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Gel–sol transition of poly(vinyl alcohol) hydrogels formed by freezing and thawing

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Abstract

Poly(vinyl alcohol) (PVA) hydrogels were prepared by freezing and thawing. Freezing and thawing cycle (*n*) was varied from 1 to 5. Gel–sol transition of the above hydrogels was measured using a highly sensitive differential scanning calorimeter (DSC). Phase transition of hydrogels was also investigated by simultaneous X-ray diffractometry (XRD) and DSC. Gel–sol transition temperature was observed in a temperature range from 55 to ca. 90 °C. Enthalpy of gel–sol transition was varied in a range from ca. 0.4 to $2\,\mathrm{J\,g^{-1}}$. Peak temperature and enthalpy of gel–sol transition increased with increasing *n*. By simultaneous measurement of X-ray diffractometry (XRD) and DSC, it is confirmed that no structural change is observed for either ice or water before and after gel formation. It is concluded that PVA molecules are aggregated during ice formation and hydrogen bonding is established between molecular chains. By increase of freezing and thawing cycle, residual free molecular chains are successively included in junction zones.

Keywords: PVA hydrogels; Freezing and thawing; DSC; Gel–sol transition; XRD–DSC

1. Introduction

Aqueous poly(vinyl alcohol) (PVA) solution forms hydrogels by γ-ray or electron-beam irradiation [1,2], freezing and thawing [2–9] or mixing with dye, such as Congo Red [11,12]. Hydrogels prepared by γ-ray irradiation are categorized as chemical gels, and those prepared by freezing and thawing or mixing with dye as physical gels. In our previous study on PVA hydrogels formed by freezing and thawing, it was found that intermolecular hydrogen bonding formed adjacent molecular chains which act as crosslinking points [4]. When the above physical gels are heated at a temperature higher than ca. 70 °C, clear sols are obtained. However, distinct gel–sol transition has not previously been observed by thermal analysis, since using ordinarily differential scanning calorimeter (DSC) transition enthalpy caused by dissociation of hydrogen bonding cannot be detected when the number of hydrogen bonding is small [4]. Other types of calorimeter, such as Privalov type calorimeter [13] cannot measure hydrogels since the structure of sample holder is only applicable to solutions.

PVA have been used in various fields [10], such as adhesives, glues and surface coating agents in textile and paper industries. Recently PVA hydrogels are considered as intelligent materials, and have been applied to specific fields, such as controlling agents for water release in order to improve soil, seeding beds for easy handling of young plants in agriculture, and artificial organs. On this account, gel formation and gel–sol transition behaviour of PVA hydrogels have received considerable attention.

In this study, gel–sol transition of PVA hydrogels prepared by freezing and thawing is measured using a highly sensitive

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differential scanning calorimeter. Phase transition of water restrained by gel network is investigated by simultaneous measurement of wide angle X-ray diffractometry and DSC (XRD–DSC) [14,15].

2. Experimental

2.1. Sample preparation

PVA was obtained from Polyscience Inc., USA. Molecular weight was 1.08×10^5 and degree of hydration 99.7 mol%. PVA aqueous solution was prepared as follows: (1) 10 ml of 5 and 10 wt.% of aqueous solutions were prepared in a stainless autoclave, which was maintained at 120 °C for 2 h. PVA sol thus obtained was divided into five portions and put in a glass vessel with a polyethylene inner lid and a plastic outer lid. (2) Vessels were directly transferred to a freezer whose temperature was −15 °C and maintained for 24 h. (3) Frozen samples were defrozen at 25 °C. This process took more than 3 h. (4) The above freezing and thawing was repeated from one to five times. In this study, the number of freezing and thawing cycles is stated as "*n*". After freezing and thawing, the samples were stored at 8 °C.

2.2. Scanning electron microscopy (SEM)

A JEOL JSM 35CF scanning electron microscope was used. Samples for scanning electron microscopy were prepared as follows; samples in glass ware were embedded in dry ice powder and freeze dried for 2 days. Fracture surface was coated by Au–palladium in vacuo using a JEOL JFC-1600 spattering apparatus.

2.3. Differential scanning calorimetry

A Seiko Instruments differential scanning calorimeter DSC 120 was used Ag pan (70 μl in volume) was used. Sample mass was ca. 50 mg, heating rate was 1 °C min^{-1}. Temperature ranges from 0 to 100 °C.

2.4. Simultaneous measurement of X-ray diffractometry–differential scanning calorimetry (XRD–DSC)

A Rigaku X-ray–DSC simultaneous instrument, analyzer RINT ULTIMAII/PC linked with XRD-DSCII, was used. Details of the above apparatus are found elsewhere [14,15]. X-ray scanning range (2θ) was from 2° to 42°, scanning speed was 20° min^{-1}. DSC heating rate was 2 °C min^{-1} and cooling rate 5 °C min^{-1}. Temperature range was from −50 to 100 °C in an ordinary atmosphere. PVA hydrogels with 10% concentration and $n = 1$ and 5 were measured in an open type sample holder.

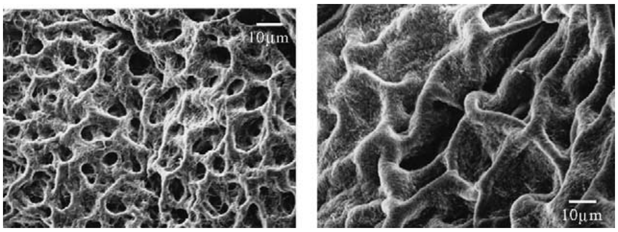

Fig. 1. Scanning electron micrographs of PVA hydrogels. Left: $n = 2$; right, $n = 5$, concentration of sol = 5%, scale bar shows 10 μm.

3. Results

PVA hydrogels formed by freezing and thawing are strong and flexible. Due to difficulties in sample preparation, the sample was frequently drawn and oriented thread like patterns were observed. Scanning electron micrographs shown in Fig. 1 are representative among various kinds of fracture surfaces. As shown in the photos, pores are observed. With increasing *n*, pore walls become thicker and the size of the pore increases. It is clear that morphology of gels varies by repeating of freezing and thawing. It is preferable if photos of the sample in sol state are used for the comparison. However, as described in the experimental section, each sample was necessarily freeze dried and the gel formation is thought to occur during this process.

Fig. 2 shows stacked DSC heating curves of PVA hydrogels (concentration of sol = 10%) measured at 1 °C min^{-1}. As clearly seen the peak temperature of gel–sol transition shifts to the low temperature side and peak size increases with increasing *n*. Several sharp peaks observed at around 70–80 °C are attributable to part of the gel in Ag vessel that moves and was detected as an artifact peak. Due to the above peaks, it was difficult to define the exact temperature of peak end.

As already reported in our previous study [4], PVA hydrogels show syneresis when sol concentration is lower than 5%. On this account, it is difficult to prepare gels with concentrations lower than 5%. When the concentration of sol decreased, gel–sol transition is hard to detect. Fig. 3 shows

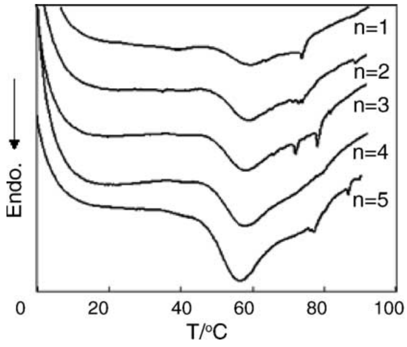

Fig. 2. Stacked DSC heating curves of PVA hydrogels. Numerals in the figure show freezing and thawing cycles. Concentration of sol, 10 wt.%; heating rate = 1 °C min^{-1}.

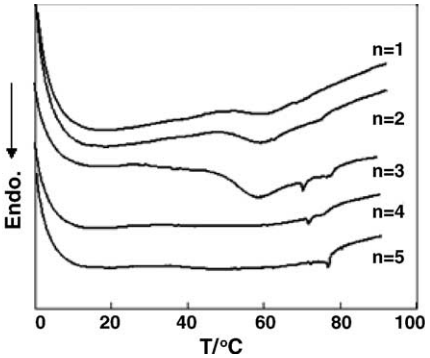

Fig. 3. Stacked DSC heating curves of PVA hydrogels. Numerals in the figure show freezing and thawing cycles. Concentration of sol, 5 wt.%; heating rate = 1 °C min^{-1}.

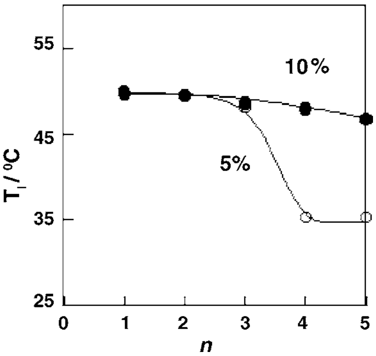

Fig. 4. Relationship between starting temperature of gel–sol transition (T_i) and number of freezing and thawing cycles. Numerals in the figure show concentrations.

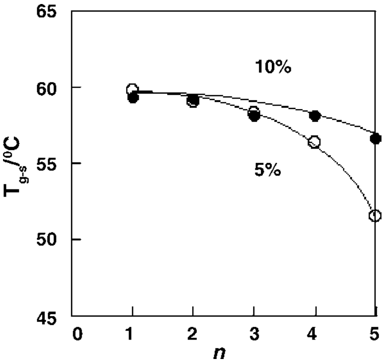

Fig. 5. Relationship between peak temperature of gel–sol transition ($T_{g–s}$) and number of freezing and thawing cycles. Numerals in the figure show concentrations.

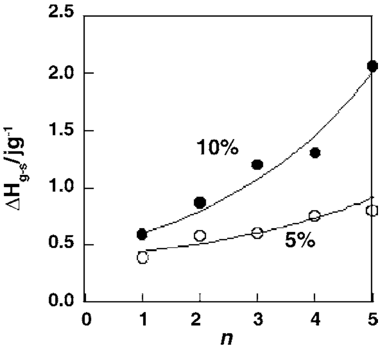

Fig. 6. Relationships between enthalpy of gel–sol transition ($\Delta H_{g–s}$) and number of freezing and thawing cycles. Numerals in the figure show concentrations.

stacked DSC heating curves of PVA hydrogels whose concentration is 5%. Gel–sol transition occurs in a similar temperature range as that of the gel with 10% concentration, however, enthalpy of transition is smaller. When freezing and thawing cycle exceeds 4, transition is observed in a broad temperature range. Even if DSC curves were magnified in the analytical procedure using a computer, exact starting temperature (T_i) becomes difficult to define. On this account, T_i values had ±3 °C error and accordingly values of gel–sol transition enthalpy ($\Delta H_{g–s}$) contain a certain ±0.1 J g^{-1} errors.

Figs. 4 and 5 show relationships between T_i or peak temperature ($T_{g–s}$) of gel–sol transition, and freezing and thawing cycles *n*. These figures indicate that both T_i and $T_{g–s}$ of the sample with 10% concentration gradually decrease, in con-

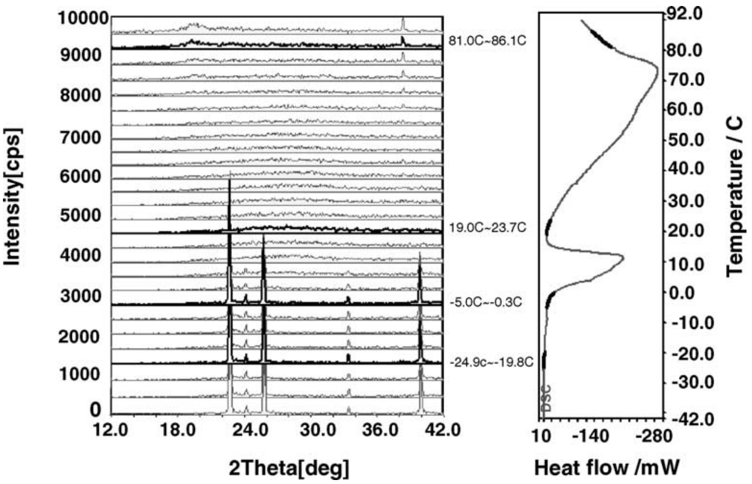

Fig. 7. DSC curve (right column) and X-ray diffraction patterns (left column) of PVA hydrogel with 10% concentration ($n = 5$) recorded in ordinary atmosphere.

trast, temperature decrease of the sample with 5% is markedly observed.

Fig. 6 shows relationship between gel–sol transition enthalpy ($\Delta H_{\text{g–s}}$) and n. $\Delta H_{\text{g–s}}$ increases from ca. 0.5 to 2 J g^{-1} for gels with 10% concentration, on the other hand, $\Delta H_{\text{g–s}}$ was ca. 0.4 to 0.7 J g^{-1} for gel with 5% concentration.

The DSC heating curve and X-ray diffraction patterns of PVA hydrogel with 10% concentration ($n = 5$) recorded during heating at 2 °C min^{-1} is shown in the right column of Fig. 7. The DSC curve indicates a broad endotherm due to melting of ice formed in the hydrogel. A large shoulder peak indicated that freezing bound water is formed in the gel. A large endothermic peak due to vaporization of water is detected. Endotherm due to gel–sol transition is completely masked by vaporization. X-ray patterns corresponding to each point on the DSC curve with the same temperature range are plotted on the left side of the figure. As shown in X-ray pattern, diffractions of ice completely disappear after the melting of free water.

4. Discussion

As shown in schematic illustration (Fig. 8), the molecular motion of PVA segments in the solution (Fig. 8(I)) ceases when water freezes. With decreasing temperature, size of ice increases (Fig. 8(II)) and the hydroxyl groups of PVA molecules participate in hydrogen bonding. Loose crosslinking networks are formed in the first freezing and thawing cycles (Fig. 8(III)). In the network, the polymer chains are restricted to limited regions because of the presence of permanent elastic constraints and the segment exhibits limited thermal fluctuation around fixed average positions [16]. On this account, the number of crosslinking points increases and molecular chains aggregate with increasing freezing and thawing cycles. Changes in the macroscopic structure of hydrogels are also observed in scanning electron micrographs as shown in Fig. 1. The cell walls of PVA hydrogels become thicker with increasing freezing and thawing cycles.

As already described in our previous study [4], PVA sol showed clear solution whose concentration is lower than 10%. Clear gels were not obtained when concentration increased. In contrast, when concentration is lower than 5%, excess water is spontaneously separated at the time of thawing. This indicates that hydrogels whose concentration is lower than 5% do not form readily. Several researchers reported PVA gels whose concentrations are higher than 10% [5,6]. Crystallites are detected in the above high concentration hydrogels by X-ray diffractometry. In the X-ray diffractograms shown in Fig. 7, after melting of water, no crystalline peak was detected. The amount of enthalpy of gel–sol transition ($\Delta H_{\text{g–s}}$) and X-ray results suggest the crosslinking points of hydrogels used in this study are attributable to hydrogen bonding formed between PVA molecular chains.

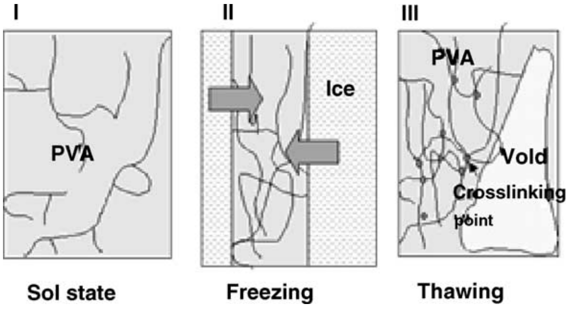

Fig. 8. Schematic illustration of gel formation by freezing and thawing.

As clearly seen in Figs. 2, 3 and 6, $\Delta H_{\text{g–s}}$ of 10% concentration hydrogels linearly increases with increasing number of freezing and thawing cycles. When concentration is 5%, $\Delta H_{\text{g–s}}$ slightly increases. This indicates that the number of inter-molecular hydrogen bonding depends on the potential for attaching two adjacent molecules. The results of Figs. 4 and 5 suggest that the crosslinking zone is firstly formed between molecules in relatively parallel arrangement and then residual molecular chains are included into the crosslinking zone with increasing freezing and thawing cycles.

The state of water restrained by PVA hydrogels has been investigated by various techniques, such as DSC [1,4,6,17] and nuclear magnetic resonance spectrometry (NMR) [1,6,18]. As shown in Fig. 7, in X-ray diffractograms, crystalline peaks of hexagonal ice in PVA hydrogels are observed at a temperature lower than melting. In DSC curves, a broad melting peak with shoulder at the low temperature side is observed. Immediately after melting, a vaporization peak with shoulder peak is observed. When it is considered that transition enthalpy of gel–sol transition is 0.4–2.0 J g^{-1}, whereas in contrast heat of vaporization of water is ca. 1700 J g^{-1}, it is quite reasonable that gel–sol transition is completely masked by the vaporization peak. The low temperature shoulder peak observed in melting suggest the presence of freezing bound water. At the same time, vaporization curves with shoulder peak suggests two different types of water, since bound water vaporized at a temperature higher than free water. Both melting and vaporization curves strongly suggest the presence of a large amount of bound water [4,19,20], although X-ray results show no distinct changes.

5. Conclusions

Poly(vinyl alcohol) (PVA) hydrogels were prepared by freezing and thawing. Gel–sol transition of the above hydrogels was measured using a highly sensitive DSC and XRD–DSC. Gel–sol transition temperature was observed in a temperature range from ca. 55 to 90 °C and enthalpy of gel–sol transition was varied in a range from ca. 0.4 to 2 J g^{-1}. It is concluded that PVA molecules are aggregated during ice formation and hydrogen bonding is formed between molecular chains. By increase of freezing and thawing cycle, residual free molecular chains are successively included in junction zones.

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