

The Concentration Dependence of Sodium Acrylate on the Phase Transition Behavior of Low Water Content NIPA/SA Gel

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We have already reported that the transition behavior of NIPA gel (700mM) in low water contents ($w_c = 0.01 - 1.7$) is complicated, depending on the w_c . The thermogram shows the glass transition, an endothermic peak around 34°C and peaks related to the melting and recrystallization of water. In the present study, the concentration dependence of sodium acrylate (SA = 0 - 100mM) on the phase transition behavior of low water contents ($w_c = 0.01 - 1.8$) NIPA/SA gel was studied by differential scanning calorimetry. The total monomer concentration of the gels at the preparation is fixed to be 700mM. SA concentration has little effect on the glass transition temperature. The endothermic peak temperature increases as SA concentration increases. This behavior is similar to that of the volume phase transition temperature observed for NIPA/SA gel in high water content.¹⁾ Moreover, the endothermic peak intensity decreases with increasing SA concentration.

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

1. INTRODUCTION

Gel shows peculiar properties, such as the volume phase transition,¹⁾ by changing the interaction of the two components; polymer network and solvent. Therefore, it is very interesting how the gel behaves when the solvent is going to disappear. Since the first report on gel-to-glasslike transition in egg-white gel by dehydration by Takushi *et al.*,²⁾⁻⁵⁾ extensive investigations on the property changes in the transition have been carried out. 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 the usual glass transition.⁶⁾ In the small angle X-ray scattering (SAXS) measurement, Sugiyama *et al.*⁷⁾ found a prominent peak in the SAXS profile probably attributed to the microphase separation during the dehydration of *N*-isopropylacrylamide/sodium acrylate(NIPA/SA) gel.

In the differential scanning calorimetry (DSC) measurements, we have reported that the transition behavior of NIPA gel (700mM) in low water contents ($w_c = 0.01 - 1.7$) is complicated, depending on the w_c .⁸⁾ In the heating process, the DSC thermogram shows the heat capacity gap (ΔC_p) by glass transition in the range from $w_c = 0.01$ to

1.5, an endothermic peak (II) around 34°C at $w_c = 0.35$ and above, an endothermic peak (III) by melting of water above $w_c = 0.85$, and an exothermic peak (IV) appearing in the lower temperature side of the peak III at the range from $w_c = 1.0$ to 1.5.

In the present study, the concentration dependence of sodium acrylate (SA = 0 - 100mM) on the phase transition behavior of low water contents ($w_c = 0.01 - 1.8$) NIPA/SA gel was studied by DSC measurements.

2. EXPERIMENTALS

Gels were prepared by a free radical copolymeriza-

tion. *N*-isopropylacrylamide (NIPA, 700 - 600 mM), the linear constituent, SA(0 - 100 mM), ionic group, *N,N'*-methylenebisacrylamide (BIS, 8.6mM), the tetra-functional cross-linking constituent, ammonium 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 total monomer concentration of the gels at the preparation is fixed to be 700mM. 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 ob-

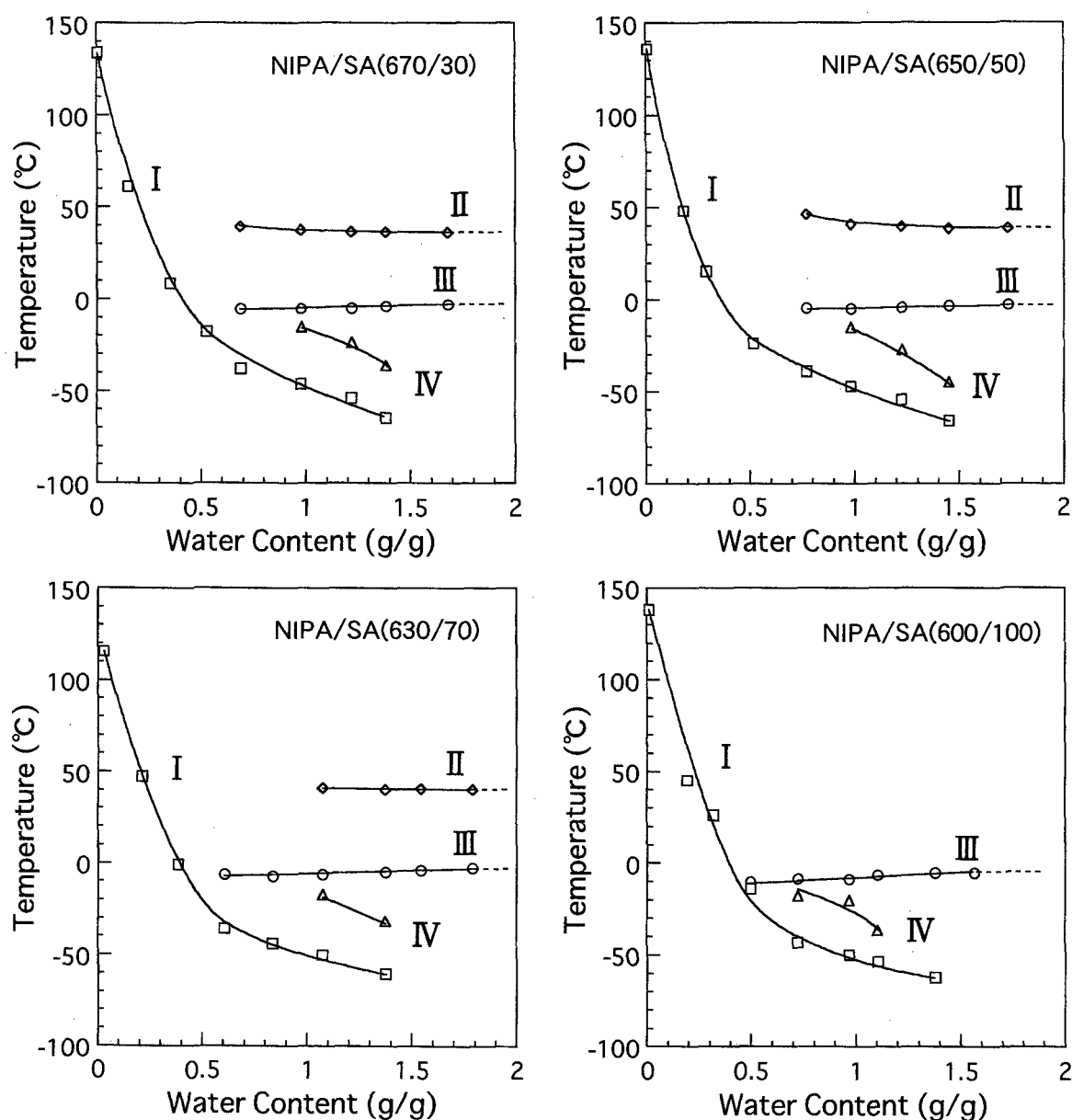


Figure 1. The w_c dependence of the heat capacity gap (I) temperature, the endothermic peaks(II , III) temperatures and exothermic peak (IV) temperature with various SA concentrations obtained from the DSC thermograms in the heating process.

tained dried NIPA/SA gel by dehydrating the gel under atmosphere after cutting in the shape of a disk.

The water content of the samples were varied by adding deionized and distilled water to the dehydrated NIPA/SA 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:

$$w_c = W_{\text{water}} / W_{\text{dried gel}}$$

where W_{water} and $W_{\text{dried gel}}$ represent the weight of water in the gel and the gel network, respectively. The w_c was varied from 0.01 to 1.8.

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 $\pm 0.001\text{mg}$.

3. RESULTS AND DISCUSSION

Figure 1 shows the w_c dependence of the heat capacity gap(I) temperature, the endothermic peak(II, III) temperatures and exothermic peak(IV) temperature with various SA concentrations obtained from the DSC thermograms in the heating process. The transition behavior is analogous to that of NIPA = 700mM of previous study⁸⁾ except for NIPA/SA = 600/100mM. The heat capacity gap I temperature decreases rapidly with increasing water content up to $w_c = 0.6$, and then decreases gently. It disappears around $w_c = 1.5$. Moreover, it is noticed that the slope of the w_c dependence of the gap I becomes gentle after the appearance of the endothermic peak III as shown in the figure. The endothermic peak II was not observed in NIPA/SA = 600/100mM. The peak IV is observed only within the range from $w_c = 1.0$ to 1.5 except for NIPA/SA = 600/100mM, and it decreases as w_c increases. It disappears at the w_c exceeding 1.5. In the NIPA/SA = 600/100mM, the peak IV is observed within the range from $w_c = 0.7$ to 1.1. In addition, a heat capacity gap was observed in the lower temperature side of the exothermic peak IV during the heating process with various SA concentrations, which is similar to the NIPA = 700mM gel of previous study.⁸⁾

From the above results, we would like to discuss the SA concentration dependence. Figure 2 is shown for comparison with the gap I temperature of various SA concentrations. As can be seen from the figure, SA concentration has little effect on the glass transition temperature. It is notice in Figure 1 that the peak III of the melting of the freezing water is not observed in steep slope region.

In addition, the crystallization peak of free water was not observed up to $w_c = 1.5$ in the cooling process (not shown here). Therefore, it is thought that the steep slope of the w_c dependence is attributed to the nonfreezing water. In this region, the water molecule seems to work as a plasticizer.

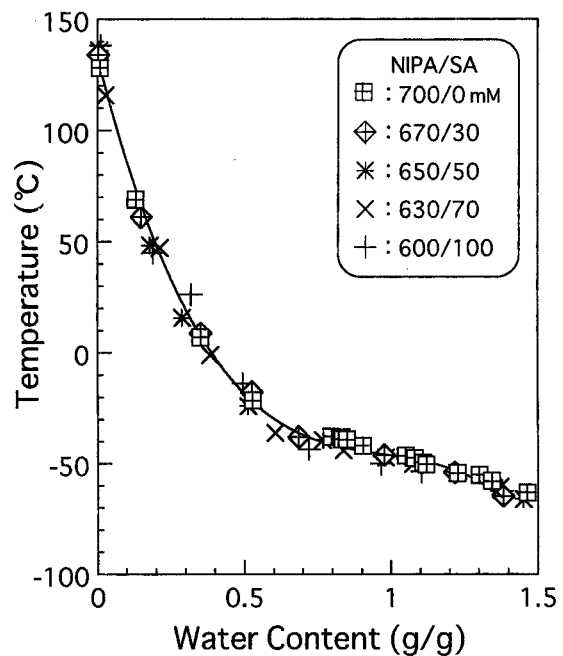


Figure 2. The w_c dependence of the heat capacity gap(I) temperature with various SA concentrations obtained from the DSC thermograms in the heating process.

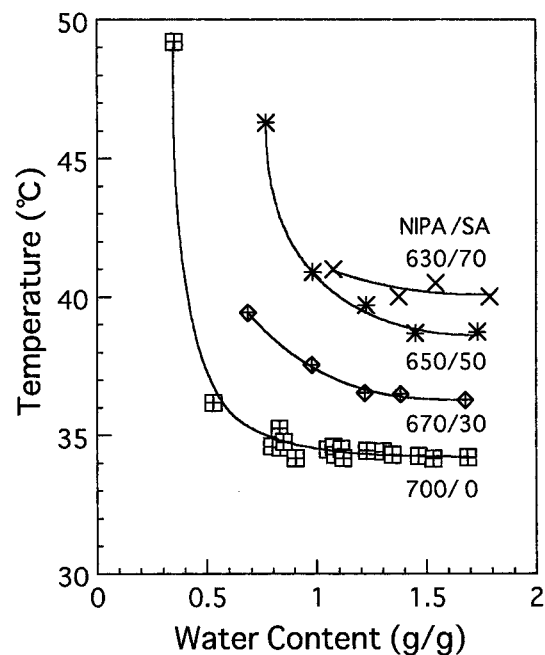


Figure 3. The w_c dependence of the endothermic peak temperature (II) with various SA concentrations obtained from the DSC thermograms in the heating process. The enlarged view of the plot in Figure 1.

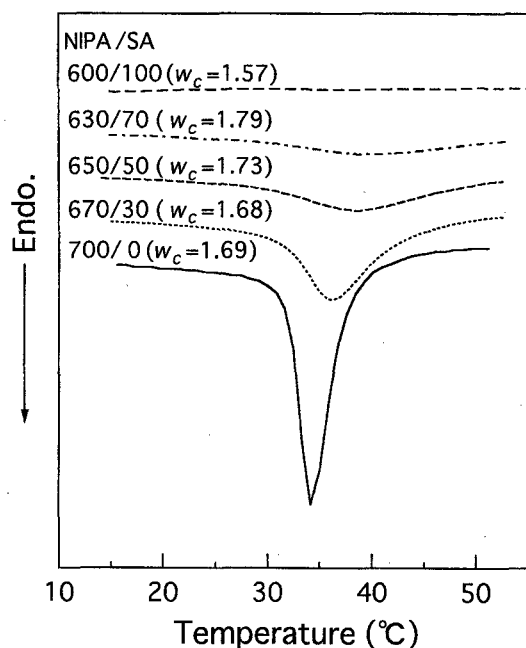


Figure 4. DSC heating thermograms of endothermic peak II of low w_c NIPA/SA gel with various SA concentrations.

The enlarged view of the plot (Figure 1) of the endothermic peak II is shown in Figure 3. The endothermic peak temperature increases as SA concentration increases. This behavior is similar to that of the volume phase transition temperature observed for gel in high water content.¹⁾ The endothermic peak II temperature increases rapidly with decreasing w_c , and then it disappears.

DSC heating thermograms of endothermic peak II of low w_c gel with various SA concentrations is shown in Figure 4. The endothermic peak intensity decreases with increasing SA concentration. The endothermic peaks appear reversibly around the same temperature region as the volume phase transition, although this volume phase transition is observed at much higher w_c . The endothermic peak II might be the origin of the volume phase transition of the gel. The peak II shifts toward a higher temperature with increasing SA concentration. It is thought that these phenomena are caused by the intermolecular interaction between the water molecules and the ionic hydrophilic groups.

Figure 5 shows the w_c dependence of the endothermic peak temperature III obtained with various SA concentrations, which is the enlarged view of the Figure 1. With increasing SA concentration the peak III shifts toward a lower temperature. It is clear that the ionic group influences the melting of water. To clarify this transition behavior, it is necessary to consider molecular-water interaction (e.g., electrostatic interaction of hydrophilic group, hydrogen bonding etc.) in the gel.

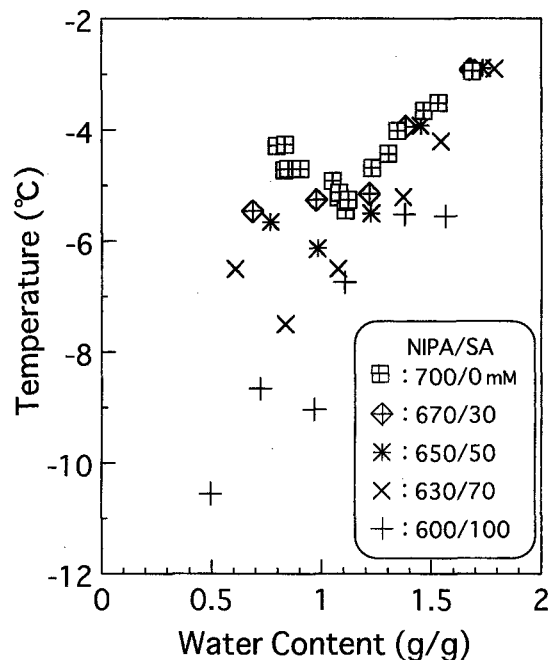


Figure 5. The w_c dependence of the endothermic peak temperature III obtained with various SA concentrations from the DSC thermograms in the heating process. The enlarged view of the plot in Figure 1.

The detailed investigations by infrared spectroscopy, Raman spectroscopy and light scattering experiments as well as the thermal behavior study are now in progress.

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