

Effects of non-uniform solvation on thermal response in poly(*N*-isopropylacrylamide) gels

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Abstract

The quantitative analyses on the dehydration of poly(*N*-isopropylacrylamide) (NIPA) hydrogels were conducted by means of differential scanning calorimetry (DSC) as a function of polymer volume fraction, ϕ . It was found that the thermal properties of NIPA gels were strongly dependent on the history of the gel treatment before DSC measurements. In particular, a disagreement in the hydrophobic dissociation temperature at which an endothermic peak appears, T_{hd} , and in the enthalpy of dehydration, ΔH , was clearly detected between gels having different histories: one prepared by adding a given amount of water to a dried gel (non-equilibrated gels) and the other made by gradual shrinking along the isobar line by heating (equilibrated gels). The phase diagram, i.e. the plot of T_{hd} vs. ϕ , for the equilibrated gels has a convex function of ϕ , whereas that of the non-equilibrated gel shows an anomalous dip for $\phi > \phi_{\text{st}} \approx 0.4$ (i.e. above the stoichiometric concentration of NIPA-water hydration). The values of ΔH for the non-equilibrated gels are less than those for the equilibrated gels in the concentration regime of $\phi > \phi_{\text{st}}$. This implies that the non-equilibrated gels have a higher degree of non-uniform solvation than the equilibrated gels. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-isopropylacrylamide) gels; Hydrophobic dissociation; Equilibrated gel

1. Introduction

Water soluble polymers bearing hydrophobic side groups dissolve in water with the aid of hydrophobic association of water molecules around the hydrophobic groups. Such polymers usually exhibit a lower critical solution temperature (LCST) behavior in water, i.e. the polymers are soluble in water at low temperatures and demix at elevated temperatures. Among them, poly(*N*-isopropylacrylamide) (poly-NIPA) aqueous solutions have been one of the most extensively studied systems since it was first reported by Heskins and Guillet [1]. The characteristic features of poly-NIPA are reviewed by Shild [2]. Particularly, a study on volume phase transition of poly-NIPA gels (hereafter we simply call NIPA gels) by Hirokawa et al. [3] triggered extensive studies on NIPA gels [4], including thermal [5] and mechanical properties [6–8], structure [9], and kinetics of gel swelling/shrinking [10]. As regards the thermal properties, Li and Tanaka treated the heat capacity of NIPA gels as a critical phenomenon [11]. Otake et al. studied the thermal properties of polymer gels and solutions from the thermodynamic point of view [5]. Lele et al. proposed the lattice-fluid-hydrogen-bond (LFHB) theory in order to interpret the

volume phase transition of thermosensitive polymer gels [12,13]. The LFHB theory, which considers the hydration layers of water molecules surrounding the hydrophobic groups on polymer networks, seems to reproduce well the volume phase transition. However, there still remain a large number of interesting questions about its physical properties.

Recently, it has been found that the importance of spatial inhomogeneities (or heterogeneities) in gels [14–18] may affect their physical properties, such as swelling kinetics and mechanical properties, and thermal response. However, to our knowledge, the thermal properties of NIPA gels have not yet been discussed in relation to the structural inhomogeneities.

In one of our previous papers, we reported the importance of the structure relaxation in differential scanning calorimetry (DSC) [19]. Because the time required for structure relaxation is, in most cases, longer than the scanning rate of temperature DSC thermograms have to be examined with the knowledge of its structure relaxation. We also discussed the preparation temperature, T_{prep} , dependence of the heat of hydrophobic dissociation of NIPA gels, ΔH , and the number of water molecules associated with the hydrophobic bonding. The conclusion was that ΔH does not depend on T_{prep} but the number of water molecules does [20]. In this paper,

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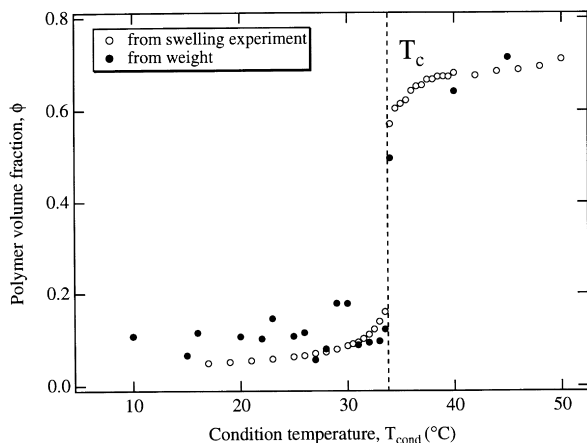


Fig. 1. Plots of the polymer volume fraction, ϕ , vs. condition temperature, T_{cond} , determined by swelling experiment and by weighing the gel. T_c denotes the volume phase transition temperature.

we report that the thermal response of gels is dependent on the history of gel conditioning.

2. Experimental section

2.1. Gel preparation and conditioning

NIPA gels were prepared in a micropipette with the inner diameter of 1.8 mm. The NIPA monomer, kindly supplied by Kohjin Chemical Co. Ltd., Japan, was purified by recrystallization before use. The monomer concentrations were 690 mM NIPA and 8.62 mM *N,N'*-methylenebisacrylamide (BIS). The polymerization temperature was 20°C and one day was allowed for complete polymerization. The details of sample preparation were the same as described elsewhere [8,21]. Two types of sample conditioning methods (i.e. concentration adjusting methods) were employed: in method I, gels prepared in a test tube were washed with an excess amount of water, cut into small pieces, and then completely dried in a vacuum oven. After weighing and adding a given amount of water, the gel was sealed in a sample pan for the DSC run and homogenized in the pan for more than 1 day. By contrast, in method II, a gel was made in a micropipette with the inner diameter of ca. 1.8 mm. The diameter of the micropipette mold employed here was chosen to be much larger than in the previous work (0.466 mm) in order to handle the gel samples more easily for DSC measurements. Gels were taken out from the micropipette and cut into small pieces of about 2.5–5 mm long. By immersing in deionized water, the gels were allowed to swell to ca. 2 mm in diameter at 10°C. These gels were further conditioned at 10°C in a glass bottle filled with deionized water. Then, the temperature of the gel was increased stepwise with a step of 1°C up to desired temperatures, T_{cond} (the conditioning temperature). It took about 2–24 h for a gel to reach an equilibrium by a change

of 1°C. Above 33°C, where the temperature is close to the volume phase transition temperature, the step was reduced to 0.1°C in order to assure thermal equilibrium. In total, it took about 1 month for sample conditioning for DSC experiments. Fig. 1 shows the polymer volume fraction, ϕ , for the gel conditioned by method II (equilibrated gels) as a function of T_{cond} . The values of ϕ were determined by swelling (open circles) and weight measurements (closed circles), where simple-additivity and no-volume change on mixing were assumed. Note that the values of ϕ obtained by the two methods are close to each other and are enough to certify the accuracy of the concentration determination of the gels used in this study. This figure shows the equilibrium volume fraction of the gel, ϕ , at a given temperature. A volume transition took place at $T_c = 34.1^\circ\text{C}$ for the NIPA gels studied here. The conditioned and equilibrated gels at the desired temperatures were taken out from the water reservoir and sealed in an aluminum pan for DSC measurements. Note that excess water droplets on the gel surface were wiped off before sealing.

2.2. Differential scanning calorimetry experiments

DSC measurements were carried out on a DSC3100 (Mac Science Co. Ltd., Tokyo) with a heating rate of 3°C/min under N_2 purge. The temperature scanning range was restricted from 20 to 50°C in order to avoid water evaporation. The polymer concentration was determined by weighing the sample. No noticeable weight loss was detected after a DSC scan. Therefore, it was assumed that no water evaporation was involved during a DSC run. The same experiments were repeated at least three times to check reproducibility.

3. Results and discussion

3.1. Analysis of differential scanning calorimetry thermograms

It is known that there are at least three types of water in hydrogels, i.e. non-freezing water, free water, and bound water [22,23]. The last two types are freezable water although they have different freezing temperatures, i.e. the same as that of pure water (free water) and a different temperature (bound water). Therefore, these waters can be classified by thermal analysis around the freezing temperature of water. In the case of hydrogels bearing hydrophobic groups, e.g. NIPA gels, the bound water may be further classified into two types of bound water: water molecules bound to hydrophilic groups of the gel (via hydrogen bonding; hydrophilic bonding) and water molecules bound to hydrophobic groups (via iceberg formation among the water molecules; hydrophobic bonding). As already shown in Fig. 1, the volume phase transition of NIPA gels takes place around 34°C. It is clear that the free water has

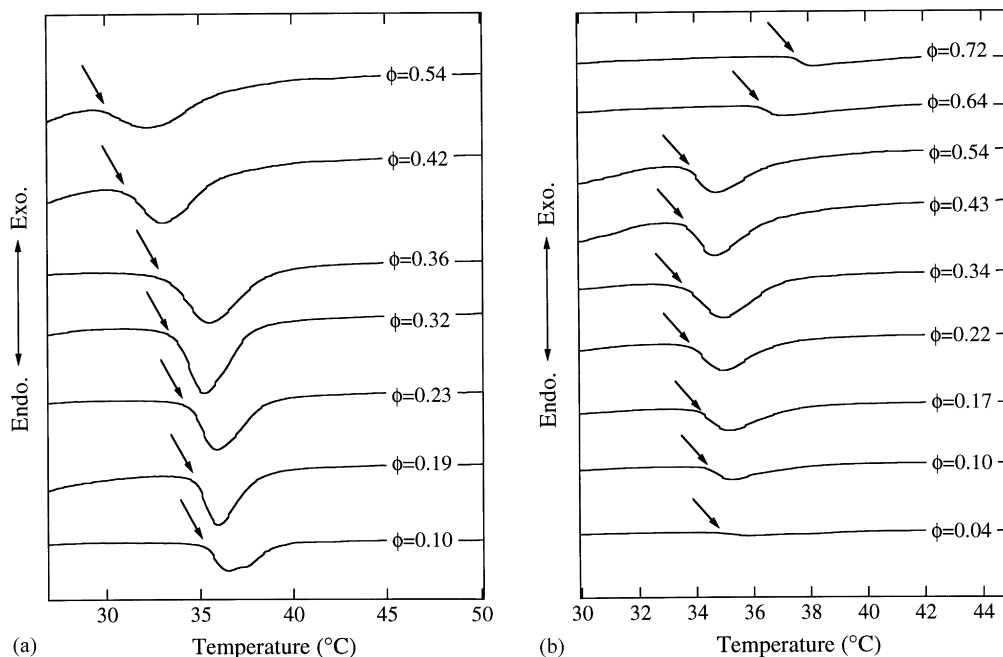


Fig. 2. DSC thermograms of NIPA gels having different polymer volume fractions, ϕ 's. The arrows indicate the hydrophobic dissociation temperature, T_{hd} . (a) The gels were prepared by method I (gels prepared from dried state; non-equilibrated gels). (b) The gels were prepared by method II (gels prepared by gradual shrinking along the isobar line; equilibrated gels).

nothing to do with the hydrophobic bonding and simply contributes to swelling.

Let us assume that water molecules with the number of n per NIPA monomer unit are bound to an NIPA polymer chain. It should be noted, however, that a considerable number of water molecules per NIPA monomer unit, with the number of n_0 , are present even in a shrunken gel via hydrogen bonding to the hydrophilic groups of NIPA. This is proved by the fact that even in the shrunken state, the volume fraction of polymer remains far below unity. Therefore, the number of water molecules responsible for the volume phase transition is estimated to be $(n - n_0)$ instead

of n . By taking this fact into account, we proposed a method to estimate n and n_0 from the enthalpy of dehydration per mole of gel, ΔH [21],

$$\Delta H = \begin{cases} \Delta H_N \left(\frac{1 + n_0}{n - n_0} W - \frac{n_0}{n - n_0} \right) & \left(\frac{n_0}{1 + n_0} < W \leq W_{st} \right), \\ \Delta H_N (1 - W) & (W_{st} < W < 1) \end{cases} \quad (1)$$

where ΔH_N is the enthalpy of dehydration per mole of NIPA-monomer unit. W_{st} is the water mole fraction at the stoichiometric relation between the NIPA segments and water molecules. The meaning of “the stoichiometric” number of water molecules is the largest number of water molecules capable of hydrophobic solvation with one hydrophobic monomer unit. Therefore, by plotting ΔH as a function of W , one obtains a triangular-shape plot. This type of analysis was proposed by Guenet and McKenna for thermoreversible gels [24]. In our previous papers [8,21], we also reported that the variations of ΔH with W are well represented by Eq. (1). The water mole fraction, W , is converted to the polymer volume fraction, ϕ , by the following equation,

$$\phi = \frac{v_{NIPA}(1 - W)}{v_{NIPA}(1 - W) + v_{water}W} \quad (2)$$

where v_{NIPA} and v_{water} are the molar volumes of NIPA and water, respectively.

Fig. 2 shows the DSC thermograms of NIPA gels with different gel concentrations ϕ 's prepared by (a) method I and by (b) method II. The arrows indicate the onset of the

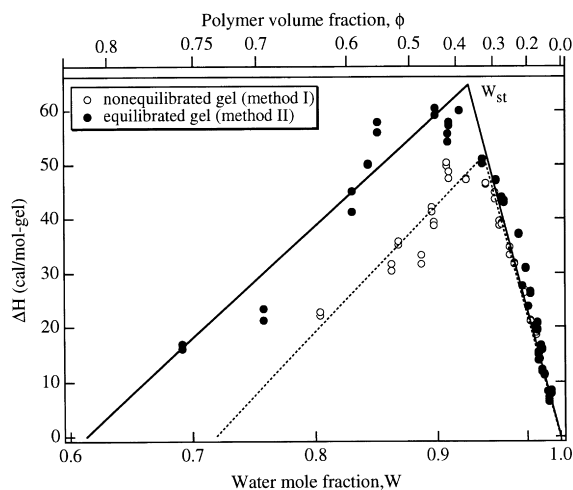


Fig. 3. Water mole fraction, W , dependence of the enthalpy of hydrophobic dissociation, ΔH for gels prepared by method I (○) and II (●).

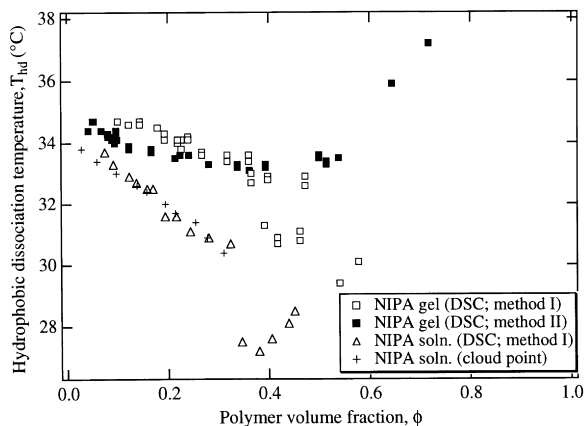


Fig. 4. Polymer volume fraction, ϕ , dependence of the hydrophobic dissociation temperature, T_{hd} , for gels prepared by method I (\square) and II (\blacksquare), and a comparison of the ϕ dependence of T_{hd} , for NIPA gels (squares) and poly-NIPA solutions (triangles). The cloud point temperature, T_{cloud} , for the poly-NIPA solutions is also plotted as a function of ϕ .

endotherm, obtained as the crossing point of the two tangents of the curve. We define this temperature as the hydrophobic dissociation temperature, T_{hd} . As shown in the figure, T_{hd} seems to be a decreasing function of ϕ for the gels prepared by method I, while that prepared by method II has a minimum around $\phi = 0.37$. Therefore, it is clear that T_{hd} is dependent on the history of sample conditioning. Note that the DSC runs were conducted not at the isobaric condition along the swelling curve (Fig. 1) but at the isochoric condition, as the scanning rate of DSC was usually much faster than the time required for the gel to adjust to new equilibrium. Therefore, ϕ is more or less fixed at the concentration at conditioning. This fact was confirmed in our previous paper, where the effect of structure relaxation during DSC runs was discussed [19].

Fig. 3 shows the plot of ΔH as a function of W for the equilibrated (closed circles) and non-equilibrated gels (open circles). As shown here, each of the data sets nicely falls on to a triangle function of W . This triangular plot indicates that the mechanism of hydrophobic dissociation changes from a water-deterministic (polymer-rich) process to a polymer-deterministic (water-rich) process at W_{st} . The top corner of the triangle corresponds to W_{st} (or ϕ_{st}), at which the water mole fraction of the hydrophobically bound water reaches a maximum. It is rather surprising that the triangular plot is dependent on the history of sample preparation. It should be noted that both sets of data coincide for $W > W_{st}$, i.e. the concentration region where excess water molecules are present around NIPA segment moiety. However, a distinct discrepancy in ΔH is detected for $W < W_{st}$. This indicates that the structure of the gels prepared by the two methods may be different. In the case of the non-equilibrated gels (prepared by method I), the value of W_{st} is pushed towards a higher value of W . This indicates that instability of phase separation takes place at a lower concentration (i.e. at a

larger value of W) for the gels prepared by method I. This finding will be verified in the following discussion in connection with Fig. 4.

3.2. Phase diagram of poly-NIPA aqueous systems

A disagreement is also found in the values of T_{hd} . Fig. 4 shows ϕ -dependence of the hydrophobic dissociation temperature, T_{hd} , for the gels prepared by method I (open squares) and II (closed squares), and of corresponding poly-NIPA solutions (open triangles). The cloud point temperature at which the phase separation takes place, T_{cloud} , is also shown with crosses for the poly-NIPA solutions. The cloud point was determined visually. As regards the comparison of T_{hd} for both the gels, the disagreement is more pronounced at $\phi = \phi_{st}$ (≈ 0.37). While T_{hd} is a convex function of ϕ having a minimum at $\phi = \phi_{st}$ for the gels prepared by method II, it has an anomalous dip at ϕ_{st} for the gels prepared by method I. It should be noted that T_{hd} was not detectable for $\phi > 0.8$ due to the absence of an endothermic peak. The results shown in Figs. 3 and 4 clearly suggest the following facts: the gels whose concentrations are adjusted by adding a given amount of water to the dried gels (method I) have more inhomogeneous structure than those prepared from equilibrated ones (method II). This may be due to the non-uniform distribution of water molecules over the gel. The gels I and II were prepared by the same method and have the same polymer volume fraction. The only difference was the method of concentration conditioning. Therefore, the remarkable difference in the thermal properties between the two systems must be related to the structure, i.e. more rigorously speaking, spatial inhomogeneities. According to our previous work on the preparation temperature dependence of NIPA gels on the static inhomogeneities [25] and on the thermal properties [20], it is reasonable to conjecture that different sample conditioning leads to different inhomogeneities. By taking account of this fact, we deal only with the gels prepared by method II, i.e. concentration-equilibrated gels for the discussion of hydrophobic dissociation. It should also be noted that the variations of T_{hd} and ΔH are strongly correlated with ϕ . T_{hd} and ΔH have a minimum and a maximum at ϕ_{st} , respectively, if the gel is conditioned through the equilibrated process (i.e. method II).

It is more suggestive to compare the T_{hd} between NIPA gels and the corresponding polymer solutions. In the case of poly-NIPA solutions, the polymer concentration was adjusted by adding water to dried poly-NIPA. Therefore, the data for poly-NIPA solutions correspond to the NIPA gels prepared by method I rather than by method II. As a matter of fact, the T_{cloud} curve falls on to the T_{hd} curve for the gel prepared by method I. It should be noted that method II could not be applied to the poly-NIPA solutions as it is based on the nature of gel, i.e. equilibrium swelling. T_{hd} 's for both NIPA gels and poly-NIPA solutions conditioned by method I have a steep dip at $\phi = \phi_{st}$. It is also worth noting that T_{cloud} is very close to T_{hd} of poly-NIPA solution for

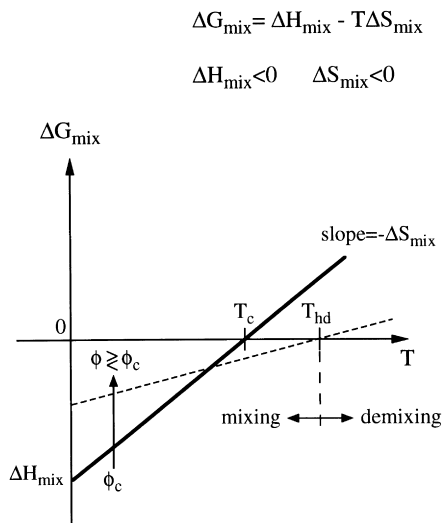


Fig. 5. Schematic diagram showing the free energy change by mixing, ΔG_{mix} , as a function of temperature. As both ΔH_{mix} and ΔS_{mix} are negative, ΔG_{mix} is an increasing function of T having a negative intercept. The absolute values of ΔH_{mix} and ΔS_{mix} becomes largest at $\phi = \phi_c$. This leads to the lowest value of $T_{\text{hd}} = T_c$ at ϕ_c .

$\phi < 0.35$ as shown in the figure. This strongly indicates that the onset of the endotherm of a DSC curve is identical to T_{cloud} . Therefore, T_{hd} can be regarded as the temperature at which a phase separation takes place. Marchetti et al. [26,27] also observed a cloud point curve for poly-NIPA aqueous solutions. Though their result is similar to the T_{cloud} curve in Fig. 4, the minimum is located around $\phi = 0.15$ (their work) instead of 0.4 (this work). Though the reason for this disagreement is not clear at this stage, it may also be due to the non-uniform solvation in the sample. Although the convexity is ascribed to the LCST nature of the poly-NIPA-water binary system, the location of the critical value of ϕ ($\equiv \phi_c$) is very important, where ϕ_c is the critical

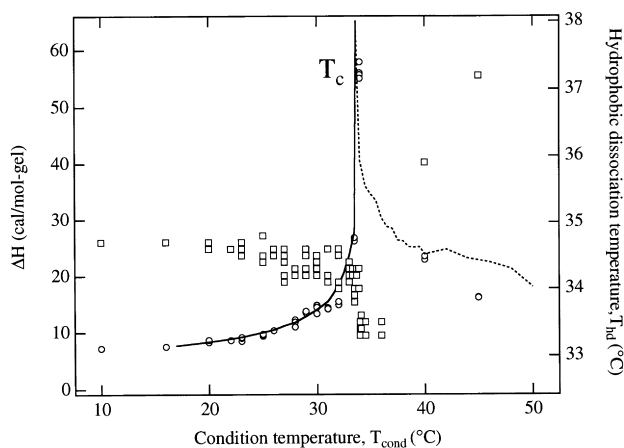


Fig. 6. T_{cond} dependence of the enthalpy, ΔH , (○) and temperature of hydrophobic dissociation, T_{hd} , (□) for the gels prepared by method II. The solid and dashed curves indicate ΔH calculated with Eq. (1) for $T_{\text{cond}} < T_c$ (i.e. $\phi < \phi_c$) and for $T_{\text{cond}} > T_c$ (i.e. $\phi > \phi_c$), respectively. The volume phase transition temperature, T_c , is also shown.

polymer concentration for phase demixing in the context of thermodynamics for binary solutions.

3.3. Thermodynamic consideration of hydrophobic interaction

Now we discuss the phase diagram of poly-NIPA aqueous solutions and gels. It is well-known that ϕ_c moves towards $\phi = 0$ on increasing the molecular weight of the polymer [28]. This is due to the fact that the translational entropy of polymers approaches zero by increasing the molecular weight. Therefore, it is expected that $\phi_c = 0$ for gels as the molecular weight of a gel is infinite. However, as shown in Fig. 4, both T_{hd} and T_{cloud} have a minimum at $\phi_c \approx 0.4$. This clearly indicates that the phase behavior is mainly governed by the hydrophobic interaction rather than the translational entropy. The Gibbs free energy for mixing ΔG_{mix} is written as

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}, \quad (3)$$

where ΔH_{mix} and ΔS_{mix} are the enthalpy and entropy of mixing, respectively. However, in the case of polymer-water system having hydrophobic interaction, ΔH_{mix} and ΔS_{mix} are decomposed into two contributions from polymer-water contact (p-w) and hydrophobic bonding of water molecules (HB) (in other words, iceberg formation), which can be symbolically written as

$$\Delta H_{\text{mix}} = \Delta H^{\text{p-w}} + \Delta H^{\text{HB}}, \quad (4)$$

$$\Delta S_{\text{mix}} = \Delta S^{\text{p-w}} + \Delta S^{\text{HB}}. \quad (5)$$

In the present case, as the polymer-water interaction is repulsive and the formation of iceberg is exothermic, the following inequality relations are derived,

$$\Delta H^{\text{p-w}} > 0, \quad \Delta H^{\text{HB}} < 0. \quad (6)$$

On the other hand, as the entropy of mixing is always positive but iceberg formation leads to a lowering of entropy, Then,

$$\Delta S^{\text{p-w}} > 0, \quad \Delta S^{\text{HB}} < 0. \quad (7)$$

As the phase behavior of the poly-NIPA water system is characterized by an LCST, the signs of ΔH_{mix} and ΔS_{mix} should be as follows,

$$\Delta H_{\text{mix}} < 0, \quad \Delta S_{\text{mix}} < 0. \quad (8)$$

Hence, ΔG_{mix} is an increasing function of T as schematically shown in Fig. 5. This figure indicates that the polymer is miscible at $T < T_{\text{hd}}$ and immiscible at $T > T_{\text{hd}}$. As T_{hd} is uniquely determined by

$$T_{\text{hd}} = \frac{\Delta H_{\text{mix}}}{\Delta S_{\text{mix}}}, \quad (9)$$

one can discuss the variation of T_{hd} as a function of ϕ . It is reasonable to expect that both $|\Delta H_{\text{mix}}|$ and $|\Delta S_{\text{mix}}|$ are largest

at ϕ_c and the plot of ΔG_{mix} vs. T has the lowest intercept and the largest slope at $\phi = \phi_c$.

3.4. Condition temperature, T_{cond} , dependence of ΔH and the relation between T_{hd} and T_c

In Fig. 6, ΔH is plotted as a function of the condition temperature, T_{cond} , at which the gel was conditioned. The variation of T_{hd} with respect to T_{cond} is also shown along the right axis. Interestingly, ΔH has a steep maximum around $T_{\text{cond}} = T_c$, i.e. the volume phase transition temperature, T_c . This figure shows a λ -shape transition of the specific heat reported by Li and Tanaka for NIPA gels [11]. However, they studied the heat capacity of a gel on an isochore line where the volume of the gel was fixed. In our case, in contrast, the λ -shape transition of ΔH is ascribed to the fact that the gels are on an isobar where an abrupt change in the gel volume is involved. This indicates that the largest amount of heat is required for the gel conditioned at T_c , and the value of ϕ conditioned at this temperature corresponds to the stoichiometric volume fraction, ϕ_{st} . The solid and dashed curves denote the ΔH curves calculated using Eq. (1) for $T_{\text{cond}} < T_c$ (i.e. $\phi < \phi_{\text{st}}$) and for $T_{\text{cond}} > T_c$ (i.e. ϕ_{st}), respectively. The following values, determined by the triangular plot in Fig. 3, were used to reproduce the ΔH vs. T_{cond} plot; $\Delta H_N = 851.8$ cal/mol-NIPA segment, $n = 12.4$, and $n_0 = 1.53$. Note that the gels prepared by method I give a smaller value of ΔH_N and larger values of n and n_0 ; $\Delta H_N = 820.5$ cal/mol-NIPA segment, $n = 15.2$, and $n_0 = 2.57$, which are in reasonable agreement with those reported in the previous paper [21]. However, it is disclosed in this work that ΔH_N becomes larger by careful conditioning. This means that a larger number of water molecules are involved in the hydrophobic dissociation in the case of the gels conditioned by method II than those conditioned by method I. However, ill-conditioned gels (prepared by method I) require more water molecules per NIPA segment, on an average, to stabilize the hydrophobic bonding because of the presence of excess water molecules which do not participate in the hydrophobic bonding. This is the reason why the value of n for the gels prepared by method I is larger than those prepared by method II. The same rule applies to the discussion on n_0 .

4. Conclusion

The enthalpy, ΔH , and the temperature of hydrophobic dissociation, T_{hd} , were studied as a function of polymer volume fraction, ϕ . A disagreement in the hydrophobic dissociation temperature at which an endothermic peak appears, T_{hd} , and in the enthalpy of dehydration, ΔH , was clearly detected between gels having different histories: one prepared by adding a given amount of water to a dried gel (non-equilibrated gels) and the other prepared by gradual shrinking by heating along the isobar line (equilibrated gels).

The phase diagram of the gels exhibited an LCST

behavior, typical of the hydrophobic polymer–water systems. However, the non-equilibrated gel shows an anomalous dip in the T_{hd} vs. ϕ plot around the stoichiometric volume fraction for hydrophobic bonding ($\phi = \phi_{\text{st}}$), indicating the presence of non-uniform solvation in the gel conditioned by a non-equilibrium process. Therefore, it is demonstrated that the non-uniform solvation in gels leads to an anomalous thermal response at ϕ_{st} . A similar phenomenon was also observed for poly-NIPA aqueous solutions. Regarding the LCST behavior, the presence of LCST at $\phi = \phi_{\text{st}} \approx \phi_c$ is successfully explained with a discussion on the mixing free energy where the contribution of the enthalpy and entropy of hydrophobic bonding (i.e. iceberg formation) is larger than that of polymer–water mixing.

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