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# Pressure Effects on Cononsolvency Behavior of Poly(*N*-isopropylacrylamide) in Water/DMSO Mixed Solvents

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## ■ INTRODUCTION

Cononsolvency is defined as a phenomenon that a polymer, being soluble in two pure solvents, becomes insoluble in their mixture depending on the composition.<sup>1–6</sup> For solutions of poly(*N*-isopropylacrylamide) (PNIPA) in water/methanol (MeOH) mixtures,<sup>1,2,7,8</sup> the lower critical solution temperature (LCST) decreases upon addition of MeOH and then increases by further addition of MeOH. A theoretical investigation by Tanaka et al. showed that the origin of this phase behavior was the reentrant change of the total number of hydrogen bonding along the chain because of the competitive attachment and detachment of the two solvents.<sup>9,10</sup> On the other hand, in water/dimethyl sulfoxide (DMSO) mixtures, PNIPA shows an upper critical solution temperature (UCST) in the high DMSO mole fraction,  $\phi_{\text{DMSO}}$ , in addition to the LCST in the low  $\phi_{\text{DMSO}}$ .<sup>3,4</sup>

Hydrostatic pressure compresses the molecular volume and modulates the interaction between the solution components. Water-soluble polymers usually show an LCST phase behavior by heating due to breakage of hydrogen-bonding between the polymer and water molecules. The phase diagrams of these polymers are convex upward curves in the pressure–temperature ( $P$ – $T$ ) plane. The LCST increases in the low pressure region and then decreases with further increase in the pressure.<sup>11–15</sup> Nonaqueous polymers do not have the specific interactions, such as hydrogen bonding, and usually show a UCST phase behavior by cooling due to the positive contribution of the enthalpic term in the Flory–Huggins equation. Their phase diagrams are convex downward curves in the  $P$ – $T$  plane. The UCST decreases in the low pressure region and then increases with further increase in the pressure.<sup>16–18</sup>

To our knowledge, there have been few reports about the effects of pressure on polymers in mixed solutions of aqueous and nonaqueous solvents. When a nonaqueous solvent is added to an aqueous polymer solution, some of the nonaqueous solvent molecules may be preferentially adsorbed on the polymers in competition with the hydrating water molecules. In particular, for PNIPA in water/DMSO mixtures, the phase behavior can be controlled between LCST and UCST by tuning  $\phi_{\text{DMSO}}$ , and hence, this is the possible model system to investigate the effect of pressure on the different phase behavior with one polymer. In this study, to investigate the pressure effects on the cononsolvency, we constructed the  $P$ – $T$  phase diagrams of PNIPA in water/DMSO mixtures with different  $\phi_{\text{DMSO}}$  by using light transmission measurements. In addition, to elucidate the molecular origin of the pressure effect on the

phase behavior, we used differential scanning calorimetry (DSC) at ambient pressure.

## ■ EXPERIMENTAL SECTION

PNIPA ( $M_n = 3.9 \times 10^4$  and  $M_w/M_n = 1.45$ ) purchased from Polymer Source Inc. was used without further purification. The polymer was dissolved in a mixture of hydrogenated water and DMSO, in which the mole fraction of DMSO was varied. Concentration of the polymer in the solutions was constant at 7 wt %.

A He–Ne laser (22 mW,  $\lambda = 6328 \text{ \AA}$ ) and a FieldMaster-GS (COHERENT, Co. Ltd., Japan) were used to monitor beam intensity. Pressure dependent experiments were carried out with an inner-cell type pressure cell having a set of optical windows (PCI-400, Teramex, Co. Ltd., Kyoto, Japan).<sup>19,20</sup> DSC measurements were carried out with a DSC8230 (Rigaku Co. Ltd.) at ambient pressure. The polymer solution was crimped in a sealed pan, and DSC thermograms were taken with a heating rate of 3 °C/min. No noticeable change in the weight of the sample pan before and after a DSC run was observed, indicating that no water evaporation occurred during the DSC run.

## ■ RESULTS AND DISCUSSION

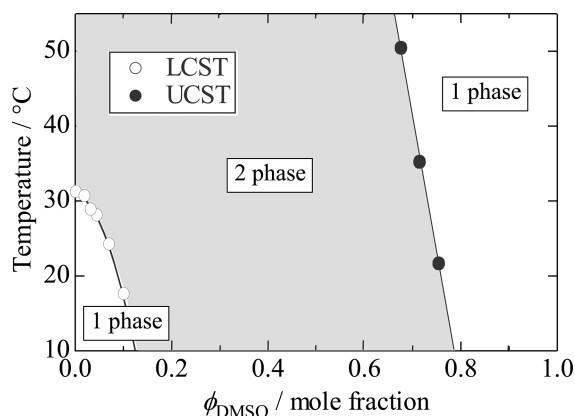
At ambient pressure, the solutions of PNIPA (7 wt %) in water/DMSO were transparent at low temperature with low mole fraction of DMSO ( $0 < \phi_{\text{DMSO}} < 0.1$ ). The transmission rapidly decreased at the lower critical solution temperature ( $T_{\text{LCST}}$ ) by heating.  $T_{\text{LCST}}$  monotonically decreased as  $\phi_{\text{DMSO}}$  increased. On the other hand, with high mole fraction of DMSO ( $0.65 < \phi_{\text{DMSO}} < 0.76$ ), the solutions were transparent at high temperature. The transmission decreased at the upper critical solution temperature ( $T_{\text{UCST}}$ ) by cooling, and  $T_{\text{UCST}}$  monotonically but drastically decreased as  $\phi_{\text{DMSO}}$  increased. The obtained phase diagram with both  $T_{\text{LCST}}$  and  $T_{\text{UCST}}$  is shown in Figure 1. On the basis of this phase diagram, we conducted the following measurements under hydrostatic pressure.

Figure 2 shows the  $P$ – $T$  phase diagram of PNIPA in water/DMSO obtained by *in situ* transmission measurement under (a) LCST conditions ( $0 < \phi_{\text{DMSO}} < 0.1$ ) and (b) UCST conditions ( $0.65 < \phi_{\text{DMSO}} < 0.76$ ). In Figure 2 (a), an upward-convexity of  $T_{\text{LCST}}$  with respect to the pressure is observed as reported for other water-soluble polymers.<sup>11,13–15</sup> It is noteworthy that the phase curve shifted toward higher temperature and pressure as  $\phi_{\text{DMSO}}$  increased while  $T_{\text{LCST}}$  at ambient pressure monotonically decreased. Especially, a subtle addition of DMSO ( $\phi_{\text{DMSO}}$

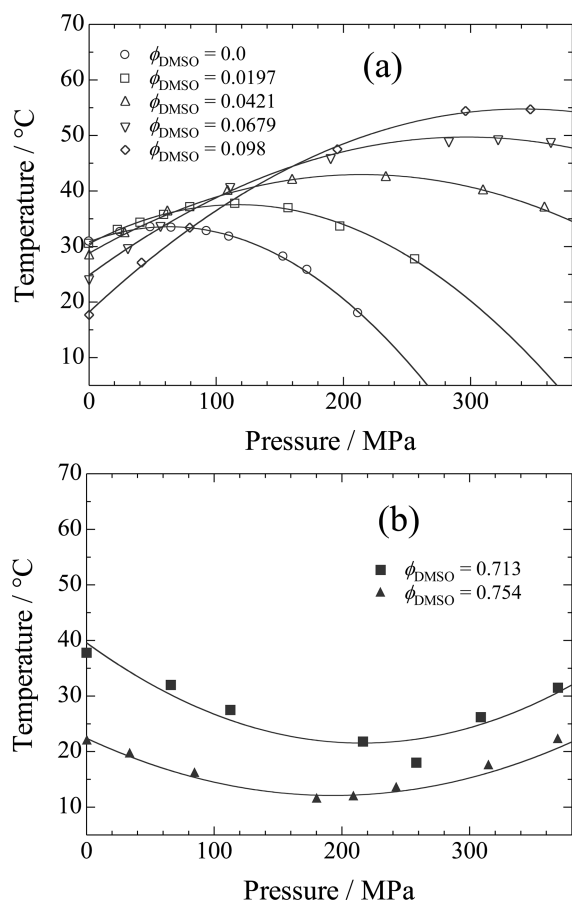
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**Figure 1.** Phase diagram of PNIPA (7 wt %) in water/DMSO mixed solvents with various  $\phi_{\text{DMSO}}$ 's at ambient pressure. Open circles indicate the LCST points ( $\phi_{\text{DMSO}} < 0.1$ ) and closed circles indicate the UCST points ( $0.65 < \phi_{\text{DMSO}} < 0.76$ ).



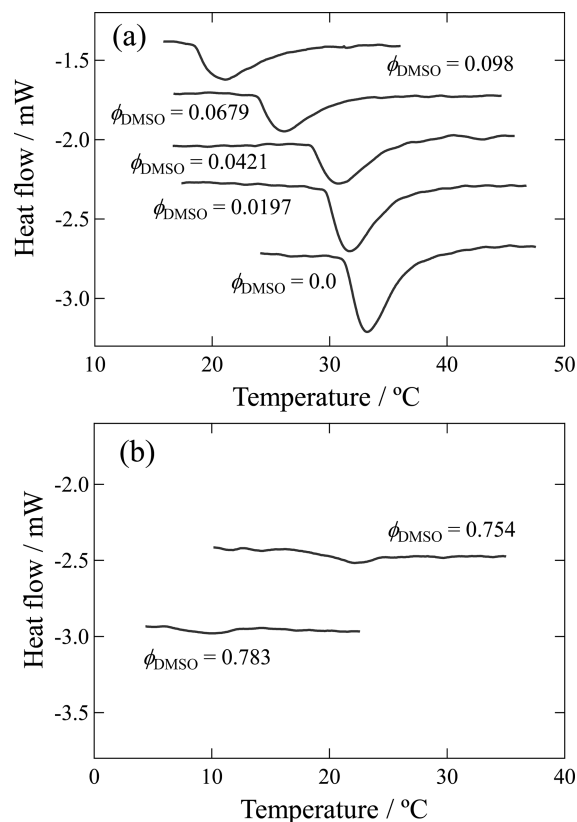
**Figure 2.** (a) Upward-convexity and (b) downward-convexity phase diagrams in the  $P$ - $T$  plane of PNIPA (7 wt %) in water/DMSO mixed solvents under the LCST ( $\phi_{\text{DMSO}} < 0.1$ ) and the UCST conditions ( $0.65 < \phi_{\text{DMSO}} < 0.76$ ), respectively. The solid lines at various  $\phi_{\text{DMSO}}$ 's are fits by quadratic functions.

= 0.098) shifted the pressure at the maximum point,  $P_{\text{max}}$  from 55 MPa ( $\phi_{\text{DMSO}} = 0.00$ ) to 340 MPa.

On the other hand,  $T_{\text{UCST}}$  first decreased in the low pressure region and then increased with further increase in the pressure (Figure 2b). In contrast with the behavior under LCST conditions, the downward-convexity of  $T_{\text{UCST}}$  with respect to the pressure is observed. The phase diagram shifted slightly

toward lower temperature as  $\phi_{\text{DMSO}}$  increased. The thermodynamic origin of the shift depending on  $\phi_{\text{DMSO}}$  was investigated by DSC at ambient pressure.

Figure 3a shows the DSC results of PNIPA in water/DMSO with various  $\phi_{\text{DMSO}}$ 's upon heating under the LCST conditions

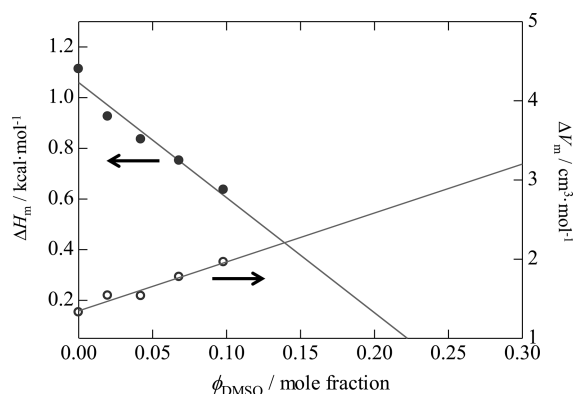


**Figure 3.** DSC measurements of PNIPA (7 wt %) in water/DMSO mixed solvents by heating at a rate of 3 °C/min under the (a) LCST condition and (b) UCST condition at ambient pressure.

at ambient pressure. The endothermic peaks shifted toward lower temperature as  $\phi_{\text{DMSO}}$  increased and the onset temperatures of the endotherm agreed with the  $T_{\text{LCST}}$  determined by transmission measurements. As  $\phi_{\text{DMSO}}$  increased, the endothermic peak became smaller and the transition behavior became broader. The endothermic heat is required to break the hydrogen-bonding between the solvent and PNIPA. Addition of DMSO into the solutions reduced the total number of hydrogen bonding along the chain because of the competitive attachment and detachment of the two solvents.<sup>9,10</sup> Therefore, reduction of the number of hydrogen bonding and the resulting decrease in the cooperativity of the hydrating solvents were reflected in the reduced endothermic heat and the broader transition, respectively.

$\phi_{\text{DMSO}}$  dependence of molar endothermic heat,  $\Delta H_{\text{m}}$ , obtained by the DSC measurements at ambient pressure is shown on the left in Figure 4. This data now allow an estimate of change in the molar volume of PNIPA with the hydrating solvents,  $\Delta V_{\text{m}}$ , at ambient pressure under the LCST conditions by using the Clausius–Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H_{\text{m}}}{T_{\text{LCST}} \Delta V_{\text{m}}} \quad (1)$$



**Figure 4.**  $\phi_{\text{DMSO}}$  dependence of molar endothermic heat in the left axis obtained by DSC measurements and change of molar volume in the right axis obtained by using eq 1.

where  $dP/dT$  is the inverse of the slope of the phase separation curve in the  $P$ – $T$  plane shown in Figure 2. Although this Clausius–Clapeyron equation is originally derived for the phase transition of the single component system,<sup>21</sup> this equation is often applied to many polymer solution systems. Especially, for PNIPA/water systems, the mixing molar volume estimated by the Clausius–Clapeyron equation showed good agreement with one obtained by the volumetric measurements at ambient pressure.<sup>11,22</sup> Furthermore, the solvent is a mixture and can be treated as a solvent because water and DMSO mixes at any compositions. Therefore, we assumed that this Clausius–Clapeyron equation is approximately applicable to our system to estimate the molar volume of PNIPA in the low mole fraction region of DMSO at ambient pressure. Monotonic increase of  $\Delta V_m$  with  $\phi_{\text{DMSO}}$  at ambient pressure obtained by using eq 1 is shown on the right in Figure 4. Since molar volume of DMSO (72 cm<sup>3</sup>/mol) is larger than that of water (18 cm<sup>3</sup>/mol),  $\Delta V_m$  increases with  $\phi_{\text{DMSO}}$  by attachment and detachment of more hydrating DMSO molecules from PNIPA. It should be noted that the maximum point in the  $P$ – $T$  phase curve corresponds to  $dT/dP = 0$  from eq 1, which leads to  $\Delta V_m = 0$ . In general, pressurizing a system decreases the volume. Since  $\Delta V_m$  increases with  $\phi_{\text{DMSO}}$ , higher pressure is needed to reduce the larger  $\Delta V_m$  to zero. This may be the possible thermodynamic origin of the shift of the phase curve toward the higher pressure as  $\phi_{\text{DMSO}}$  increases. In addition, as  $\phi_{\text{DMSO}}$  increases, the total number of hydrogen bonding along the chain decreases and a hydrogen bonding between the C=O group of PNIPA and the methyl group of DMSO is weaker than one between the C=O group of PNIPA and the hydroxyl group of H<sub>2</sub>O.<sup>4</sup> These facts suggest that the shift of the maximum point with  $\phi_{\text{DMSO}}$  is determined by the change in the hydrating volume not by the interaction between polymer and the hydrating solvents. With respect to the shift of the maximum point toward higher temperature,  $T_{\text{LCST}}$  increases up to  $\Delta V_m = 0$  in the low pressure region. The increased slope of the phase curve at ambient pressure and the shift of the maximum points toward the higher pressure with increase of  $\phi_{\text{DMSO}}$  will shift the maximum point toward higher temperature.

On the other hand, under the UCST conditions, significant enthalpic heat was not obtained from the DSC measurements at ambient pressure (Figure 3b). This result suggests that the origin of the UCST phase behavior is not related to the hydrating solvents. UCST phase behavior is usually driven by

the positive enthalpic term in the Flory–Huggins equation, such as van der Waals type interaction. At ambient pressure, a subtle addition of DMSO into the mixed solution decreased  $T_{\text{UCST}}$  by specifically modulating the nonspecific interaction.<sup>3</sup> However, the shape of the  $P$ – $T$  phase curve was almost the same irrespective of  $\phi_{\text{DMSO}}$  except for the shift toward lower temperature. This suggests that the compression effect by the hydrostatic pressure did not significantly modulate the nonspecific interaction. In the future, the detailed mechanism for the shifts will be investigated using *in situ* scattering and spectroscopy measurements under high pressure.

## CONCLUSIONS

In summary, the effect of pressure on the phase behavior of PNIPA (7 wt %) in water/DMSO was investigated using *in situ* transmission measurements under hydrostatic pressure and DSC measurements at ambient pressure. Under the LCST conditions with low  $\phi_{\text{DMSO}}$ , the  $P$ – $T$  phase diagrams were convex upward curves and shifted drastically toward both higher pressure and temperature as  $\phi_{\text{DMSO}}$  increased. By contrast, under the UCST conditions with high  $\phi_{\text{DMSO}}$ , the  $P$ – $T$  phase diagrams were convex downward curves and shifted toward lower temperature as  $\phi_{\text{DMSO}}$  increased. On the basis of the Clausius–Clapeyron equation, the drastic shift of the phase curve with  $\phi_{\text{DMSO}}$  under the LCST conditions was attributed to the increased molar volume of PNIPA at ambient pressure. For the UCST phase behavior under pressure, addition of DMSO modulated the nonspecific interaction such as van der Waals interaction, and the hydrating solvents were not important.

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### Notes

The authors declare no competing financial interest.

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