Effects of the Gel Size on the Thermal Behavior of *N*-isopropylacrylamide Gels in Relation to the Volume Phase Transition

Hideya Kawasaki, Shigeo Sasaki, and Hiroshi Maeda*
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

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Effects of the gel size on the thermal behavior and the shrinking profile of poly(N-isopropylacrylamide)(NIPA)gel in water were investigated by differential scanning calorimetry(DSC) and the volume measurement at the same heating rate. The DSC thermogram of NIPA gel of the smallest size gave double endothermic peaks and the gel underwent a discontinuous volume phase transition during DSC run. On the other hand, a single endothermic peak was observed for NIPA gel of the largest size and the gel shrank only slightly during DSC run due to the slow volume change.

It is well known that (*N*-isopropylacrylamide)(NIPA)gels in water exhibit a discontinuous volume change between a swollen state and a collapsed state (*i.e.*, volume phase transition of gels) at about 34 °C.[1] Thermal analyses by differential scanning calorimetry (DSC) on the transition of NIPA gel showed a single endothermic peak at the transition with increasing temperature.[2-5] The endothermic transition heat has been suggested to originate from dehydration of NIPA chains at the transition (release of the structured water around the hydrophobic residue).[2] Time required to reach the equilibrium volume of gels has been known to be proportional to the square of a characteristic length of the typical size of gels due to the collective diffusive process of gel-network.[6] Hence, in order to investigate the thermal behavior associated with the volume phase transition of NIPA gel, low heating rate and small sample gel-size are both required in the DSC measurements. In this study, the thermal behavior of NIPA gels in water was mainly investigated by DSC experiments at a heating rate of 0.1 °C/min, using the gels of 0.3, 1.2 and 3 mm diameters at their preparation. The thermograms of the NIPA gels were compared with the volume change profiles at the same heating rate of 0.1 °C/min.

NIPA gels were prepared by free radical copolymerization in the aqueous solutions of NIPA(696.5 mM) and N,N'-methylenebis(acrylamide) (3.5 mM). The polymerization was initiated by ammonium persulfate(APS), accelerated by *N',N',N',N'*-tetramethylethylendiamine(TEMED) and carried out at 5 °C for 24 h. NIPA gel thus prepared in a capillary of a diameter D(mm) is denoted as NIPA(D)gel. Dried NIPA (0.3) gel, NIPA (1.2) gel and NIPA (3) gel were cut into the length of about 0.5, 1 and 2.5 mm, respectively. The dried sample gels of about 2 mg were immersed in water for a week before the DSC measurement. DSC experiments were carried out with a DSC 120 calorimeter (Seiko Inc). In the swelling measurement, gel volume (V) was estimated from the gel diameter, d, measured with an optical microscope coupled with a video monitor system. The temperature in swelling measurement was controlled within ± 0.02 °C.

Figure 1(a) shows a shrinking profile of NIPA (0.3)gel at a heating rate of 0.1 °C/ min as a function of temperature. For comparison, equilibrium swelling ratios of the sample gel are also shown in Fig. 1(a) with open squares. The two swelling curves coincide with each other in the temperature range lower than 33.8 °C, the transition temperature obtained from the equilibrium swelling measurement. In the temperature range of 34.5 - 36 °C, the gel undergoes an inhomogeneous shrinking process : a discontinuous volume shrinkage starts from the edge part extruding in the solution phase where the diameter is d_{min}, while the remaining part of the gel has a large diameter of d_{max}. The gel collapses completely at about 36 °C. The shrinking profile indicates that the size of NIPA(0.3) gel is small enough for the discontinuous volume change to occur at about 34.5 °C during DSC run of the heating rate of 0.1°C/min. In Fig. 1(b), DSC thermogram of NIPA (0.3)gel at the same heating rate of 0.1 °C/min is shown. The thermogram of NIPA(0.3) gel gives double endothermic peaks. From the comparison of DSC thermogram with the shrinking profile of of NIPA(0.3) gel at the same heating rate, we can say that the endothermic heat associated with the discontinuous volume phase transition of NIPA gel is characterized by double endothermic peaks.

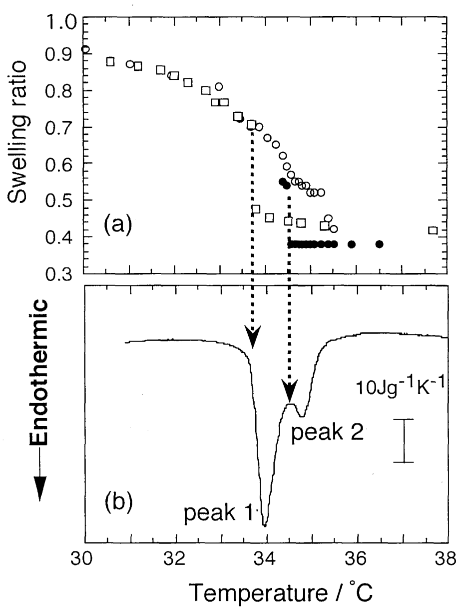

Figure 1. The shrinking profile (a) and the DSC thermogram (b) of NIPA (0.3) gel at a heating rate of 0.1 °C/ min. (O): The shrinking profile of the gel at the heating rate. For comparison, the equilibrium swelling ratios of NIPA (0.3) gel are also shown with open squares(□). Swelling ratio is defined as (d /d_0) where d_0 is a diameter of the gel at 25 °C.

In the case of inhomogeneous shrinking process that took place at about 34.5 °C, two diameters (d_{min}, d_{max}) were recorded for the gel. Here, d_{min} and d_{max} denote, respectively, the diameters of the shrunken and the swollen regions of the gel at a given temperature. These swelling ratios, (d_{min}/d_0) and (d_{max} /d_0) are represented by closed (●) and open circles(O), respectively.

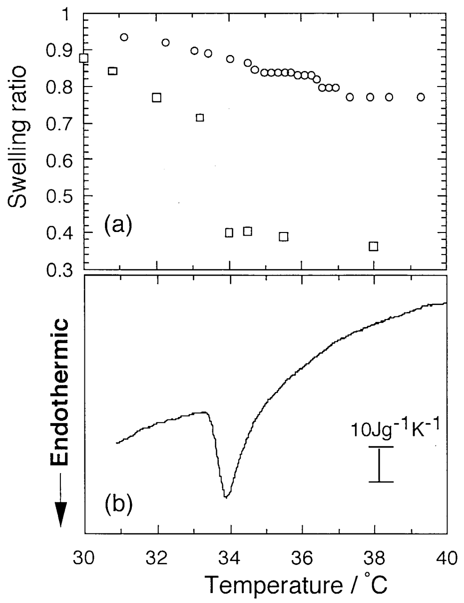

Figure 2. The shrinking profile (a) and the DSC thermogram (b) of NIPA (3) gel at the heating rate of 0.1 °C/ min. (O): The shrinking profile of the gel at the heating rate. For comparison, the equilibrium swelling ratios of NIPA (3) gel are also shown with open squares (□).

The results of the similar experiments on NIPA(3) gel are shown in Figure 2(a) and 2(b). NIPA(3) gel shrinks only slightly during DSC run due to the slow volume change. The thermogram of NIPA(3) gel gives a single broad endothermic peak. This indicates that dehydration of NIPA chains takes place under the almost constant volume condition of NIPA(3)gel. The endothermic peak of NIPA(3) gel is considered to correspond to the dehydration of NIPA chains due to the spinodal decomposition of NIPA gel into two phases with different network concentration (phase separation), which has been reported by Li et. al for NIPA gel at an isochore path.[7] A single endothermic peak of NIPA gel due to the phase separation has been also suggested by Shibayama et.al.[8] The finding that NIPA(3) gel became opaque abruptly in the almost constant volume region in Fig. 2 suggests the occurrence of a phase separation inside NIPA(3) gel. We expect that the peak at the lower temperature side of NIPA(0.3) gel (peak 1) also relates to the phase separation. To clarify the relation between the peak 1 and the phase separation, further experiments are necessary.

The satellite endothermic peak of NIPA(0.3) gel (peak 2) most likely originates from the cooperative dehydration of NIPA chains accompanying the discontinuous volume shrinkage during the DSC run by the following reasons. (1) The peak 2 position corresponded to the discontinuous volume shrinkage at the same heating rate as the DSC as shown in Fig. 1 (2) No satellite peak was observed for NIPA(3)gel that underwent little volume shrinkage during the DSC run. (3) For another NIPA (0.3) gel sample of the small size but of a high cross linker mole fraction of 0.04, a continuous volume change was found in the equilibrium swelling measurement. This gel showed a single endothermic peak at the transition (not shown).

We also examined a possibility that the double endothermic peaks of NIPA(0.3) gel originated from a consequence of the difference in the packed condition from NIPA(3) gel. However, this possibility can be ruled out by the following reasons. (1) To avoid the anticipated loose thermal contact, the DSC experiments were performed with the samples gels immersed in water. (2) If a large temperature distribution within the sample is responsible for the double endothermic peaks of NIPA(0.3) gel, it is expected that clear double endothermic peaks should be observed at faster scan rates in DSC. However, faster scan rates actually made the double peak into single peak with a shoulder(not shown).

References and Notes

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