Adsorption of water to double-network polymers having a hierarchical structure

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Abstract. Double-network hydrogels (DN-gels) have cross-linked aqueous polymer networks which result in unique mechanical properties [1,2]. Although the structure of the hydrophilic polymer networks have been previously determined [3,4,5], it was not clear how water molecules are adsorbed to the polymer network. We prepared freeze-dried DN-gels (DN-polymers) made of polyacrylamide and sodium salt of poly(2-acrylamido-2-methylpropane sulfonic acid), and small-angle neutron scattering (SANS) experiments were conducted to determine the humidity dependence of the nanoscale structure. The SANS results show that water molecules adsorb on larger structures than the mesh size of polymer networks at low relative humidity (RH), and adsorb gradually on the segmental scale of polymers with increasing RH.

1. Introduction

Soft matter has a hierarchical structure on the scale of angstroms up to nanoscale and macroscale. Additionally it is known that the physical properties of soft matters are greatly influenced by water. Synthetic hydrogels are good materials to study the effect of water adsorption because they contain an abundance of water. In fact, most hydrogels, which have a three-dimensional polymer network, can adsorb more than 90 wt% of water. Nevertheless, most hydrogels are composed of 90 wt% water, which means only 10 wt% of the polymer network governs its mechanical properties. Although there are a number of studies on water in hydrogels, there is little experimental study on the water near the polymer network.

Double-network hydrogels (DN-gels) [1,2] are water-soluble synthetic polymer gels that have high mechanical strength equivalent to cartilage. Several studies on polymer networks of DN-gels have been conducted using small-angle neutron scattering (SANS) [3,4,5] so far. However, it was not determined how water molecules are adsorbed to the polymer network.

In this study, we performed SANS measurements to investigate the humidity dependence of the nanoscale structure of the freeze-dried DN-gels (DN-polymers) to clarify the mutual relationship between a polymer network and water.
2. Experiments

2.1. Materials
The water-swollen DN-gels [1,2] were prepared with 2-acrylamido-2-methylpropanesulfonic acid (Toagosei Co., Ltd, Japan) and were neutralized by NaOH. 2-Acrylamide-2-methylpropanesulfonic acid sodium salt was used as the monomer for first network, purified acrylamide was used as the monomer for the second network and purified N,N’-methylenebisacrylamide was used as the crosslinker for the first network with 2-oxoglutaric acid as the UV initiator (Wako Pure Chemical Industries, Ltd., Japan). The DN-gels were then freeze-dried by EYELA FDU-2100 (Tokyo Rikakikai Co., Ltd., Japan), which creates the DN-polymers [6]. The DN-polymer samples were placed in a dry state with a glove box evacuated by a turbo-pump (VPT-030, ULVAC Kiko, Inc., Japan) to remove light water. After the drying process, heavy water (435767-100G, Aldrich Chemical Company) vapours were introduced into the system for more than an hour to generate a certain relative humidity (RH). The humidity conditions were as follows: 0% (dry state), 23%, 40%, 68% and 79%. Measurements of all humidity conditions were prepared by the same sample, and we confirmed the reproducibility of SANS results shown below.

2.2. Small-Angle Neutron Scattering (SANS) measurements
The SANS measurements were performed with a small- and wide-angle neutron scattering instrument, TAIKAN (BL15), which is in the Materials and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC). The pinhole collimator set before the sample was 10 mm in diameter. All SANS measurements were performed at 25 °C. The wavelengths of the incident neutrons ranged from 0.07 nm to 0.76 nm, and the time of flight-method was used.

2.3. Pore size determination
The specific pore size distribution of the DN-polymers was determined with the BELSORP-mini II (BEL Japan, Inc.). Nitrogen gas adsorption–desorption isotherm analysis was performed at 77.4 K.

3. Results and Discussion
The SANS profiles of the DN-polymers under various RH conditions are shown in Fig. 1. The intensity below \(q = 0.2 \text{ nm}^{-1}\) increases with increasing RH. The power law behaviour is observed in this \(q\)-range with an exponent of approximately \(-3.1\) for all RH conditions. The samples studied here are dried, porous materials synthesized via radical polymerization and intrinsically have a random structure. Therefore, it is reasonable to assume that the SANS intensities originate from the nanoscale interfaces of polymer networks.

The pore size distribution is determined by the nitrogen gas adsorption–desorption measurements. Fig. 2 shows the BJH-plot of the DN-polymers, where \(d_p\) is the pore diameter in nanometers, and \(V_p\) is the pore volume in \(\text{cm}^3\text{g}^{-1}\). From this plot, it is known that the number of pores larger than 30 nm in diameter is more than the number of nanoscale pores. This spatial scale corresponds to the \(q\)-range lower than \(q = 0.2 \text{ nm}^{-1}\). Thus, we could say that the origin of the SANS intensities in the region following the power-law behaviour are due to the density fluctuation of the pores.

To clarify the effect of water adsorption on the SANS profiles, the profiles measured between 23% RH and 79% RH were divided by the profile measured at 0% RH as shown in Fig. 3. The scaled intensity increases with increasing RH below \(q = 0.8 \text{ nm}^{-1}\). When the RH is less than 68%, the scaled intensity does not change above \(q = 0.8 \text{ nm}^{-1}\), but when it is more than 68%, the scaled intensity decreases with increasing RH. This threshold, \(q = 0.8 \text{ nm}^{-1}\), corresponds to the correlation length of the DN-polymers, which is approximately 8 nm [5].
Figure 1. SANS profiles obtained from the DN-polymers under different humidity conditions. The relative humidity is 0% (dry state, closed circle), 23% (open circle), 40% (triangle), 68% (square) and 79% (diamond).

The adsorption behaviour of water molecules in the polymer network of the DN-polymers could be interpreted as follows: There is no change in the polymer network structure larger than \( d = \frac{2\pi}{q} = 20 \) nm, which is comparable to the pore size below 79% RH. Below 79% RH, water molecules adsorb onto a larger polymer structure than a mesh size scale, which is greater than 8 nm, in the dry state of
When the RH is 68%–79%, water molecules adsorb not only on the large polymer structure but also on internal structures such as polymer segments that are smaller than the mesh size. A detailed structure analysis of the SANS results is beyond the scope of this proceedings and will be presented in a forthcoming article with SAXS data.

![Figure 3. The relative SANS profile divided by the SANS profile measured at 0% RH. The relative humidity is 23% (open circle), 40% (triangle), 68% (square) and 79% (diamond).](image)

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