Thermal Properties of Copolymer Gels Containing *N*-Isopropylacrylamide

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ABSTRACT: The phase transition of gels containing *N*-isopropylacrylamide (NIPA) was investigated by differential scanning calorimetry (DSC) and swelling measurements. The enthalpy of dissociation of the hydrophobic interaction per molar unit of NIPA chains (ΔH_N), the transition temperature (T_c), and the number of water molecules associated with an NIPA monomer, (n) were evaluated as a function of polymer concentration. Significant differences in ΔH_N and T_c were found between two systems: poly(NIPA-*ran*-acrylic acid) (NIPA/AAc; a weakly charged gel) and poly(NIPA-*ran*-dimethylacrylamide) (NIPA/DMAA; a neutral gel). ΔH_N decreases with increasing comonomer concentration. However, a larger decrease in ΔH_N was observed for NIPA/AAc than for NIPA/DMAA, which is accounted for by the strong hydrophilic effect of the charged AAc comonomers. No noticeable copolymer concentration dependence in n was observed in both systems. It is suggested that there are two types of water molecules, i.e., one associated with the phase transition, ($n - n_0$), and the other the lower limit for the hydrophobic hydration, n_0. The roles of these water molecules are discussed in relation to the volume phase transition.

Introduction

It is well known that poly(*N*-isopropylacrylamide) (PNIPA) gels undergo a volume phase transition in water at the transition temperature, T_c, from a swollen state to a shrunken state by increasing temperature.[1,2] This is due to dissociation of the hydrophobic interaction between NIPA segments and water. By copolymerizing NIPA with acrylic acid (AAc), one can obtain a gel which has a higher T_c and a larger swelling power at $T < T_c$.[3] This phenomenon is well elucidated by microscopic structure investigations by means of small-angle neutron scattering (SANS).[4] The SANS analysis disclosed an interesting feature of concentration fluctuations. Above the Θ temperature of PNIPA, which is about 34 °C, strong concentration fluctuations of the order of a few tens of nanometers appeared. These concentration fluctuations grew with increasing temperature until a macroscopic shrinking transition took place. This phenomenon was explained with two antagonistic interactions, i.e., electrostatic interaction and hydrophobic interaction.

Not only in polymer science but also in other fields of science, studies of hydrophobic interaction are of great significance. For example, many kinds of foods, such as gluten and fish paste, are materials coagulated with hydrophobic and/or hydrogen-bonding interactions. Therefore, control of the hydrophobic interaction is one of main themes in food science and/or processing.[5] PNIPA gels are regarded as typical model systems to study the mechanical and thermal properties as well as processability of these kinds of food.[5,6]

Thermal analysis of the demixing transition of linear PNIPA's was first reported in the literature by Heskins and Guillet in 1969.[7] Shild and Tirrell reported that the transition was found to be independent of heating rate of ≤30 °C/h.[8] However, they observed a large difference in the shape and height of the endotherms in PNIPA's having different molecular weight distributions. In the case of PNIPA gels, Otake et al. reported the enthalpy change related to the volume phase transition[9,10] and proposed a theory for the transition.[9]

In a previous paper,[11] we employed differential scanning calorimetry (DSC) to investigate the hydrophobic interaction of poly(NIPA) and found that about 750 cal/mol of NIPA monomer units is required for the dissociation of the hydrophobic interaction and about 13 water molecules are released from an NIPA monomer unit. In the present paper, we extend this analysis to two types of copolymers: poly(NIPA-*ran*-acrylic acid) (NIPA/AAc; a weakly charged gel) and poly(NIPA-*ran*-dimethylacrylamide) (NIPA/DMAA; a neutral gel).

Experimental Section

Samples. *N*-Isopropylacrylamide (NIPA) and *N*,*N*-dimethylacrylamide (DMAA) monomers were kindly supplied by Kohjin Chemical Co. Ltd., which were purified by recrystallization. Acrylic acid of special grade (AAc) was purchased from Wako Chemical Co. and used without further purification. The prescribed amounts of the monomers were dissolved in deionized water and then mixed with *N*,*N*′-methylenebis(acrylamide) (BIS) (cross-linker) and ammonium persulfate (APS) in deionized water. The polymerization was initiated with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) at 20 °C after degassing the pregel solution. The concentrations of these reagents were 22.4 (BIS), 1.75 (APS), and 8 mM (TEMED) for NIPA/DMAA, which were the same as those employed in the previous paper.[11] In the case of NIPA/AAc gels, the concentrations were 8.6 (BIS), 1.88 (APS), and 32 mM (TEMED), which are typical concentrations for the preparation of acrylamide gels for electrophoresis except for the TEMED concentration. The TEMED concentration was raised so as to keep a basic atmosphere in the presence of AAc. Table 1 shows the sample codes as well as the compositions for the NIPA/DMAA and NIPA/AAc copolymer gels. The total monomer concentrations were fixed to be 700 mM. Gels prepared in micropipettes were washed with deionized water (pH ≈ 5.6). Special care was paid for washing the gel since it affected the transition temperature, particularly in the case of the NIPA/AAc copolymer gels.[4]

Shrinking Curve Measurements and DSC. The shrinking curve was obtained with a Nikon inverted microscope coupled with an image analyzing system, which allowed us to precisely determine the gel diameter with an error of less than ±5 μm. DSC measurements were carried out with a DSC3100 (Mac Science Co. Ltd.). The polymer concentration in a gel was adjusted by deswelling the gel at $T > T_c$. Gels having

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Table 1. Sample Codes and Compositions

code	NIPA/DMAA (mM/mM)	code	NIPA/AAc (mM/mM)
D0	700/0		
D35	665/35	A4	696/4
D70	630/70	A8	692/8
D105	595/105	A12	688/12
D140	560/140	A16	684/16
D175	525/175	A32	668/32
D210	490/210	A64	636/64
D245	455/245		

polymer concentrations higher than that in the shrunken state were prepared by moisturizing a dried gel in a weighing bottle. A piece of thus prepared gel of about 3 mg was crimped in a sealed pan, and the DSC thermogram was taken with a heating rate of 3 °C/min. The temperature range was 20−80 °C. No noticeable change in the sample pan before and after a DSC run was detected, indicating no water evaporation took place during the DSC run. The concentration was determined by weighing the gel before and after drying.

Results

Since NIPA/AAc gels have acrylic groups on the network chain, the swelling power is expected to vary with pH. Thus, we examined the pH dependence of the swelling power of NIPA/AAc gels prior to the temperature dependence experiments. Figure 1 shows the variation of d/d_0 with pH of NIPA/AAc gels (A32) observed at 15 °C, where d/d_0 is the reduced gel diameter with respect to the mold diameter, d_0 (=466 μm). pH was varied by adding HCl or NaOH. As shown here, d/d_0 is strongly dependent on pH, which is due to the pH dependence of the ionization of the acrylic groups on the chain. The highest swelling power is obtained around pH 7−9. The decrease in d/d_0 at higher pH is due to the ionic screening effect of added NaOH. The pH of the deionized water employed was around 5.6, at which the degree of ionization of the acrylic groups seems to be limited. In order to avoid complexity, no further experiments by varying pH were conducted in this work, and the degree of ionization of acrylic acid was stable enough to assume an invariance with temperature as well as polymer concentration.

Figure 2 shows d/d_0 vs temperature plots (shrinking curves) for (a) NIPA/DMAA and (b) NIPA/AAc gels on the heating process. At least four characteristic features are disclosed by this experiment. (1) NIPA/DMAA gels have a continuous transition, whereas NIPA/AAc gels have a discontinuous transition from the swollen to the shrunken state. (2) The degree of swelling at $T < T_c$ for NIPA/DMAA does not depend on the DMAA content, whereas that for NIPA/AAc is strongly AAc composition dependent. The higher the AAc composition, the larger the swelling ratio at $T < T_c$. (3) No hysteresis with respect to temperature was found for NIPA/DMAA, whereas a biphase state, i.e., coexistence of swollen and shrunken states, was observed near T_c for NIPA/AAc gels. (4) The diameters of the shrunken gels seem to be roughly equal irrespective of the kind of comonomer and the comonomer concentration. The value of d/d_0 in the shrunken state is around 0.5 (except for the case of D175), which will be discussed later. Regarding T_c for NIPA/AAc gels, a similar result was reported by Hirotsu et al.[3] However, the transition temperatures are slightly different, which is ascribed to the difference in the amount of ionized residue in the system. The presence of the biphase is also reported by Shibayama et al.[4] and Hirotsu.[12,13]

Figure 3 shows the DSC thermograms for NIPA/DMAA's. Clear endotherms are resolved for gels having zero or low DMAA compositions. These endotherms correspond to the dissociation of the hydrophobic interaction as was proved in the previous paper.[11] By increasing DMAA, the endotherm shifts to the high-temperature side and the peak becomes diminished.

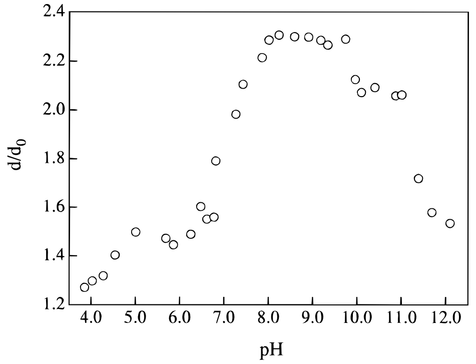

Figure 1. pH dependence of NIPA/AAc gel (A32) at 15 °C. d/d_0 denotes the reduced gel diameter, where d is the gel diameter at the given temperature and d_0 is the mold inner diameter.

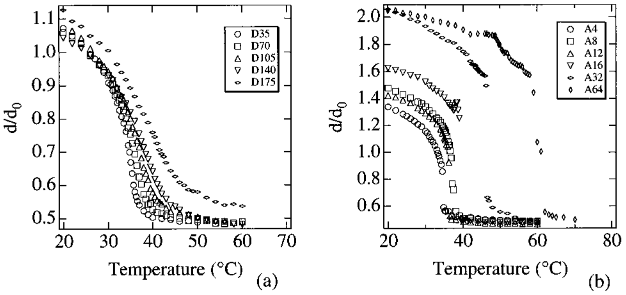

Figure 2. Shrinking curves of (a) NIPA/DMAA gels and (b) NIPA/AAc gels as a function of temperature.

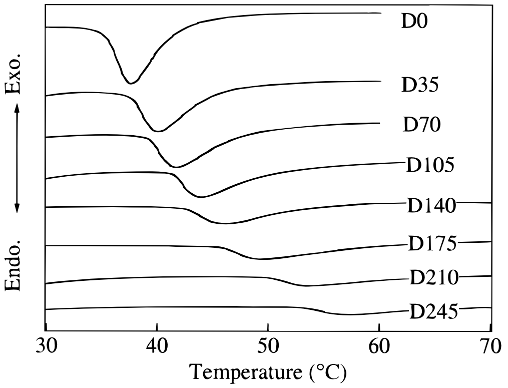

Figure 3. DSC thermograms for NIPA/DMAA gels.

A similar phenomenon is also found in NIPA/AAc's as shown in Figure 4. However, the depression of the endotherm with the comonomer content is more significant. It should be noted that the peak shift with the comonomer content is less than that of NIPA/DMAA gels.

Discussion

1. Transition Temperature. First, we examine the comonomer concentration dependence of T_c. Figure 5 shows the transition temperatures, T_c's, for NIPA/DMAA obtained from (a) the shrinking curve and (b) DSC. In the case of (a), the inflection point in the shrinking curve was taken as T_c. On the other hand, the tangential method, the crossover point of the baseline and the extrapolated line of the peak, was employed

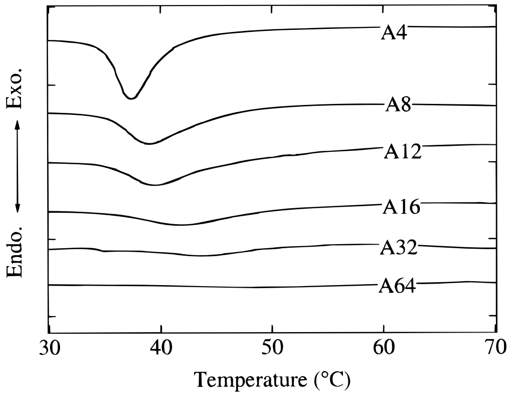

Figure 4. DSC thermograms for NIPA/AAc gels.

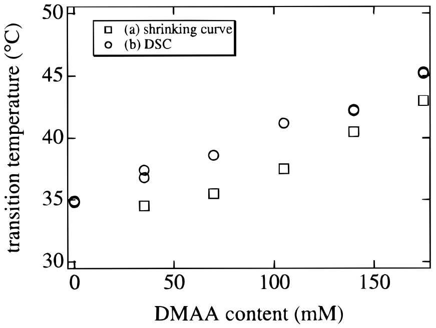

Figure 5. DMAA content dependence of the transition temperatures, T_c's, obtained by (a) the shrinking curve (squares) and by (b) DSC (circles).

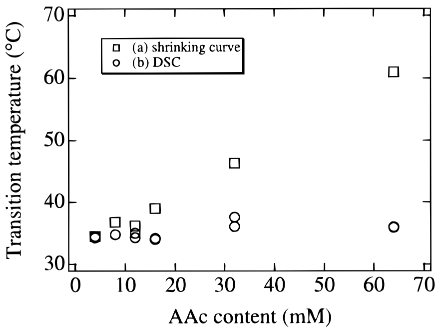

Figure 6. AAc content dependence of the transition temperatures, T_c's, obtained by the shrinking curve (squares) and by DSC (circles).

for the case of (b). As shown in the figure, the two T_c's are relatively well correlated to each other. The difference in T_c's obtained by the two methods is less than a few degrees.

Figure 6 shows T_c's for NIPA/AAc obtained from (a) the shrinking curve (the temperature at a discrete transition in the d/d_0 curve) and (b) DSC. Contrary to the case of NIPA/DMAA, the T_c determined by the shrinking curve measurement deviates from that by DSC as the AAc comonomer concentration increases. This deviation is accounted for by the presence of two transitions, i.e., one macroscopic and the other microscopic. As indicated in the SANS study,[4,14] the macroscopic transition takes place when the shrinking power (hydrophobic dissociation power) dominates the swelling power (electrostatic repulsion and Donnan potential). This is observed as a "macroscopic" volume phase transition. On the other hand, the microscopic transition is detected by the appearance of a peak in the SANS intensity profile. This is an indication of the onset of the switching-on of the shrinking power in the microscopic order (≈10 nm), i.e., emergence of the demixing power above the Θ temperature of PNIPA. Therefore the microscopic transition (dissociation of the hydrophobic association) is expected to be close to Θ (≈34 °C). This is what we observed by DSC.

2. Calorimetric Analysis. In the previous paper,[11] we proposed a convenient method to estimate the enthalpy of dissociation and the number of water molecules associated with a NIPA molecule. We assumed that there was a PNIPA gel consisting of x moles of NIPA monomer units and y moles of water molecules in the system. The enthalpy of dissociation, ΔH, for the PNIPA−water system containing $(x + y)$ moles as total, or that normalized by the total number of moles, $(\Delta H)_{\mathrm{mol}}$, is given by

$$(\Delta H)_{\mathrm{mol}} \equiv \frac{\Delta H}{x+y} = \begin{cases} \dfrac{\Delta H_{\mathrm{N}}}{n} Y & 0 < Y \le Y_{\mathrm{m}} \\ \Delta H_{\mathrm{N}}(1-Y) & Y_{\mathrm{m}} < Y \le 1 \end{cases} \tag{1}$$

where Y is the water mole fraction $[Y \equiv y/(x + y)]$ and ΔH_{N} is the enthalpy of dissociation per mole of PNIPA monomeric unit. This equation predicts a triangular function crossing the abscissa ($\Delta H = 0$) at $Y = 0$ and $Y = 1$, which has a maximum at $Y = Y_{\mathrm{m}}$, the stoichiometric water mole fraction. A similar analysis was conducted on thermoreversible gels by Guenet and McKenna.[15]

However, our experimental results did not support this prediction at $Y = 0$. Therefore, we now modify the theory by considering the presence of water molecules which do not participate in the dissociation and/or association. We define the stoichiometric numbers of water molecules per monomer unit of NIPA as n and n_0 before and after the dissociation, respectively. n_0 is the number of inert water molecules which have nothing to do with the dissociation. The enthalpy of dissociation, ΔH, is given by

$$\Delta H = \mathrm{d}H_{\mathrm{w}} x(n - n_0) \qquad \text{for } nx \le y \tag{2a}$$

$$\Delta H = \Delta H_{\mathrm{w}}(y - n_0 x) \qquad \text{for } n_0 x \le y < nx \tag{2b}$$

where ΔH_{w} is the enthalpy for dissociation of the hydrophobic interaction allotted to 1 mol of water. Figure 7 schematically shows (a) the shrinking curve and (b) the enthalpy change as a function of Y. At $T < T_c$, some of the water molecules are in the ordered state (as illustrated with linked circles). However, at $T > T_c$, water molecules are dissociated to free water molecules. It is obvious that the observed enthalpy is related to this dissociation. Equation 2a corresponds to a gel having water molecules in addition to the hydrophobically associated water molecules, of which the dissociation process is indicated by the path i. On the other hand, eq 2b represents a deswollen gel having fewer water molecules than the stoichiometric condition for the hydrophobic association (path ii). By rearranging eqs 2a and 2b, one gets

$$(\Delta H_{\mathrm{mol}}) = \Delta H_{\mathrm{w}}(n - n_0)(1 - Y) \qquad \text{for } Y_1 \le Y \le 1 \tag{3a}$$

$$(\Delta H)_{\mathrm{mol}} = \Delta H_{\mathrm{w}}[(1 + n_0)Y - n_0] \qquad \text{for } Y_0 \le Y \le Y_1 \tag{3b}$$

Therefore, by plotting $(\Delta H)_{\mathrm{mol}}$, which is obtained by DSC, as a function of Y, one gets a triangular-shape

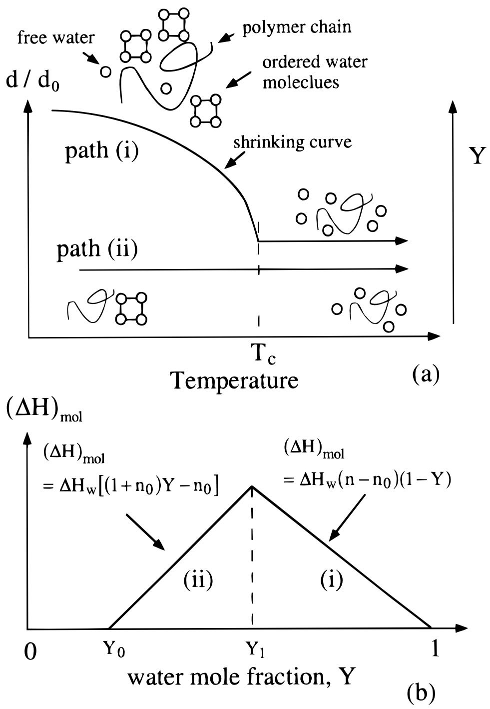

Figure 7. Schematic representation of the transitions: (a) shrinking curve and (b) the enthalpy function, $(\Delta H)_{mol}$, vs the water mole fraction, Y. Path i indicates a DSC measurement along the shrinking curve, and path ii denotes that on an isochore (equiconcentration) line.

function having the peak at $Y = Y_1$ and crossing the abscissa at $Y = Y_0$ as shown in Figure 7b. From Y_0 and Y_1, one can easily estimate n and n_0 with the following equations:

$$Y_0 = \frac{n_0}{1 + n_0}, \qquad Y_1 = \frac{n}{1 + n} \tag{4}$$

ΔH_w can be converted to the enthalpy for dissociation of the hydrophobic interaction per mole of NIPA, ΔH_N, which is given by

$$\Delta H_N = (n - n_0)\Delta H_w \tag{5}$$

On the other hand, by letting $Y_0 = 0$, eq 3 becomes identical to eq 1 and the one derived by Guenet and McKenna.[15]

Figure 8 shows the plots of $(\Delta H)_{mol}$ vs the water mole fraction, Y, for NIPA/DMAA gels (D35, D70, and D105). As predicted by eqs 3a and 3b, data points fit well to a triangular function, which are indicated with two lines. Note that the extrapolated line toward the lower Y side does not cross the abscissa at $Y = 0$ but at $Y = Y_0$. From the intercept of the extrapolated line, the Y value at the peak ($=Y_1$), and Y_0, the values of ΔH_N, n, and n_0 were evaluated with eqs 4 and 5, which are also shown in the figures.

A similar analysis was also conducted for NIPA/AAc gels (Figure 9), where the fact $Y_0 \neq 0$, is clearly seen. In the cases of Guenet and McKenna[15] and our previous paper,[11] the presence of water (solvent) molecules after the transition was neglected. Thus Y_0 was set to be zero. However, in reality, the polymer mole fraction never reaches unity even after the shrinking transition but approaches a finite value. The classic theory of volume phase transition[2,3,16] does not predict this upper limit of the polymer volume fraction. Though Grosberg explains this with a crumpled globule model,[17] it still seems to be an open question.

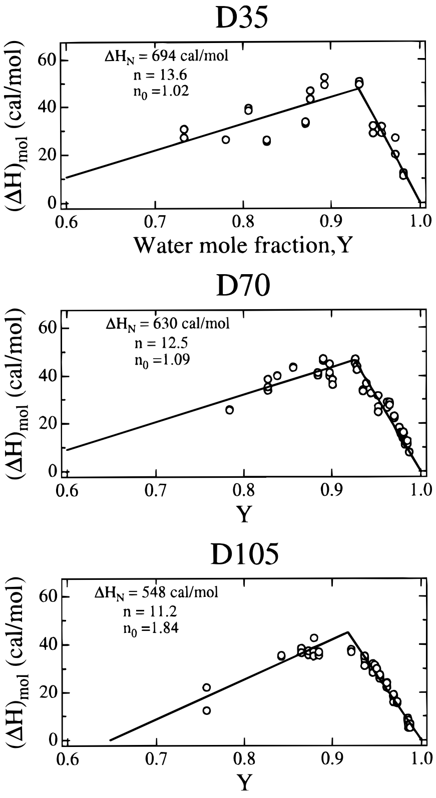

Figure 8. $(\Delta H)_{mol}$ vs the water mole fraction, Y, plots for NIPA/DMAA gels.

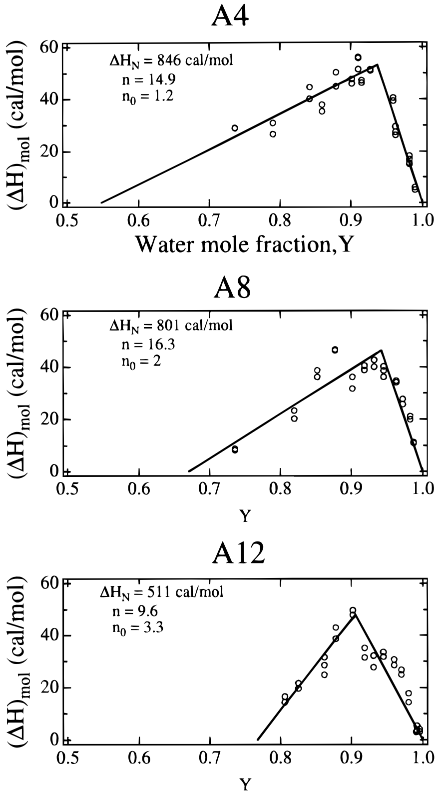

Figure 9. $(\Delta H)_{mol}$ vs the water mole fraction, Y, plots for NIPA/AAc gels.

Figure 10 shows the comonomer concentration dependence of ΔH_N for (a) NIPA/DMAA and (b) NIPA/AAc gels. Although both of them are decreasing functions of comonomer concentration, that of the NIPA/AAc gels

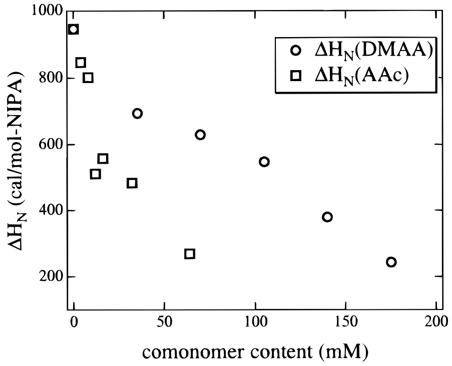

Figure 10. Comonomer concentration dependence of $(\Delta H)_N$ for NIPA/DMAA and NIPA/AAc gels.

is more strongly dependent on the comonomer concentration. This is accounted for by the strong hydrophilicity of the AAc comonomer since it can be charged in aqueous medium. On the other hand, DMAA comonomers serve as a deactivating (deteriorating) reagent of the hydrophobicity of NIPA. Thus a rather gradual decrease in ΔH_N is observed. The value of ΔH_N for zero comonomer concentration (i.e., the case of pure NIPA gels) is estimated to be 0.858 kcal/mol-NIPA (3.59 kJ/mol-NIPA). In our previous paper,[11] we reported ΔH_N = 0.747 kcal/mol-NIPA. However, it turned out that it was slightly underestimated due to a calibration error. The value ΔH_N = 0.858 kcal/mol-NIPA was obtained after calibration of the DSC instrument with the melting enthalpies of lead and indium. The obtained ΔH_N is in good agreement with those by Otake et al. (3.3−4.5 kJ/mol-NIPA).[10] It should be noted here that ΔH_N for PNIPA gels is significantly smaller than that for PNIPA linear polymer solutions, e.g., 6.3 kJ/mol (Schild et al.)[8] and 4.8−6.1 kJ/mol (Otake et al.),[10] which may be ascribed to a lowering of "the degree of hydrophobic hydration" in the gels by introducing the cross-linked structure. Schild et al. assigned this enthalpy change to hydrogen bond interaction. However, as discussed in the present paper, it seems more reasonable to assign this endotherm as the dissociation enthalpy of the hydrophobic interaction. Regarding the comonomer concentration dependence, one expects that ΔH_N does not depend on the comonomer concentration if the comonomers behave merely as noninteracting additives and are not involved in the hydrophobic dissociation. However, ΔH_N decreases with comonomer concentration in both NIPA/DMAA and NIPA/AAc gels. This indicates that the introduction of these comonomers affects the local environment of the NIPA chains; i.e., the hydrophobic atmosphere is significantly modified as evidenced by NMR[18] and Fourier transform infrared spectroscopy.[4]

Figure 11 shows the number of water molecules associated with the NIPA monomer units, n and n_0, for NIPA/DMAA gels. The number of water molecules released at the shrinking transition is $(n - n_0)$ and slightly decreases from 13 to 9 with increasing DMAA content; the reason for this change is not clear at this stage. The important finding is the presence of n_0 ($\approx$1), whose physical meaning will be discussed in the next section.

In the case of NIPA/AAc gels, the data points of n and n_0 are rather scattered as shown in Figure 12. This is due to the difficulty of the evaluation of $(\Delta H)_{mol}$. Though the comonomer dependence of n and n_0 is not clear, the presence of n_0 is clearly shown. The value of n_0 is about 1−3, which seems to be slightly larger than that for NIPA/DMAA gels.

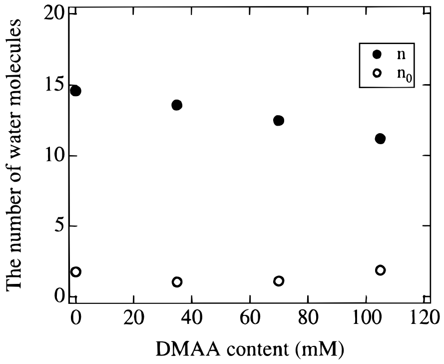

Figure 11. DMAA content dependence of n and n_0 for NIPA/DMAA gels.

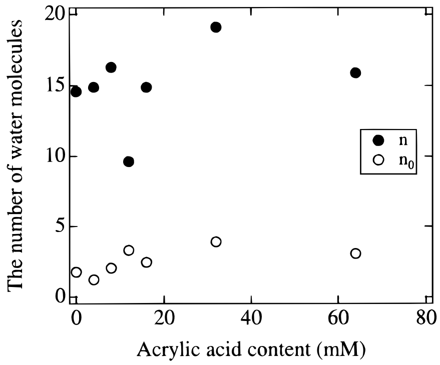

Figure 12. DMAA content dependence of n and n_0 for NIPA/AAc gels.

Table 2. Comparison of the Polymer Volume Fractions at the Shrunken State

code	$\phi_{shrunken}$	ϕ_n	ϕ_{n_0}
D35	0.671	0.315	0.860
D70	0.667	0.332	0.851
D105	0.659	0.355	0.770
A4	0.705	0.296	0.839
A8	0.684	0.278	0.758
A12	0.742	0.394	0.654
A16	0.710	0.295	0.722
A32	0.671	0.245	0.613
A64	0.616	0.277	0.662

3. Stoichiometry of Hydrophobic Hydration. In this section, we discuss the physical meaning of n and n_0. Since these are related to the hydrophobic dissociation, it is reasonable to expect that they are also correlated to the polymer concentration at the shrunken state. Table 2 shows polymer volume fractions at the shrunken state estimated by several methods; $\phi_{shrunken}$ (from d/d_0 at the shrunken state, i.e., $\phi_{shrunken} = \phi_0(d_0/d)^3$, ϕ_0 being the polymer volume fraction at gel preparation), ϕ_n (from the n or Y_1 value of DSC), and ϕ_{n_0} (from the n_0 or Y_0 value of DSC). Although we expected an agreement between $\phi_{shrunken}$ and ϕ_n, these values were quite different. $\phi_{shrunken}$ is much higher than ϕ_n. This indicates that there are some water molecules which do not participate in the shrinking transition but are extruded from the gel by the transition. By reexamining Figure 2 of the previous paper,[11] it is clear that $\phi_{shrunken}$ is dependent on the cross-linker (BIS) concentration. The higher the BIS concentration, the higher the $\phi_{shrunken}$. This clearly indicates that the introduction of cross-links to a hydrophobically associated system, e.g., an NIPA aqueous solution, reduces the degree of collapsing (shrinking), probably due to a reorganization of hydrophobic clusters, i.e., a larger cluster formation with a lower entropy loss. This speculation is supported by the fact that ΔH_N's for gels are much lower than that of the corresponding solution (the values reported by Shild[8] and Otahe et al.[10]).

In the case of DSC runs for a gel having a polymer concentration higher than ϕ_{shrunken}, a DSC endotherm is still observable up to a concentration corresponding to the water mole fraction of Y_0. Therefore, n_0 can be assigned to the lowest number of water molecules per NIPA monomeric unit above which a hydrophobic association can take place. It is interesting to compare the values of n_0 between NIPA/DMAA gels and NIPA/AAc gels. n_0 is 1−2 for NIPA/DMAA gels and 1−3 for NIPA/AAc gels. This indicates that NIPA/DMAA gels are better suited for hydrophobic hydration compared to NIPA/AAc gels. In other words, hydrophobic hydration is easily attained in NIPA/DMAA gels because of their strong hydrophobic nature. In the case of NIPA/AAc gels, a comonomer concentration dependence in n_0 is clearly observed, which is again explained with the strong hydrophilicity of charged AAc groups. In order to initiate hydrophobic hydration, more water molecules are required since some of the water molecules are taken by the charged AAc groups.

It should be noted here that calorimetric studies were conducted without taking account of the degree of ionization of the acrylic groups. However, as described in the Results section, it varies with the polymer concentration as well as with pH. A preliminary study discloses that a systematic variation in ΔH_N is obtained at different pHs, which will be reported shortly.

Conclusions

Thermal analysis was conducted on copolymer gels containing *N*-isopropylacrylamide as one component. The gels underwent a shrinking transition by increasing temperature. In the case of NIPA/dimethylacrylamide (NIPA/DMAA) gels, the transition was continuous, while that for NIPA/acrylic acid (NIPA/AAc) gels was discontinuous. The transition temperature, T_c, increased with the comonomer concentration. However, in the case of NIPA/AAc, the difference in T_c's estimated by the shrinking curve and by DSC became larger with increasing AAc concentration. T_c(shrinking curve) was higher than T_c(DSC). The former corresponds to the macroscopic transition and the latter to the microscopic transition. The effect of the introduction of comonomers is stronger in NIPA/AAc gels than in NIPA/DMAA gels, which is due to the strong hydrophilic nature of the charged AAc segments. The enthalpy of dissociation of the hydrophobic interaction, ΔH_N, was estimated as a function of the comonomer concentration. ΔH_N decreases with the comonomer concentration. For NIPA homopolymer gels, ΔH_N was estimated to be 0.858 kcal/mol-NIPA, which is in good agreement with the literature value. The numbers of water molecules associated with the dissociation was estimated to be 10−15/NIPA segment. The lower limit of the number of water molecules necessary for hydrophobic hydration, n_0, was also found. n_0 was 1−2 for NIPA/DMAA gels and 1−3 for NIPA/DMAA gels, which increased with decreasing the hydrophobic atmosphere by introducing charged comonomers, i.e., AAc groups.

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References and Notes

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