated in the upper right corners of the respective graphs before dehydration.

The SAXS experiments were carried out at room temperature with a SAXS apparatus (SAXES) installed at BL10C of Photon Factory in Institute of Materials Structure Science (IMSS), 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 of SAXES and

the intensity distribution of the scattered X-ray was sensed with a scattering vector ranged from 6.0×10^{-3} to $2.0 \times 10^{-1} \text{Å}^{-1}$. 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. By these correction and normalization, the value of final data straightforwardly corresponds to the scattering efficiency.

III RESULTS AND DISCUSSION

Figure 3 shows a part of SAXS profiles of NIPA/SA gels dehydrated after absorbing respective additive ions. As can be seen from the figures, a clear and intense side peak was observed in the respective SAXS profiles, regardless of ionic charge numbers of the additive cations. This feature demonstrates that a fundamental nano-scale structure which exists in the dehydrated NIPA/SA gel does not receive destruction by the ion-addition.

Table I shows atomic numbers (*Z*) and normalized ones (described as [*Z*]) by the value of carbon which is the most abundant element in the specimens except for hydrogen to which the X-ray is almost insensitive. Because the amplitude of the coherently scattered X-ray is proportional to the spatial-fluctuation magnitude of electron density, one can easily understand that most of the coherently scattered X-ray intensity comes from the hydrophilic site where the relatively additive high-*Z* ions are thought to disperse in the lower-*Z* matrix of the DIMSS as confirmed in the previous anomalous-dispersion study of copper-ion added dehydrated NIPA/SA gel [19].

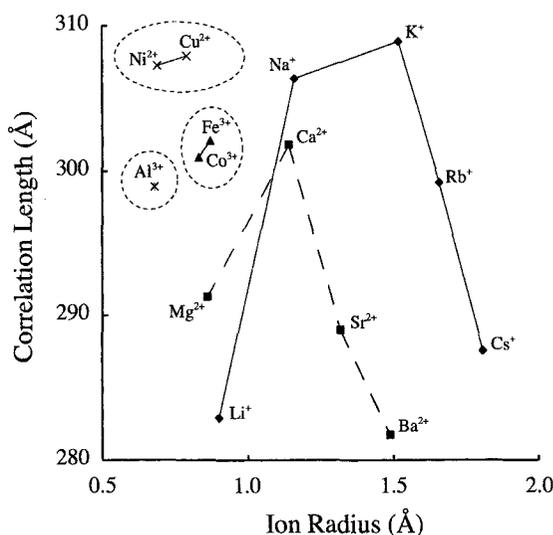


Fig.4 Variation of correlation length derived from SAXS profiles of NIPA/SA (400mM/300mM) gels which are dehydrated after absorbing metal ions.

Table I Atomic Numbers (*Z*) and [*Z*]=(*Z*/*Z*_C) of the Elements in the Specimens of the Present Study

	Hydrophilic Site														Hydrophobic Site					
	Li	Na	K	Rb	Cs	Mg	Ca	Sr	Ba	Al	Fe	Co	Ni	Cu	SO ₄	Cl	C	H	O	N
<i>Z</i>	3	11	19	37	55	12	20	38	56	14	26	27	28	29	48	17	6	1	8	7
[<i>Z</i>]	0.5	1.8	3.2	6.2	9.2	2.0	3.3	6.3	9.3	2.3	4.3	4.5	4.7	4.8	8.0	2.8	1.0	0.2	1.3	1.2

Figure 4 shows ion-radius dependences of the correlation length (ξ) derived from the side peak positions in the SAXS profiles: the authors adopted data of the ion radius in the 6-coordination structure reported by Shannon [20]. With a close examination, 5 sets of systematic variation of ξ can be perceived according to the groups in the periodic table:

- Alkali Metal Ion Group

Relatively a large variation in ξ is observed. With increasing ion-radius, ξ increases and shows a maximum between the sodium and potassium ions; then ξ decreases up to the cesium ion.

- Alkaline-Earth Metal ion Group

Similar to the alkali metal ion group, relatively a large variation in ξ is observed. Beside, ξ also shows a similar ion-radius dependence to that of the alkali metal ion group. Especially from calcium to barium ion, gradients ($\Delta\xi/\Delta$ ion-radius) to the corresponding alkali metal ions which are located in the same series in a periodic table reveal to be almost identical.

- Transition Metal Ion Groups $\{\text{Cu}^{2+}, \text{Ni}^{2+}\}, \{\text{Co}^{3+}, \text{Fe}^{3+}\}$

ξ 's with additive ions of the same ionic charge numbers do not change so much in the ion radius, which may reflect the resemblance of the chemical property. However, the groups with different ionic charge numbers ($\{\text{Cu}^{2+}, \text{Ni}^{2+}\}$ versus $\{\text{Co}^{3+}, \text{Fe}^{3+}\}$) show a noticeable distance in the figure.

- Aluminum Ion

ξ of Al^{3+} lies in the neighborhood of $\{\text{Co}^{3+}, \text{Fe}^{3+}\}$, which indicates that the ionic charge number may have important role to determine the correlation length of the DIMSS.

In addition to these qualitative characteristics, it should be mentioned that almost of ξ 's are smaller than that of sodium, which may come from the fact that the pure NIPA/SA gel originally contains sodium ion.

In summary, in the present study, the authors have found systematic variations of the nano-scopic correlation length in the NIPA/SA gel dehydrated after absorbing additive ions, of which the fashion seems to considerably depend on ionic charge number and ion radius. Though the detailed mechanism of this systematic variation of ξ is not clear so far, the authors convince that it can be quite important and interesting to investigate the ξ -variation more intensively for clarifying the stabilization mechanism of the DIMSS with absorbed ions, which is in progress now.

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