

# Effect of Hydrophobic Substances on the Volume-Phase Transition of *N*-Isopropylacrylamide Gels

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Received: July 10, 2000; In Final Form: January 31, 2001

The effects of the addition of hydrophobic substances on the volume-phase transition of *N*-isopropylacrylamide (NIPA) hydro gels were investigated. The volume transition temperature of NIPA gel was reduced by adding hydrophobic substances, such as benzoic acid (BA) and phenol (Ph), into the solution surrounding the gel. The degree of binding of BA or Ph to the NIPA gel was found to increase in a transition-like manner simultaneously with discontinuous volume shrinkage. The lowering of the transition temperature relates to the degree of binding of BA and Ph to the NIPA gel in the collapsed state. Fourier transform infrared (FT-IR) spectra of the Ph binding gel suggest that the hydrogen bond forms between the amide group of the NIPA and the hydroxyl group of Ph.

## 1. Introduction

The volume-phase transition of gel is a phenomenon of discontinuous volume change in continuously varying physical conditions such as temperature and solvent composition. In the course of the transition, the solvent molecules transitionally enter or escape the gel network under varying conditions. This phenomenon has been actively studied for possible application to chemical switching and drug delivery.<sup>1–3</sup> However, there remains much to be unsolved regarding the interaction between the small molecules and the gel chains in the transition.

*N*-Isopropylacrylamide (NIPA) hydro gel is well-known to exhibit volume-phase transition at about 34 °C.<sup>4</sup> The transition temperature decreases with the addition of inorganic salts<sup>5</sup> or saccharide<sup>6</sup> to the gel system. Our recent studies<sup>6–8</sup> have revealed that the chemical potentials of water molecules estimated for the salt solutions at the transition points are almost identical. The volume-phase transition occurs when the chemical potential of the water molecules in bulk becomes lower than that of the water molecules hydrated to the polymer chain. Raising the temperature has the effect of decreasing the chemical potential of water molecules in bulk to lower than that at the transition point, and the transition takes place. The addition of inorganic salts<sup>5</sup> or saccharide<sup>6</sup> has the effect of reducing the chemical potentials of water molecules in bulk, thus lowering the transition temperature.

The transition temperature of the NIPA hydro gels is also reduced by the addition of alcohol and several hydrotropes to the surrounding solution of the gel.<sup>9–13</sup> From the Raman spectra of the solution, Nishio et al.<sup>10</sup> concluded that the entropy of the bulk water increases due to the disintegration of the clustered water molecules induced by the additive. The increase in entropy results in the reduction of the chemical potential of bulk water, thus destabilizing the hydration of the gel chains and causing the gel to shrink.<sup>9,10</sup> In this respect, the addition of alcohol or phenol is considered to have the same effect as inorganic salt and saccharide on the volume-phase transition. Although a qualitative explanation<sup>11</sup> for the lowering of the transition temperature has been proposed on the basis of single-liquid approximation,<sup>14</sup> as yet trials have been unsuccessful without

including the chain volume fraction dependence of the attractive interaction between water and alcohol.

In most explanations proposed to date, the binding of small molecules to the gel chain has been ignored. This binding can change the affinity of the chain to the solution and thus affect transition behavior. To clarify the mechanism responsible for the change in transition temperature, the change in the degree of binding in the transition should be evaluated. In the present experiment, the binding of benzoic acid (BA) and phenol (Ph) molecules was examined for the NIPA gel system in the vicinity of the transition. We found that discontinuous binding was accompanied with the discrete volume reduction of gel and that the lowering of the transition temperature is directly related to the extent of binding of BA or Ph to the gel. The transition temperature decreased significantly in the 10 mM BA or Ph solution, in which the chemical potentials of water molecules were found to be almost identical to that of ordinary water from osmolarity measurements. This indicates that the mechanism responsible for the lowering of the transition temperature of NIPA gel by the addition of BA and Ph differs from that of inorganic salts. In this study, the influence of the addition of BA and Ph on volume-phase transition behavior was examined. The effect of the addition of Ph on the amide group of NIPA was also examined, utilizing Fourier transform infrared (FT-IR) spectroscopy.

## 2. Experimental Section

Poly(*N*-isopropylacrylamide) (PNIPA) was prepared by radical polymerization in 10-mL aqueous solutions of NIPA (1 M) and ammonium persulfate (APS) (5 mM), with 24  $\mu$ L of *N,N,N',N'*-tetramethylethylenediamine (TEMED) at 5 °C. The PNIPA prepared was dialyzed in distilled water in order to remove the residual monomer. NIPA gels were prepared in the same way, except for the addition of *N,N'*-methylenebisacrylamide (BIS) (5 mM) as a cross-linking agent. The gels, polymerized into a plate form of 1-mm thickness or a cylindrical form of 0.3-mm diameter, were rinsed thoroughly with distilled water and dried in a vacuum. The plate and cylindrical gels were cut into small pieces (5-mm square and 10-mm length).

NIPA monomer was supplied by Kohjin Co., Ltd., and all other chemicals used were of analytical grade. Distilled water was used.

The cylindrical gel was used to obtain the dependence of gel size on both concentration and temperature because the equilibrium of the gel system was reached within several hours after altering the conditions. The gel was immersed in an aqueous solution of a given concentration of BA or Ph, at a given temperature, and allowed to stand in the solution to achieve equilibrium. The diameter of the gel was measured using a computer-aided optical microscope system.<sup>15</sup> For examining hysteresis, size measurements for one gel were made for successive steps of concentration and temperature.

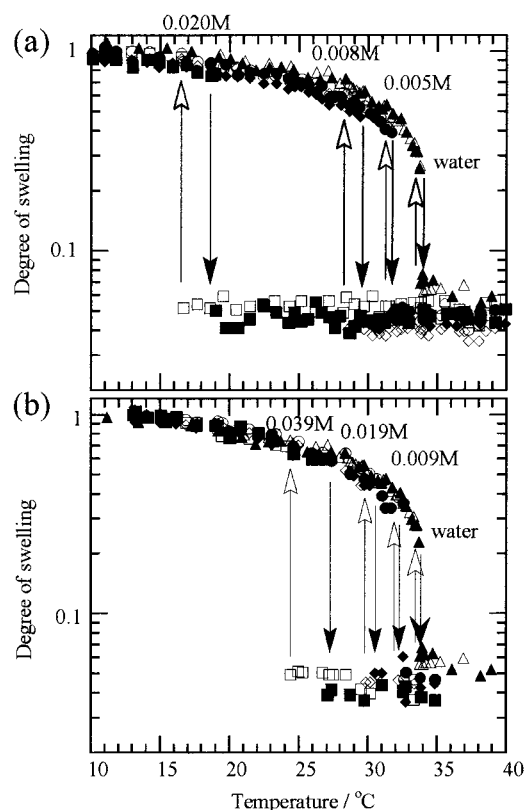
To obtain the binding isotherm of BA and Ph to the gel, the amount of these hydrophobic substances bonding to the plate gels was evaluated as follows. The gel was immersed in a solution of a given concentration of BA or Ph at 35 °C. The weight of dry gel  $w_{\text{dg}}$ , the weight of the solution  $w_{\text{sol}}$ , and the concentration of additive in the solution  $C_{\text{out}}^0$  were measured before immersing the gel in the solution. The temperature was slowly (0.1 °C/min) changed from 35 °C to a given final temperature. The gel was allowed to stand for more than 2 weeks at constant temperature to achieve binding equilibrium with the solution. The concentration of additive in the solution at equilibrium  $C_{\text{out}}$  was obtained from the optical absorbance at 226.6 nm for BA and at 269.6 nm for Ph, using a UV/VIS spectrophotometer (U-best 50, Jasco, Japan). The equilibrium weight of the gel  $w_{\text{sg}}$  was also measured. The degree of binding of the additive to one monomeric unit of gel chain  $\beta$  can be obtained from the following equation:

$$\beta = 113.16w_{\text{sol}}(C_{\text{out}}^0 - C_{\text{out}})/w_{\text{dg}} \quad (1)$$

Here, the unit of concentration used is molality. The concentration of additive in the gel fluid was assumed to equal to  $C_{\text{out}}$ . In most cases, the experiments were carried out for a small total volume of gel and solution as far as possible in order to afford a large difference between  $C_{\text{out}}$  and  $C_{\text{out}}^0$  and thus suppress the experimental errors of  $\beta$ . For ascertaining the reliability of the experiment, the amount of Ph in certain gels was examined by discharging Ph from the gels as follows. The gel, equilibrated with the Ph solution, was immersed in *N,N'*-dimethylformamide (DMF) and then the Ph concentration in the DMF solutions was obtained from the absorbance of the solution at 279.4 nm using the spectrophotometer. The difference between the results obtained from discharging and those from differentiating was within 10%. The weight of water present in the gel was evaluated by subtracting the sum of the dry gel weight and the weight of binding Ph or BA from the equilibrated gel weight.

In the experiments mentioned above, the pH of the BA solution was adjusted to 2 by adding HCl for BA to be non-ionized. The temperature dependency of the gel volume in the solution at pH 10 after such an operation as immersing the gel in the solution at pH 2 for 2 weeks was completely the same as that before the operation. This indicates that no hydrolysis of amide group is induced by the operation, since the hydrolyzed gel, the partly ionized gel, should exhibit a different temperature dependency from that observed.<sup>16</sup>

The ATR attachment (Shimadzu ATR 8100H, Shimadzu, Japan) for attenuated total reflection spectroscopy was mounted on the FT-IR spectrometer (Shimadzu FT-IR 8600, Shimadzu, Japan). The plate gel, equilibrated with a solution of a given concentration of Ph (0 and 600 mM) at 40 °C was placed on the ZnSe prism of the ATR for FT-IR measurement. A 10 wt/

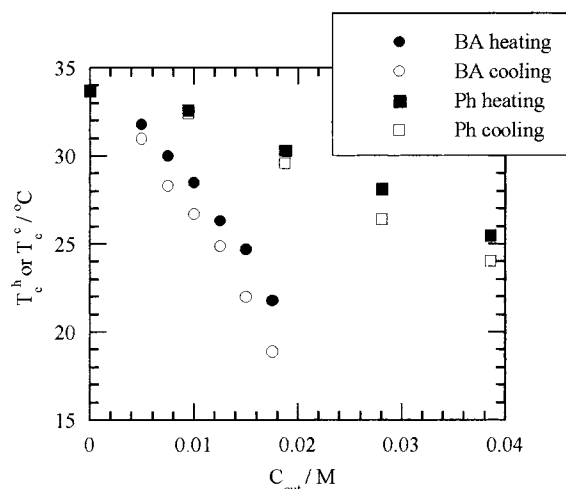


**Figure 1.** Temperature dependence of degree of swelling in solutions of (a) BA and (b) Ph.  $C_{\text{out}}$  of BA and Ph are indicated in the figure. Degree of swelling is the ratio of gel volume to volume of gel at 10 °C. Transitions are indicated by arrows. Closed and open symbols represent heating and cooling processes, respectively. pH of BA solution was adjusted to 2 by adding HCl.

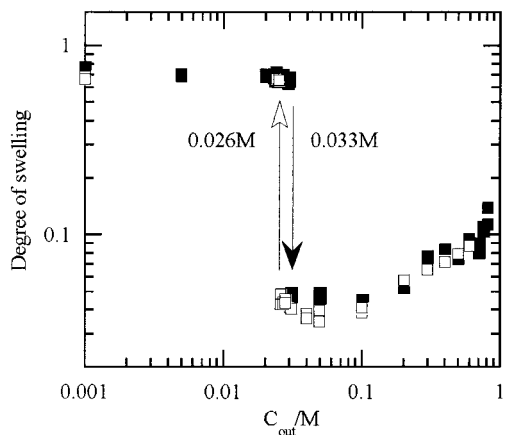
wt % PNIPA—acetone solution was cast into the film on a tetrafluoroethylene plate. The film cast was then dried in a vacuum. The KBr disk containing the solid Ph was prepared at room temperature using the compressor (hand press SSP-10A, Shimadzu, Japan) of the FT-IR apparatus. The FT-IR spectra of the NIPA gel, the PNIPA film, the solid Ph, and the PNIPA—THF solutions were obtained with a resolution of 2  $\text{cm}^{-1}$  at room temperature.

### 3. Results

Figure 1 shows the temperature dependence of the degree of swelling of the gel in the aqueous solutions for various BA and Ph concentrations. The degree of swelling of the gel,  $V/V_0$ , is defined as  $(d/d_0)^3$ , where  $d$  and  $d_0$  represent the diameters at a given temperature and at 10 °C, respectively. The degree of swelling  $V/V_0$  decreases continuously with increasing temperature. The transition temperature decreases with increasing BA and Ph concentration. This type of concentration dependence of the transition temperature has also been observed in the volume-phase transition of gel in a salt solution.<sup>5,7</sup> The decreasing tendency of  $V/V_0$  of the gel in the swollen state with increasing temperature is insensitive to the concentration of the additive, as shown in Figure 1. This differs from the shrinking behavior<sup>5,7</sup> of the gel in the salt solutions, in which the shrinking behavior of gel has a salt concentration-dependent temperature shift. There transition has a degree of hysteresis in that the transition temperature in the heating process  $T_c^h$  is significantly greater than the transition temperature in the cooling process  $T_c^c$ . It should be noted that both the amplitude of hysteresis ( $T_c^c - T_c^h$ ) and the transitional volume change increase with



**Figure 2.** Transition temperatures of NIPA gel against  $C_{out}$ . Closed and open symbols represent heating and cooling processes, respectively.  $T_c^h$  = transition temperature in heating process,  $T_c^c$  = transition temperature in cooling process.



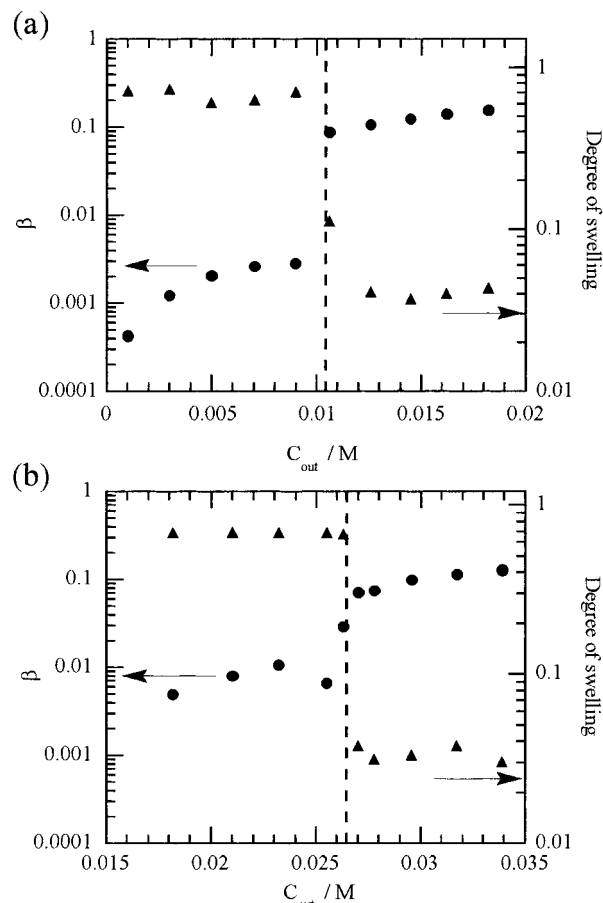
**Figure 3.** Degree of swelling of gel in Ph solutions as a function of  $C_{out}$  at 26.5 °C. Open and closed symbols represent increasing and decreasing processes in  $C_{out}$ , respectively.

increasing  $C_{out}$ . Figure 2 shows the  $C_{out}$  dependence of  $T_c^h$  and  $T_c^c$  for BA and Ph. The lowering of the transition temperature, as well as the amplitude of hysteresis in the aqueous solution of BA, is greater than for Ph at the same  $C_{out}$ .

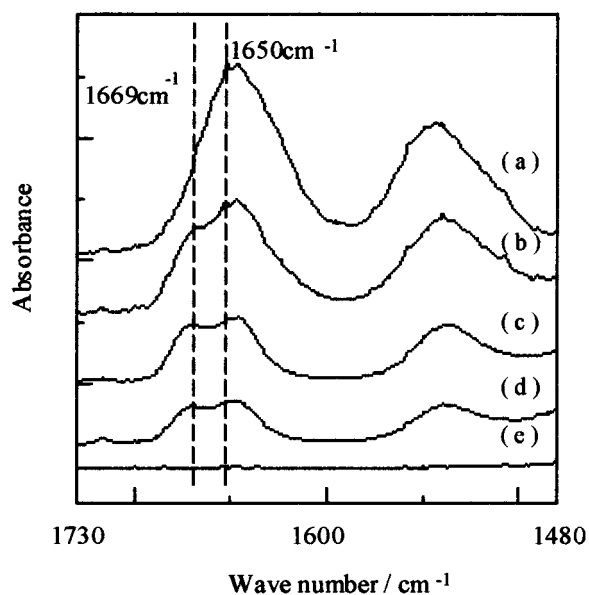
The volume-phase transition of NIPA gel was also induced for various  $C_{out}$  of Ph and BA at constant temperature, as shown in Figure 3. Hysteresis is again observed for transition concentration. The discontinuous volume shrinkage is observed at higher concentrations than that at which discontinuous volume swelling occurs. It should be noted that the volume of gel in the swelling state is independent of  $C_{out}$  and that the volume of gel gradually increases as  $C_{out}$  increases above 0.1 M.

Figure 4 shows the dependence of the degree of binding  $\beta$  on  $C_{out}$  and  $V/V_0$  for BA and Ph at 26.5 °C. The discontinuous change in  $\beta$  is observed at the same  $C_{out}$  as that at which the volume-phase transition occurs. It is notable that  $\beta$  in the collapsed state ( $\sim 0.1$ ) is always higher than that in the swelling state ( $\sim 0.01$ ).

Figure 5 shows FT-IR spectra for the PNIPA film and THF solution of PNIPA. Amide I and II bands were observed at 1650 and 1544  $\text{cm}^{-1}$ , respectively, in the spectrum of the PNIPA film. The absorbency peaks in the amide I band of the PNIPA in the THF solution split into two peaks at 1669 and 1650  $\text{cm}^{-1}$ . The split of the amide I band becomes more apparent with increasing THF concentration, as shown in Figure 5. However, no



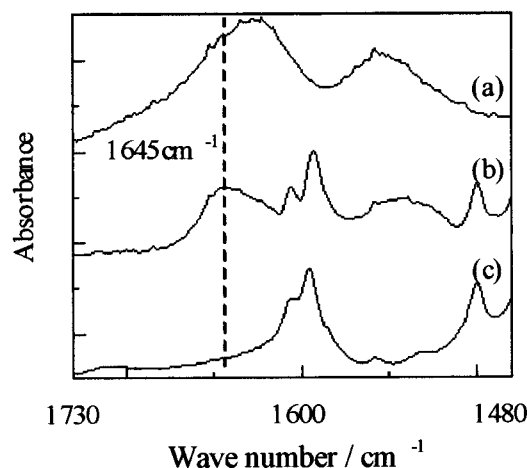
**Figure 4.** Degree of binding ( $\beta$ ) and degree of swelling against  $C_{out}$  of (a) BA and (b) Ph at 26.5 °C. Degree of swelling is the ratio of gel volume to volume of gel in nonadditive solution. Broken line indicates transition point. Closed circles and triangles represent degree of binding and degree of swelling, respectively.



**Figure 5.** IR spectra in amide I and II region obtained for NIPA-tetrahydrofuran system: (a) PNIPA film, (b) THF solution of PNIPA 20 wt %, (c) 10 wt %, (d) 5 wt %, and (e) pure THF.

significant shift of the amide II band at 1544  $\text{cm}^{-1}$  was observed in the spectra of the PNIPA-THF mixtures.

Figure 6 shows the FT-IR spectra of the solid Ph and the collapsed NIPA gels, which were both equilibrated with aqueous solutions of 0 and 600 mM Ph. Amide I and II bands were

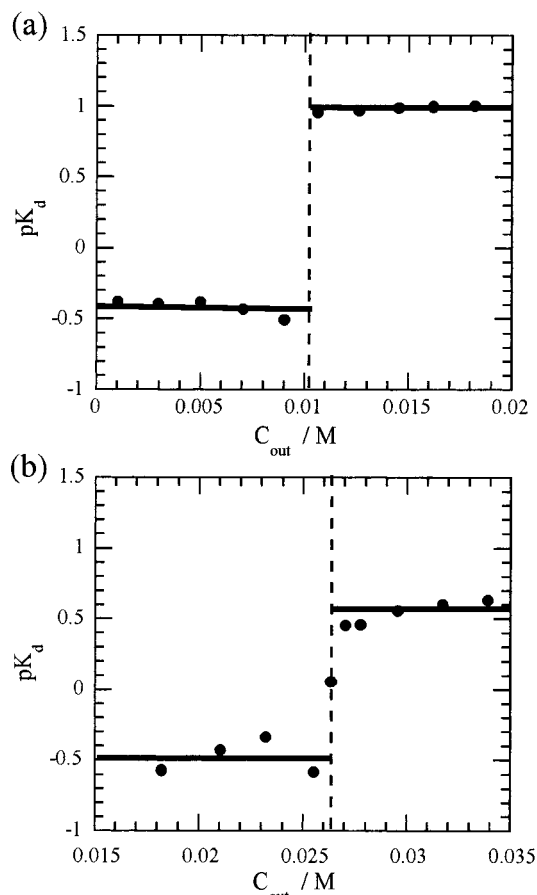


**Figure 6.** Effect of Ph on IR spectra of NIPA gels. Spectra a and b were obtained for collapsed gels, taken from (a) no-additive solution and (b) 600 mM Ph solution. Spectrum c is for Ph in the solid state.

observed at 1623 and 1558  $\text{cm}^{-1}$ , respectively, in the spectrum of the gel equilibrated with the 0 mM Ph aqueous solution. In contrast, the amide I and II bands in the spectrum of the gel equilibrated with the 600 mM Ph aqueous solution shift to higher and slightly lower frequencies, respectively, than those in the spectrum for 0 mM Ph. The peaks at 1606 and 1593  $\text{cm}^{-1}$  observed in the spectrum of the solid Ph are attributable to C—C stretching bands and are also observed in the spectrum of the gel equilibrated with the 600 mM Ph aqueous solution. The numbers of water and Ph molecules in the collapsed gel equilibrated with the 600 mM Ph aqueous solution were found to be  $0 \pm 0.3$  and  $1.3 \pm 0.1$  per NIPA monomeric unit, respectively, from the binding experiment. The number of water molecules in the collapsed NIPA gel equilibrated with 0 mM Ph solution was 2.2. Thus, it is suggested that the presence or absence of water molecules in the gel induces the amide I and II bands mentioned above.

#### 4. Discussion

The temperature dependence of  $V/V_0$  in the swelling regime is independent of  $C_{\text{out}}$ , as shown in Figure 1. Accordingly, no change in the gel volume is observed for the addition of BA or Ph in the swelling regime at constant temperature. This differs from the effect of salt, as the addition of salt causes the gel volume to decrease at constant temperature. The fact that the gel volume does not change with the addition of BA or Ph suggests that the change in the chemical potentials of water molecules in bulk induced by the BA or Ph is negligible. This was confirmed by osmolarity measurements, in which osmolarity did not exhibit any dependence on BA or Ph concentration. Another difference in the effects of BA or Ph compared to that of salt is the volume change at the transition; the volume change increases with BA or Ph concentration, whereas the volume change is insensitive to salt concentration. These facts indicate that the mechanism responsible for the drop in transition temperature that occurs with the addition of BA or Ph is different from that of inorganic salts. It should be taken into account that the binding of BA or Ph molecules to the gel chain accompanies the transition, as shown in Figure 4. However, salt has not been observed to bond with the gel at transition.<sup>17</sup> The binding of BA or Ph to the collapsed gel chain is considered to be caused by not only hydrophobic interactions between the phenyl group of the BA or Ph and the isopropyl group of NIPA but also the formation of hydrogen bonds between the functional



**Figure 7.**  $pK_d$  versus  $C_{\text{out}}$  of (a) BA and (b) Ph at 26.5 °C. Broken line indicates transition point.

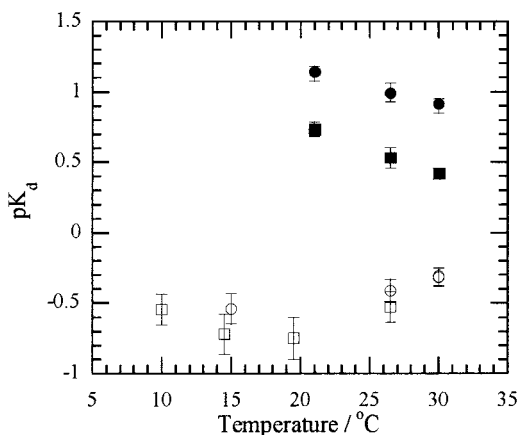
group of BA or Ph and the amide group of NIPA. The result of this is that the aqueous solution adopts a poor affinity for the gel chain, thus stabilizing the collapsed state.

The bonding state is analyzed assuming that each NIPA monomer unit contains one binding site for BA or Ph. A dissociation constant  $K_d$  is described as follows:

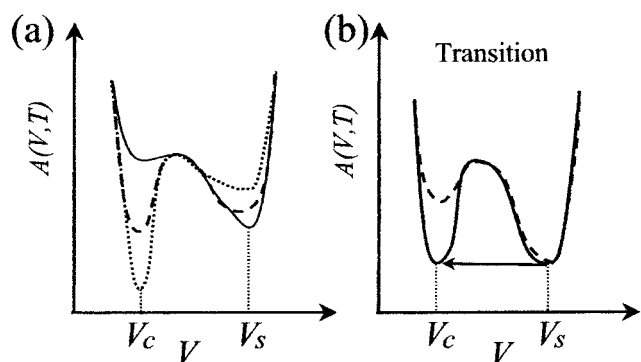
$$K_d = C_{\text{out}}(1 - \beta)/\beta \quad (2)$$

Figure 7 shows the  $C_{\text{out}}$  dependence of  $pK_d$  ( $= -\log k_d$ ) for the binding of BA and Ph at 26.5 °C. The  $pK_d$  values for the swelling and collapsed gels are found to differ from each other and to be independent of  $C_{\text{out}}$  and  $\beta$ . The constancy of  $pK_d$  is indicative of the thermodynamic independence of the binding sites or of no interaction between the BA and Ph binding sites. Figure 8 shows the temperature dependence of  $pK_d$ , from which  $pK_d$  in the collapsed state can be seen to decrease with increasing temperature, whereas  $pK_d$  in the swelling state appears to be independent of temperature. This indicates that the binding of BA and Ph to the collapsed NIPA gels is exothermic. The formation of hydrogen bonds between the amide group of NIPA and the hydroxyl group of Ph or BA in binding may explain the exothermic binding. It should be mentioned that the disruption of hydrophobic hydration and mediation of the association by hydrophobic interactions are endothermic processes.<sup>18</sup> In the binding of BA and Ph, the hydrophobic interactions are considered to fill a specific role because of their hydrophobic nature. The fact that the binding is exothermic suggests that the exothermic energy of the hydrogen bond between BA or Ph and NIPA exceeds the endothermic energy of the dehydration of BA or Ph.



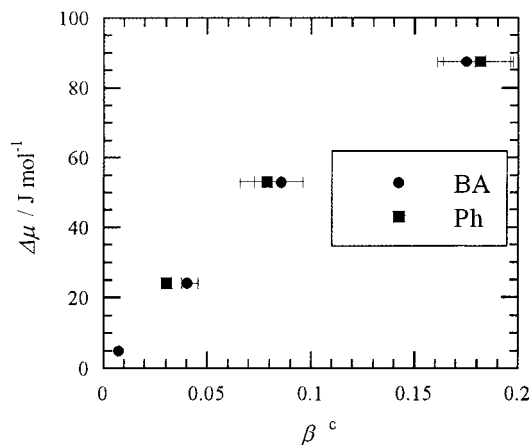


**Figure 8.** Temperature dependence of  $pK_d$ . Closed and open symbols represent collapsed and swelling states, respectively. Circle and square symbols denote BA and Ph, respectively.



**Figure 9.** Schematic volume dependence of free energy of NIPA gels for (a) constant  $\beta$  and (b) volume-phase transition induced by hydrophobic additive.  $A(V,T)$  is free energy of gel with volume  $V$  at temperature  $T$ .  $V_s$  and  $V_c$  represent  $V$  in swollen and collapsed states, respectively. (a) Solid, broken, and dotted lines represent  $A(V,T)$  of gels with null, low, and high values of  $\beta$ , respectively. Binding of additive decreases the free energy of the collapsed state and increases that of the swollen state. (b) Solid and broken lines represent  $A(V,T)$  with and without additive, respectively.  $A(V,T)$  with additives is similar to that without additives at  $V = V_s$  because  $\beta$  value of gel with additive is almost zero at  $V = V_s$  in actual systems. Arrow indicates volume-phase transition.

The free energy of the hydrated segment in the swollen gel is lower than that in the collapsed gel and that of the dehydrated segment in the collapsed gel is lower than that in the swollen gel. Hydrophobic molecules bind to the dehydrated segment, thus reducing the free energy of the dehydrated segment in the collapsed state and increasing that in the swollen state. A small section of the NIPA chain is dehydrated even in the swollen gels. The free energy of the gel as a function of gel volume and temperature  $A(V,T)$  is considered to be significantly affected by the existence of hydrophobic additives through binding. Figure 9 shows schematically the effect of additives on  $A(V,T)$ . The additive reduces the free energy of the collapsed state and increases that of the swollen state for a given number of bonds, as shown in Figure 9a. In reality, the number of bonds in the swollen state should be less than that in the collapsed state because the binding increases the free energy of the swollen state. Thus,  $A(V,T)$  in the swollen state is essentially unaffected by the additive, as shown in Figure 9b. Therefore,  $\beta$  of the swollen gel is much less than  $\beta$  of the collapsed gel, as shown in Figure 4, and the effect of additives on  $V$  in the swollen state is negligible, as shown in Figure 1.



**Figure 10.**  $\Delta\mu$  dependence of  $\beta^c$ .  $\beta^c$  is the degree of binding in the collapsed state at transition.

The chemical potential of water molecules is known to increase with decreasing temperature.<sup>7</sup> The lowering of the transition temperature with increasing  $C_{out}$ , as shown in Figure 2, indicates that the chemical potential of water molecules at the transition increases with  $C_{out}$ . The transition can be described by

$$k\mu_{H_2O} = \mu_h(\beta) - \mu_d(\beta) \quad (3)$$

where  $k$ ,  $\mu_{H_2O}$ ,  $\mu_h(\beta)$ , and  $\mu_d(\beta)$  are the number of hydrated water molecules, the chemical potential of water molecules in the solution, and the chemical potentials of the hydrated and dehydrated segments, respectively. The relationship between  $\beta$  for the collapsed gels at the transition ( $\beta^c$ ) and the difference in  $\mu_{H_2O}$  from that in the additive-free case ( $\beta = 0$ ) at the transition gives  $\mu_h(\beta)$  and  $\mu_d(\beta)$ . Figure 10 shows the relationship between the difference  $\Delta\mu$  and  $\beta^c$ . The difference  $\Delta\mu$  is evaluated from  $\mu_{H_2O}$  as a function of temperature, as estimated from the temperature dependence of the heat capacity of water,<sup>7</sup> and  $\beta^c$  is evaluated from  $K_d$  of the collapsed state and eq 5. Figure 10 shows that  $\Delta\mu$  increases linearly with increasing  $\beta^c$ . This indicates that  $\mu_h(\beta) - \mu_h(0) - \{\mu_d(\beta) - \mu_d(0)\}$  increases linearly with increasing  $\beta$ . In the actual system,  $\mu_h(\beta) - \mu_h(0) \approx 0$ , as discussed above. Thus, the experiment shows that  $-\mu_d(\beta) + \mu_d(0)$  increases linearly with  $\beta$ .

The amide I and II bands are considered to involve dominantly C=O stretching and N-H bending, respectively.<sup>19</sup> It has been found that the hydrogen bond formation of amide groups shifts the amide I vibration to low frequencies and the amide II vibration to high frequencies.<sup>19-21</sup> In Figure 5, the two peaks observed in the amide I band of the PNIPA in THF at 1669 and 1650  $\text{cm}^{-1}$  can be assigned to a hydrogen bond-free C=O stretching band and an intramolecular hydrogen bond C=O stretching band, respectively.<sup>22</sup> The amide I band observed at 1650  $\text{cm}^{-1}$  in the spectrum of the PNIPA film is attributable to the intramolecular hydrogen bond C=O stretching band. As shown in Figure 6, the amide I band wavenumber observed at 1627  $\text{cm}^{-1}$  in the spectrum of the gel equilibrated with 0 mM Ph aqueous solution is lower than that in the spectrum of the PNIPA film. This 1627  $\text{cm}^{-1}$  band can be attributed to the hydrogen bond C=O stretching band between NIPA and water molecules. The very strong hydrogen bond between NIPA and water molecules may change the frequency of the C=O band from 1669 to 1627  $\text{cm}^{-1}$ . The strong hydrogen bonds restrict

the motion of water molecules in the collapsed NIPA gel. The restriction of water motion has also been indicated by the much lower electric conductance of the NIPA gel in the collapsed state than in the swelling state.<sup>23</sup>

In the spectrum of the gel equilibrated with 600 mM Ph aqueous solution, the shift to higher frequency shown in Figure 6 can be explained by the dehydration of the amide group, because few water molecules exist in the gel. The amide I band obtained at 1645 cm<sup>-1</sup> should be assigned to intramolecular hydrogen bonds or hydrogen bonds between NIPA and the hydroxyl group of Ph. Taking into account the exothermic binding of Ph to the chain, as suggested by the temperature dependence of  $pK_d$  of the collapsed gel, we can say that hydrogen bonds form between the amide group of NIPA and the hydroxyl group of Ph.

## 5. Conclusion

The volume-phase transition temperature of NIPA hydro gels was observed to decrease with increasing  $C_{out}$  of BA or Ph. It was found that the volume of swelling gel, as a function of temperature, is independent of  $C_{out}$  and that the volume of collapsed gel is independent of both  $C_{out}$  and temperature. An increase in the discontinuous volume change at the transition was observed in the BA and Ph aqueous solutions. The degree of binding  $\beta$  increases in a transition-like manner with  $C_{out}$  simultaneously with the volume shrinkage of the gel. The synchronous binding at the transition differs from the effects of inorganic salts on the volume-phase transition of NIPA. IR spectra observed for the Ph binding gel suggest the formation of hydrogen bonds between the amide group of NIPA and the hydroxyl groups of Ph. It was also found that the binding increases the chemical potential of water molecules hydrated to the gel chain.

**Acknowledgment.** The Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists is gratefully acknowledged for partial financial support.

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