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Thermal Behavior of *N*-isopropylacrylamide Gel in Low Water Content

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The transition behavior of *N*-isopropylacrylamide (NIPA) gel in low water contents (w_c=0.01-1.7) was studied by differential scanning calorimetry. The thermograms are complicated depending on the w_c. The glass transition observed ranging from 128°C to –55°C and an endothermic peak around 34°C are noteworthy. The glass transition temperature decreases rapidly by increasing water content up to w_c = 0.6, and then levels off. It disappears around w_c =1.5. This behavior might result from the plasticization effect of water molecules. It is well known that the NIPA gel in very high water content undergoes a continuous volume change around 34.3°C[1]. The endothermic peak appears reversibly around the same temperature region as the volume transition in the heating process. In addition to those phenomena, an endothermic peak by melting of water, and an exothermic peak are observed in the range of w_c =1.0 to 1.46. This exothermic peak temperature decreases as w_c increases, and then it disappears around w_c =1.5. It is thought that this peak is occurred for crystallization of free water.

Key words: NIPA gel, low water content, glass transition, differential scanning calorimetry

1. INTRODUCTION

Since the first report on gel-to-glasslike transition in egg-white gel by dehydration by Takushi *et al.*, extensive investigations on the property changes in the transition have been carried out. [2)-5)] It is one of the characteristic feature during the dehydration process of the gel that the log weight shows a decrease proportional to the dehydration time and the slope alters at a certain time (t'_g).[2)] The linear behavior with a steep slope in the early period of the dehydration process is due to the loss of free water, while that after t'_g with a gentle slope results from the loss of bound water. Besides, with increasing temperature, the dehydrated gel shows the characteristic feature in differential thermal analysis, which is similar to usual glass transition.[6)] In the small angle X-ray scattering (SAXS) measurement, Sugiyama *et al.* found a prominent peak in the SAXS profile probably attributed to the microphase separation during the dehydration of *N*-isopropylacrylamide/sodium acrylate gel.[7)]

In the present study, in order to elucidate the thermal behavior in low water contents around t'_g, we carried out the differential scanning calorimetry (DSC) measurements. The assingnment of the transitions observed were discussed.

2. EXPERIMENTALS

Gels were prepared by a free radical copolymerization. *N*-isopropylacrylamide (NIPA, 700mM), the linear constituent, *N*,*N*'-methylenebisacrylamide (BIS, 8.6mM), the tetra-functional cross-linking constituent, ammonium

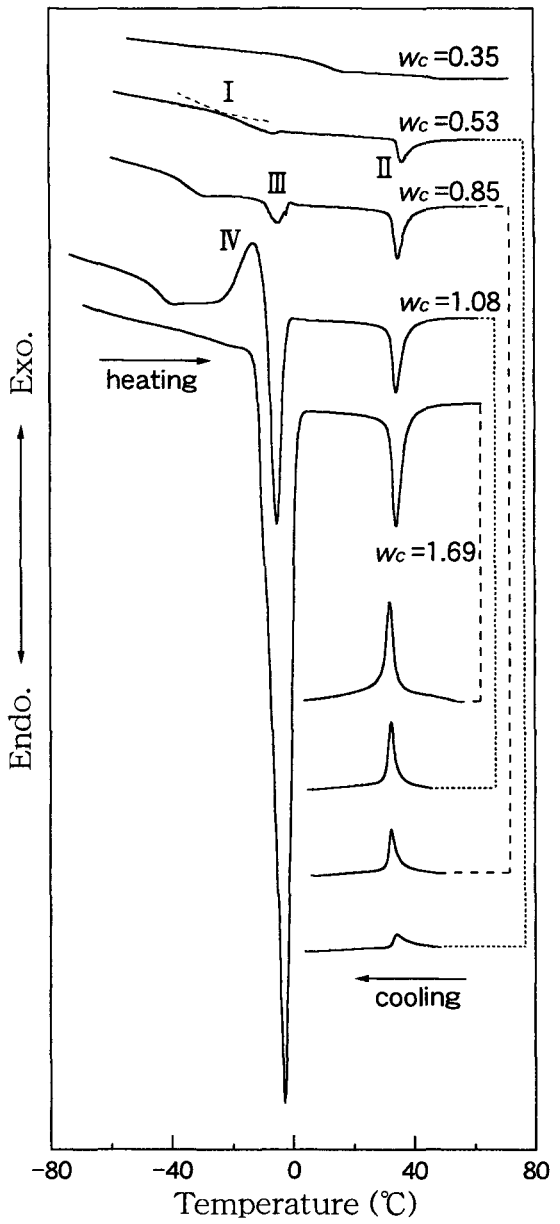


Figure 1. Typical DSC heating and cooling thermograms of dried NIPA gel with various water contents; scanning rate, 3°C/min. Ⅰ, heat capacity gap; Ⅱ, Ⅲ, endothermic peak; Ⅳ, exothermic peak. The intersection of the brokenline represent heat capacity gap temperature.

persulfate, the initiator (10mg), and sodium bisulfite (10mg), the accelerator, were dissolved in deionized, distilled, and nitrogen-saturated water at 20°C to a final volume of 50ml. The solution was then poured into glass tubes. After the gelation was completed, the gel was taken out of the glass tubes, then immersed in water in order to wash away residual chemicals. We obtained dried NIPA gel by dehydrating the gel under atmosphere after cutting in the shape of a disk.

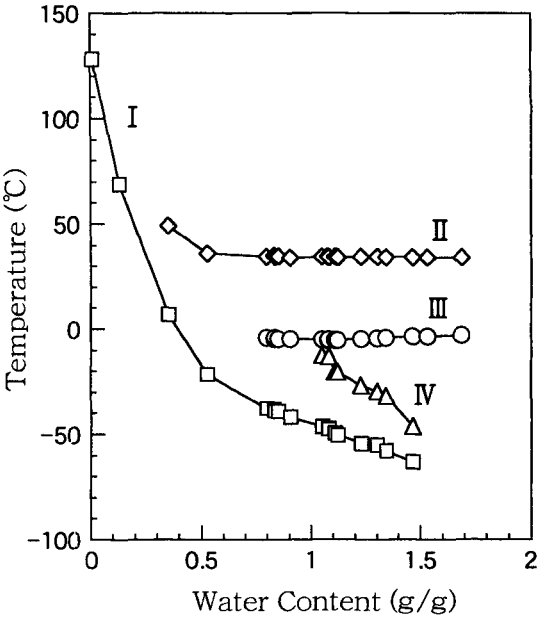


Figure 2. The w_c dependence of the heat capacity gap (Ⅰ) temperature, the endothermic peaks(Ⅱ , Ⅲ) temperatures and exothermic peak(Ⅳ) temperature obtained from the DSC thermograms in the heating process.

The water content of the samples were varied by adding deionized and distilled water to the dehydrated NIPA gels using a micro pipette. In order to homogenize the water content distribution in the sample, it was sealed in a DSC pan and left for several days. The water contents, w_c, is defined by:

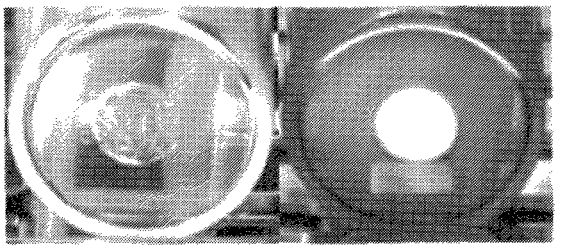
$$w_c = w_{water} / w_{dried\ gel}$$

where w_{water} and $w_{dried\ gel}$ represent the weight of water in the gel and the gel network, respectively. The w_c was varied from 0.01 to 1.7.

DSC measurements were carried out using a Seiko Denshi Model SSC/5200. The sealed type sample pans were used. DSC curves were obtained in the temperature range from - 80 to 160°C at a scanning rate of 3°C/min. The weight was measured on a microbalance (Mettler-Toledo Ltd., Model MT5) accurate to ± 0.001mg.

3. RESULTS AND DISCUSSION

Figure 1 shows typical DSC heating and cooling thermograms with various water contents of dried NIPA gel. It can be seen that the NIPA gel indicates the complex thermal behavior by changing the w_c. In the heating process, the heat capacity gap (Ⅰ) is observed in the range from w_c = 0.35 to 1.08. At w_c = 0.53 and above, the endothermic peak (Ⅱ) is observed around 34°C. In the heating curve of w_c = 0.85, the endothermic peak (Ⅲ) appears around - 4°C. In the heating curve of w_c = 1.08, the



(a) (b)

Figure 3. The photograph of visual observation of the NIPA gel of $w_c = 0.90$ at 22.4°C (a) and 43.2°C (b), respectively. These temperatures are located below and above the endothermic peak temperature (34°C).

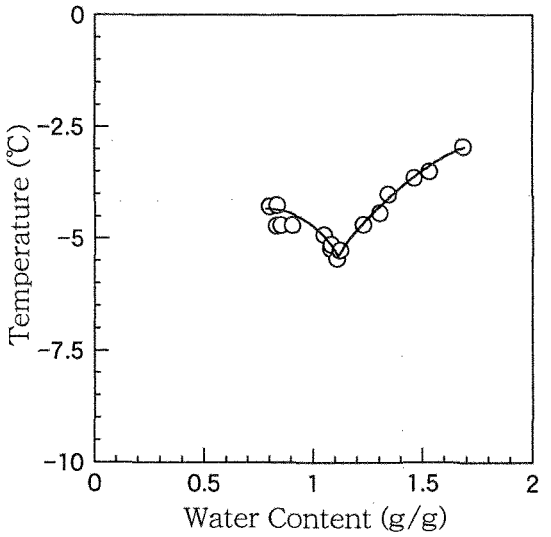


Figure 4. The w_c dependence of the endothermic peak temperature (Ⅲ) obtained from the DSC thermograms in the heating process. The enlarged view of the plot in Figure 2.

exothermic peak (Ⅳ) is observed in the lower temperature side of the peak Ⅲ. In the cooling process, the exothermic peaks are observed around 34°C at $w_c = 0.53$ and above.

The w_c dependence of the peak temperatures and the heat capacity gap temperature obtained from the DSC thermograms are depicted in Figure 2. The heat capacity gap Ⅰ decreases rapidly by increasing water content up to $w_c = 0.6$, and then levels off. It disappears at w_c above 1.46. The peak Ⅱ temperature is roughly constant at the w_c exceeding 0.35. Similarly, the peak Ⅲ temperature does not depend on the w_c above $w_c = 0.85$. The peak Ⅳ temperature is observed only within the range from $w_c = 1.08$ to 1.46, and it decreases as w_c increases. It disappears around $w_c = 1.5$.

From the above results, we would like to discuss the

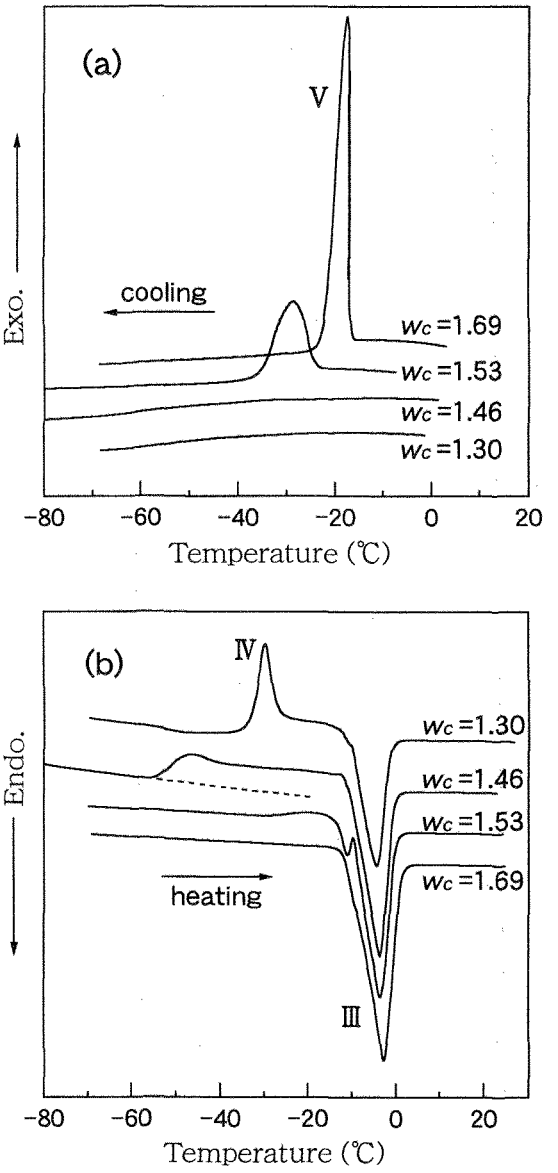


Figure 5. DSC cooling (a) and heating (b) thermograms of the samples whose w_c is ranging from 1.30 to 1.69. Each heating thermogram was successively measured after the cooling one. The brokenline represents the heat capacity gap of the base line.

assignment of these phenomena. We concluded that the heat capacity gap Ⅰ attributes to the glass transition, because the observed base line of the gap Ⅰ is similar to the phenomena of glass transition in usual glass or amorphous materials, and because the gap temperature depends on w_c, probably due to the plasticization effect of water molecules.

It is well known that the NIPA gel in very high water content undergoes a continuous volume change around 34.3°C.[1] The endothermic and exothermic peaks appear reversibly around the same temperature region as the vol-

ume phase transition, although this volume phase transition is observed at much higher w_c.

We have performed visual observation of morphological change of the NIPA gel. Figure 3 shows the photograph of the NIPA gel of $w_c = 0.90$ at 22.4°C (a) and 43.2°C (b), respectively. These temperatures are located below and above the endothermic peak temperature (34°C). It is found that the NIPA gel transforms to be transparent below the transition temperature and opaque above it. This means that the NIPA gel undergoes phase separation at 43.2°C in the order of optical light wavelength. We have confirmed that the phenomenon is reversivle, as we expected from the DSC thermogram. Consequently, the endothermic peak Ⅱ and exothermic peak are related to the phase separation of the gel and might be the origin of the volume phase transition of NIPA.

It is thought that the endothermic peak Ⅲ attribute to the melting of the freezing water. This is because it is observed at about - 4°C, and it grows as w_c increases. The enlarged view of the plot (Figure 2) of peak Ⅲ is shown in Figure 4. It is understood that the appearance of the exothermic peak Ⅳ influences the transition temperature of Ⅲ as shown in the Figure.

Figure 5 (a) and (b) show the DSC cooling and heating thermograms of the samples whose w_c is ranging from 1.30 to 1.69. Each heating thermogram was successively measured after the cooling one. With increasing the w_c, the exothermic peak Ⅳ shifts toward a lower temperature. It is clear that the exothermic peak Ⅳ of heating curves is not observed, when the exothermic peak Ⅴ (crystallization of free water) of cooling curves is observed. In addition, as shown by the brokenline in Figure 5 (b), a heat capacity gap of baseline is observed in the lower temperature side of the exothermic peak Ⅳ during the heating process. As the crystallization of water reduces specific heat, it is thought that this exothermic peak attribute to the recrystallization of water.

The detailed investigations of mesoscale structure by X-ray and neutron scattering experiments as well as the thermal behavior study are now in progress.

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