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Research paper

Change in hydrogen bonding structures of a hydrogel with dehydration

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ABSTRACT

To investigate the mechanisms of structural changes in polymer network and water during dehydration, X-ray diffraction of poly-*N*,*N*-dimethylacrylamide (PDMAA) hydrogels was measured. The variation process in the individual structures of water and PDMAA were analyzed by decomposition of the diffraction patterns to separate the respective contributions. The results show that the short-range structures of PDMAA expand during dehydration, whereas the network structure as a whole shrinks. The average length of the hydrogen bonds between water molecules increases with the process. The present results provide a direct evidence of the structural changes of water and polymer in the hydrogel during dehydration.

1. Introduction

Hydrogels are unique materials consisting of large amounts of water within three-dimensional polymer networks. Because of their characteristic properties, hydrogels have been widely used as biomaterials, medicinal products, civil engineering products, and so on [1–3]. Furthermore, hydrogels are expected as functional materials such as drug delivery systems and scaffolding of cellular cultures [4,5]. The structures of the polymer network and the included water are important factors governing the chemical and physical properties of hydrogel materials.

The water in hydrogels has been classified into three types: bound, intermediate, and free water [6]. Bound water forms hydrogen bonds with the hydrophilic groups in the polymer or interacts strongly with the polymer chains. Free water has a structure similar to that of bulk water and is ‘free’ from interactions with the surrounding polymer chains. Intermediate water exists between the bound and free water, and interacts weakly with the polymer. As a result of the differences in the structures of these three types of water, the properties of hydrogels are affected by the relative amounts of the three types of water. Because the relative amounts of the three types of water depend on water content [7], it is essential to understand the structural changes that the hydrogel undergoes during dehydration.

The dehydration processes of hydrogels have been studied using various methods. Koshoubu et al. [8] analyzed mechanical properties of white gel in heat-treated eggs, and showed that the dehydration process of hydrogel can be classified into three stages based on the differences in dehydration rates in the three types of water [9]. Sekine and Ikeda-Fukazawa [10] measured Raman spectra of poly-*N*,*N*-dimethylacrylamide (PDMAA) hydrogels and analyzed the structural changes in water and the polymer networks during dehydration. From these results, the following stages were proposed for the dehydration process of PDMAA hydrogels. In the beginning of the dehydration process (stage-I), free water mainly evaporates and the polymer network shrinks with the evaporation. Intermediate water begins to evaporate during the middle stage (stage-II). Due to a rapid reduction of water during stage-II, the polymer network collapses and undergoes a glass transition at the end of this stage. In stage-III, the remaining bound water evaporates slowly from the glassy dried gel. Using differential scanning calorimetry (DSC), Ikeda-Fukazawa et al. [11] showed that the boundaries between stages I–II and II–III for PDMAA hydrogel are 65 and 40 wt%, respectively. Although these studies indicated the macroscopic dehydration process of hydrogel, the microscopic process of structural changes of water and polymer network is less conclusive.

In order to investigate the mechanism of microscopic structural changes of water and polymer network in a hydrogel during dehydration, we measured and analyzed X-ray diffraction (XRD) of a PDMAA hydrogel. XRD is a useful tool for the analyses of short-range structure in liquid and amorphous materials, which have no long-range order structures [12–14]. Several studies of hydrogels using XRD have been previously reported. Ricciardi et al. [15] measured XRD of poly (vinyl alcohol) (PVA) hydrogels obtained using the freezing–thawing method. They showed that both the degree of crystallinity and the size of crystals in PVA hydrogels increase with an increasing number of the freezing–thawing cycles. Using XRD and small-angle neutron diffraction

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methods, Bosio et al. [16] analyzed the pore size of poly (2-hydroxyethylmethacrylate) hydrogel. The results showed that the water in the pores or micro-channels of the hydrogel exists in the unfreezable state due to interaction with three-dimensional polymer networks. These studies suggest that XRD is an efficient technique for the investigation of hydrogel structures.

2. Experimental

Poly-*N*,*N*-dimethylacrylamide (PDMAA) hydrogels were synthesized using the following procedure. *N*,*N*′-dimethylacrylamide (DMAA), *N*,*N*-methylenebis(acrylamide) (BIS), potassium persulfate (KPS), and *N*,*N*,*N*′,*N*′-tetramethylenediamine (TEMED) were used as the monomer, cross-linker, initiator, and catalyst, respectively. Distilled water was purged with N_2 gas for 3 h prior to the sample preparation in order to remove the dissolved O_2. An aqueous solution consisting of water (57 mL), BIS (0.276 g), and DMAA (5.94 g) was prepared. TEMED (48 μL) was then added to the solution. Finally, an aqueous solution of KPS (0.03 g) in water (3.0 mL) was added. The solution (8.0 mL) was dripped onto a silicon wafer with a diameter of 50 mm and a thickness of 1 mm. A radical polymerization was then preceded for 20 h at room temperature. The formed hydrogels, with a thickness of 3 mm, were soaked in pure water for 72 h in order to remove unreacted compounds. Fig. 1 shows the chemical structure of PDMAA.

For hydrogel dehydration, the samples were stored in a desiccator at 298 ± 3 K and at a humidity of 50 ± 10% for 240 h. During the dehydration process, XRD of each sample was measured. The water content (W) of the dehydrated sample was determined by

$$W = [(M_{\mathrm{gel}} - M_{\mathrm{fd}})/M_{\mathrm{gel}}] \times 100, \tag{1}$$

where M_{gel} and M_{fd} are the mass of the sample and the fully dehydrated sample, respectively. The W values of the examined 29 samples were in range of 90.0–7.76 wt%.

Diffraction patterns of the prepared hydrogels were measured using an X-ray diffractometer (Rigaku RINT-Ultima III). Using Cu Kα radiation of 1.5418 Å in wavelength, the diffraction patterns were measured in 2θ range of 3–70 deg. The scan speed and step were 1.0 deg min^{-1} and 0.01 deg, respectively. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 2 shows the XRD patterns of PDMAA hydrogels with W = 90.0, 53.0, and 7.76 wt%. The diffraction patterns have broad liquid-like features, and the band feature changes with water content. Three broad peaks are observed in the patterns for the hydrogels with water content of 53.0 and 7.76 wt% in the examined angle region. In the case of the hydrogel with W = 90.0 wt%, two well-defined peaks and the foot for the lowest-angle peak were observed. As shown in Fig. 2, the three broad peaks shift with water content.

To analyze the dependence of the observed peak positions on water content, the XRD profiles were decomposed into three peaks using Gaussian functions. The dotted lines in Fig. 2 show the fitted curves. For instance, the angles of the three fitted peaks for the hydrogel with W = 7.76 wt% are 11.10, 20.59, and 36.69 deg. Using the Cu Kα wavelength of 1.5418 Å, these 2θ values are converted into *d*-spacing values of 7.71, 4.31, and 2.45 Å respectively. Hereafter, these three peaks are referred to as p_1, p_2, and p_3, respectively.

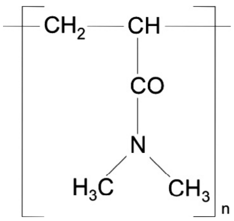

Fig. 1. Chemical structure of PDMAA.

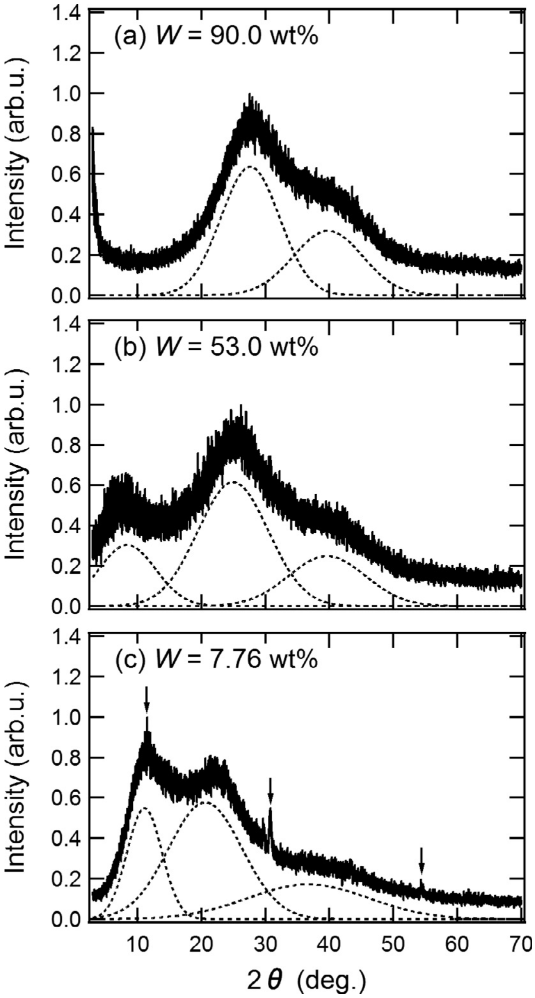

Fig. 2. X-ray diffraction patterns of PDMAA hydrogels with water content W = (a) 90.0 wt%, (b) 53.0 wt%, and (c) 7.76 wt% at 298 K. The solid and dotted lines show the intensities observed experimentally and fitted curves determined using Gaussian functions, respectively.

Fig. 3 shows the dependence of the peak positions on the water content for p_1, p_2, and p_3. The *d*-spacing of p_1 decreases with dehydration, whereas those of p_2 and p_3 increase. These shifts can be attributed to the structural changes in the polymer networks and water within the hydrogel during dehydration. These results imply that short-range structures expand due to dehydration, while a long-range structures shrink. The p_1 peak corresponds to a long-range structure between polymer chains, because the *d*-spacing of the peak is larger than 20 Å in swollen states.

In addition to the three broad peaks observed at 11.10, 20.59, and 36.69 deg (i.e., p_1, p_2, and p_3), the diffraction pattern of hydrogel with W = 7.76 wt% has three sharp peaks at 11.47, 30.72, and 54.34 deg. The arrows in Fig. 2(c) show the positions of the three sharp peaks. The peak at 30.72 deg. is assigned to the silicon wafer substrate. Because the thickness of the sample decreases as the dehydration progresses, the silicon peak was detected for the dried samples. The appearance of two peaks observed at 11.47 and