Transition Enthalpy for a Poly(*N*-isopropylacrylamide) Based Polymer Gel Estimated from the Clapeyron Equation

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ABSTRACT: The applicability of the Clapeyron equation to the polymer gel system is demonstrated. It is shown that the stress dependence curve of the transition temperature of the gels undergoing the volume phase transition can be regarded as a phase boundary between swollen and collapsed phases. The enthalpy change at the volume phase transition is estimated from the Clapeyron equation for a poly(*N*-isopropylacrylamide) (PNIPA) based polymer gel. The transition enthalpy obtained by differential scanning calorimetry (DSC) measurements is estimated for a PNIPA based polymer gel and is compared with that obtained by the Clapeyron equation. It is shown that the transition enthalpy associated purely with the volume phase transition cannot be estimated by DSC while the Clapeyron equation gives the enthalpy change for the volume phase transition.

KEY WORDS Poly(*N*-isopropylacrylamide) Gel / Volume Phase Transition / Hydrophobic Hydration / Phase Separation / Clapeyron Equation / Differential Scanning Calorimetry /

As well known, some polymer gels in solvent show a discontinuous volume (V) change at a certain temperature.¹ Poly(*N*-isopropylacrylamide) (PNIPA) based ionic polymer gels, which are usually copolymerized with an ionic monomer such as sodium acrylate (SA), show the discontinuous volume change in response to an infinitesimal change of temperature (T).^{1–4} The transition temperature for the volume phase transition (T_V) depends on the composition and/or crosslink density. These gels in water remain in a swollen phase below T_V but shows a collapsed phase above T_V . Many studies have been made to clarify the nature of the volume phase transition of the gels.⁵ For example, the enthalpy change at the transition has been evaluated by calorimetry, mostly by differential scanning calorimetry (DSC).^{6–9} However, the volume phase transition for the PNIPA based gels is accompanied with the change in hydration around T_V , and also with the phase separation at almost constant volume unless the heating rate is sufficiently low. The latter can be avoided, of course, if heating is made very slowly, but the former appears to be essential to the PNIPA based gel systems regardless of the heating or cooling rates. This suggests that the change in enthalpy surely occurs in DSC measurements even if the gel system shows the continuous volume change. At present, there appears to be no study to estimate purely the enthalpy change associated with the volume phase transition.

It has been well recognized that there exists an analogy in phase behavior between the PNIPA based polymer gels and the van der Waals fluids (or, real gases) and the volume phase transition of the gels is classified into a first-order phase transition.¹ However, a phase diagram corresponding to the liquid-gas boundary in the pressure (p)- T plane for the van der Waals fluids has not been found experimentally. It is easily understood

that the osmotic pressure for the gel systems acts as the pressure for the van der Waals fluids. This means that the phase diagram exists in the osmotic pressure-temperature plane for the polymer gels. Theoretically speaking, the phase diagram must exist for the polymer gels, but in experiments such a phase diagram cannot be obtained so easily and was not actually obtained because experiments for the volume phase transition were conducted at equilibrium, namely, at the condition of zero-osmotic pressure. In the previous paper,¹⁰ we have reported that a phase diagram exists for the PNIPA based polymer gels under tension. The phase diagram allows us to estimate the transition enthalpy associated with the volume phase transition using the Clapeyron equation. The aim of this study is to estimate the transition enthalpy of a PNIPA based copolymer gel with relatively high ion content under tension from the Clapeyron equation. Then, the enthalpy change at the volume phase transition is compared with the change in enthalpy obtained by DSC.

PHASE DIAGRAM AND HEAT OF TRANSITION FOR PNIPA BASED GELS

We have reported¹⁰ that a PNIPA homopolymer gel and a PNIPA based copolymer gel with small amount of ionic groups show the volume phase transition and T_V depends on the applied tension (or, stress). The compositions of these gels were relatively close to the critical composition. In the previous paper,¹⁰ it was suggested that the Landau-type free energy can well describe the basic feature of the volume phase transition, although the applicability is limited only to the region near the critical point. It was also found¹⁰ that the stress dependence curve of T_V can be regarded as a coexistence curve for the gels in the T - p plane if the average pressure (the pressure difference between the inside and outside of the gels, and is also expressed by p) generated by the appli-

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Figure 1. Schematic representation of the coexistence curves for PNIPA based gels (left) at swelling equilibrium in solvent and van der Waals fluids (right). Here, cp stands for the critical point.

cation of mechanical stress is used, *i.e.*, $p = -\text{Tr}\sigma/3$ (σ ; external stress). This coexistence curve divides the T - p plane into two regimes: one is a swollen phase and the other a collapsed phase of the gels. A pair of the coexistence curves, the T - p and V - T curves, for the gels allows us to calculate the transition enthalpy associated with the volume phase transition (ΔH_V). Figure 1 schematically represents a pair of the coexistence curves for the polymer gels together with those for the van der Waals fluids. The curve in the T - V plane for the gels corresponds to the p - V curve for the van der Waals fluids, and the T - p curve for the gels to the p - T curve for the van der Waals fluids. The T - p curve for the gels also starts from (or, ends at) the critical point where the gels show the continuous volume transition, as in the case of the van der Waals fluids. This is expected from the experimental data for the gel with composition close to the critical composition.¹⁰

Consider the volume phase transition of PNIPA based polymer gels in swelling equilibrium in solvent. In this case, the swollen and collapsed phases as well as the pure solvent (water) coexist at the transition point. We think that the presence of free ions in the gel is not essential to the estimation of the transition enthalpy at the volume phase transition because some of neutral PNIPA gels show a discontinuity.¹¹ The equilibrium conditions in this situation are given by

$$\mu_p^I = \mu_p^{II} \quad (1)$$

$$\mu_s^I = \mu_s^{II} = \mu_s^0 \quad (2)$$

where μ_p and μ_s are respectively the chemical potentials of the polymer network and solvent in the gel, μ_s^0 being the chemical potential of pure solvent. The superscript I

means that the chemical potential with the superscript is for the swollen phase, and the quantity with superscript II for the collapsed phase. Equation 2 is automatically satisfied as long as the transition occurs in swelling equilibrium. This may mean that we have only to focus basically on how the polymer network changes its dimension in the space where solvent molecules are fixed. In other words, the problem of the volume phase transition of polymer gels in solvent may be reduced to that of the volume transition of one-component system, namely, of the skeleton (polymer network). From eq 1, we can obtain the following Clapeyron-type equation for the polymer gel system.

$$\Delta H_V = T_V \Delta V_V \left(\frac{dp}{dT} \right)_{\text{coex}} \quad (3)$$

Here, ΔH_V and ΔV_V are respectively the changes of the partial molar enthalpy and volume of the polymer network. The quantity ΔV_V actually corresponds to the apparent volume change of the gel composed of 1 mol network polymer, because the addition of the dried network to a gel phase increases the volume of the gel and the increased volume is proportional to the amount of the network added. Namely, the apparent gel volume for 1 mol network is equal to the partial volume of the network at equilibrium. The derivative in eq 3 is the value on the coexistence curve. The fact that the T - p curve surely exists for the gel systems allows us to estimate ΔH_V of the polymer gel systems from eq 3. We think that it is better to define the heat of transition for the volume phase transition of the polymer gels by ΔH_V , because ΔH_V is related only to the conformational change or transition of the constituent polymer chains in the network. The non-zero value of ΔH_V is obtained as long as the gel specimen undergoes a discontinuous volume change, but the value becomes zero when the change becomes continuous. When a uniaxial stress is applied to the gel specimens, the above equation can be re-written as

$$\Delta H_V = -\frac{T_V \Delta V_V}{3} \left(\frac{d\sigma}{dT} \right)_{\text{coex}} \quad (4)$$

where σ is the applied stress. It is implicitly assumed here that the strains induced by the applied tension are small enough compared with those by the volume change; namely, the apparent volume change is almost isotropic.

EXPERIMENTAL

A cylindrical *N*-isopropylacrylamide (NIPA)-SA copolymer gel, coded as PNS40, was prepared by radical copolymerization technique at 20°C. Pregel solution of the amount of 100 mL was prepared using distilled water as a solvent. Molar concentrations of NIPA and SA were 1499 mM and 40 mM, respectively. *N,N'*-methylene-bis(acrylamide) (BIS) and ammonium peroxodisulfate (AP) were respectively used as a crosslinker and an initiator. Their concentrations were 25.7 mM (BIS) and 3.5 mM (AP). In the reaction, *N,N,N',N'*-

Table I. The number of metal weights, polymer concentration at 30.0°C (c), transition temperature (T_V), and changes in volume (ΔV_V) and enthalpy (ΔH_V) at T_V

No. of weight	$\Delta V_V / 10^{-6} \text{ m}^3 \text{ g}^{-1}$	$T_V / ^\circ\text{C}$	$c / \text{g cm}^{-3}$	$\Delta H_V / \text{J g}^{-1}$
0	-1.08	33.35	0.22	2.7
1	-1.06	33.55	0.21	2.6
2	-1.05	33.75	0.20	2.6

tetramethylethylenediamine (TEMED) (240 μL) was also used as an accelerator. The total monomer content prepared was 15 wt%. The pregel solution was then poured into glass tubes and the gelation was performed. After the gelation, the cylindrical specimens were immersed into distilled water to wash out the reaction residues and to achieve the equilibrium swelling. The polymer content after the equilibrium swelling was 12 wt% at 20°C. The gel specimen was fixed in a specially designed water bath, and the diameter and length were measured as a function of temperature. At 30°C, the diameter (d) of the cylindrical specimen was *ca.* 300 μm . The temperature was varied at an interval of 0.1°C. The accuracy in controlling water temperature was $\pm 0.02^\circ\text{C}$. The equilibration after the T jump of 0.1°C required 4–8 h depending on the temperature; the required time became longer with approaching T_V . For uniaxial elongation, a metal weight (35 mg) was used. The elongation was carried out in the water bath. The concentration (c) of the gel under and without loading is tabulated in Table I; c decreases slightly with increasing load. The DSC measurements were carried out using a Seiko DSC6200 on heating. The weight of the specimen was *ca.* 20 mg and the heating rate (v) ranged from 1 to 10°C min $^{-1}$.

RESULTS AND DISCUSSION

Figure 2 shows the plot of V against T for PNS40. The gel shows the swollen state at low temperatures and the collapsed state at high temperatures. The volume V increases with increasing σ , namely, increasing the number of weights in the swollen state. The order is reversed in the collapsed state. This may be due to the downward shift of the transition region: the region moves to the smaller volume side as the tension increases, although we do not know the reason of the downward shift at present. Each of the V - T curves shows no hysteresis and T_V , determined as an average of the onset and completion temperatures, increases with increasing σ . The change in volume of the gel specimen per unit mass of the network, which we also write ΔV_V , is summarized in Table I together with T_V . The quantity ΔV_V is almost constant independently of σ . The stress dependence of T_V is shown in Figure 3. In this experiment, tension was kept constant because one or two pieces of metal weights were stuck on the gel. This means that tension was kept constant over the T range examined while the stress acting on the gel is T -dependent because the cross-sectional area of the specimen changes with T . Then, the true stress at 30°C (designated as σ_{30}) is used here as a stress measure. The transition temperature T_V increases linearly as σ_{30} increases. As stated previously, the plot corresponds to the coexistence curve for the gel, and the gel remains in the swollen state below the line while the

Figure 2. Temperature (T) dependence of volume (V) for PNS40. **Figure 3.** Plots of transition temperature for volume phase transition (T_V) against true stress at 30.0°C (σ_{30}) for PNS40.

region above the line corresponds to where the collapsed phase emerges. Since the slope of the line is estimated to be $2.43 \times 10^4 \text{ Pa K}^{-1}$, we can calculate the change in enthalpy per unit mass of polymer network at the transition (here, we re-define it as ΔH_V) for the gel from eq 4. The calculated value of ΔH_V is also tabulated in Table I. As can be seen from the table, the value remains almost constant lying around 2.6 J g^{-1} .

In the DSC thermograms on heating, two kinds of the transitions (namely, the changes in enthalpy) may appear for the PNIPA based gels. In this case, the overall change per unit mass of a polymer network (ΔH_{DSC}) must be divided into the two terms: one is related to the partial molar enthalpy of solvent, the other corresponding to the partial molar enthalpy of the network.

$$\Delta H_{\text{DSC}} = \Delta H_{\text{DH}} + \Delta H_{\text{VC}} \quad (5)$$

Here, ΔH_{DH} is the enthalpy change due to the dehydration of the hydrophobic hydration. The term ΔH_{VC} is the enthalpy change due to the conformational transition of the network detected by the DSC measurements, and is expected to approach ΔH_V at $v \rightarrow 0$. Basically, ΔH_{DH} will

Figure 4. A DSC thermogram of PNS40 at a heating rate of $1^{\circ}\text{C min}^{-1}$.

be independent of v and always contributes to ΔH_{DSC} , although we do not know the detailed nature of the dehydration. In some cases, the PNIPA based gels become opaque around a certain temperature on heating while the volume change progresses continuously, resulting from the formation of a domain structure due to the spinodal decomposition occurring in the gels. This is because v is not balanced with the rate of the volume change during the DSC runs. When v is high enough (namely, when the phase separation occurs), the transient effects due to the spinodal decomposition, which are believed to contribute to ΔH_{DSC} as a change in the internal energy,⁹ becomes large. For the PNIPA based gels investigated in this study, the equilibration of the volume initiated by the change of T of 0.1°C required several hours, as stated in the experimental section. This gives the estimation that v showing the limiting value of ΔH_{VC} (ΔH_{V}) is smaller than the order of $10^{-4}^{\circ}\text{C min}^{-1}$, which can never be attained by our DSC apparatus.

A typical DSC thermogram of PNS 40 at $v = 1^{\circ}\text{C min}^{-1}$ is shown in Figure 4. In the figure, a broad endothermic peak is observed at about 38°C . The rather large broadening may be explained by the superposition of the two dominant transitions, the change in hydration and the phase separation, although we can not clarify at present whether they actually differ in transition temperature. Actually, a broad peak, just similar to the one in Figure 4, has also been observed on the DSC thermograms for PNIPA based polymer gels measured under an isochore condition. The transition temperature determined at the

Table II. Summary of DSC experiments. The heating rate (v), transition temperature determined at the onset point (T_{DSC}), and the transition enthalpy (ΔH_{DSC})

$v/^{\circ}\text{C min}^{-1}$	$T_{\text{DSC}}/^{\circ}\text{C}$	$\Delta H_{\text{DSC}}/\text{J g}^{-1}$
1	35.7	10
2	36.0	10
5	36.4	11
10	37.1	10

onset point (T_{DSC}) and ΔH_{DSC} are summarized in Table II. The temperature T_{DSC} is slightly higher than T_{V} without loading (Table I), and also increases with increasing v . The enthalpy change ΔH_{DSC} remains almost constant, around 10 J g^{-1} independently of v . This value is much larger than ΔH_{V} , the enthalpy change for the equilibrium volume phase transition (see Table I). Even if a DSC measurement is made at sufficiently low v , the enthalpy change obtained must contain ΔH_{DH} other than ΔH_{V} , and each of them cannot be estimated separately by calorimetry. At present there may exist no method other than the use of the Clapeyron equation to estimate pure ΔH_{V} .

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