Effects of Cononsolvency on Preferential Adsorption Phenomenon in Poly(N-isopropylacrylamide) Ternary Solutions

Jean-Hong Chen,[1] Hsiu-Hsiu Chen,[2] Ying-Xun Chang,[1] Pei-Ying Chuang,[1] Po-Da Hong[2]

[1]Department of Polymer Materials, Kun Shan University, Tainan 71003, Taiwan, Republic of China
[2]Graduate School of Polymer Engineering, National Taiwan University of Science and Technology, Taipei 10672, Taiwan, Republic of China

ABSTRACT: In this work, the effect of cononsolvency on the phase transition and preferential adsorption phenomenon behaviors of poly(N-isopropylacrylamide)/methanol/water ternary solutions was studied. In this cononsolvent system, the $\Delta\overline{V}^E$, $\Delta\overline{G}^m$, and χ_{12} values show a nonlinear behavior and the minimum values of $\Delta\overline{V}^E$ and $\Delta\overline{G}^m$, while the maximum value of χ_{12} at ϕ_2 is around 0.7. These facts indicated that one water molecule could directly bond with one methanol molecule to form the $H_2O-MeOH$ complex. The $H_2O-MeOH$ complex structure was found to remarkably affect the phase transition of poly(N-isopropylacrylamide) (PNIPAM) in ternary solution. However, at the composition of mixed cononsolvent, $\phi_2 < 0.2$, the PNIPAM molecules may preferentially adsorbed pure water molecules; therefore, the LCST decreases slightly with composition of mixed cosolvent and this may be because of the small amount of $H_2O-MeOH$ complexes in the mixed cononsolvent. While, at $\phi_2 > 0.7$, the PNIPAM molecules may preferentially adsorbed pure methanol molecules. PNIPAM ternary solutions were transparent and no transition occurred in this region. This indicates that the PNIPAM coils exhibited a much-extended conformation in solutions. In contrast, at $0.2 < \phi_2 < 0.4$ and $0.4 < \phi_2 < 0.7$, PNIPAM molecules preferentially adsorbed water and methanol molecules, respectively, and also adsorbed large amount of $H_2O-MeOH$ complexes. In these regions, the clathrate-like structure around the side chain of PNIPAM molecule became more defected with adsorbing $H_2O-MeOH$ complex. Therefore, we considered that the various thermodynamic behaviors between PNIPAM and mixture solvents must be related different preferential adsorption phenomena, which were mainly related to different degrees of polymer–solvent interaction and structures of solvent used. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2732–2742, 2008

Key words: cononsolvent; preferential adsorption coefficient; poly(N-isopropylacrylamide)

INTRODUCTION

The microstructure and conformation of polymer chains in polymer solutions have been extensively studied for the several decades. The main progress has been investigated in the equilibrium issues of the fundamental of polymer binary solution, as reported recently.[1–4] Poly(N-isopropylacrylamide) (PNIPAM) could be soluble in aqueous and in many organic solvents as long as the PNIPAM attracts solvents with hydrogen bonding or with hydrophobic force.[5–12] These phenomena indicated that the interaction force can classify mechanisms of polymers binding together, interaction between polymer and solvent, and that between solvents. However, the temperature-induced phase transition of PNIPAM in ternary solution is same as the lower critical solution temperature (LCST) behavior that occurred in PNIPAM aqueous solution.[13,14] In our previous study, we reported that the PNIPAM molecules undergo a simultaneous intermolecular aggregation and intramolecular coil-to-globule transition to form a dynamically mesostable globule particle in PNIPAM/water solution. However, for the PNIPAM/methanol solution, no transition occurred at measurement range. The different thermodynamic behaviors between PNIPAM/water and PNIPAM/methanol solutions must be related to different degrees of polymer–solvent interaction that mainly related to the structure of PNIPAM molecule and the different structures of solvent used.[15]

The thermodynamic behavior of polymer ternary solutions reflected the balance of the interactions between polymer and the mixed cosolvent mole-

cules. Compared with the polymer–solvent interaction in the binary solutions, the interactions undoubtedly become more complicated in the ternary solutions. For example, the composition of mixed cosolvent was related to the polarity of the solvent medium, which plays a significant role in changing the degree of the affinity between polymer and cosolvent. It is interesting that the PNIPAM in mixed solvent system, mixture water with those organic solvents, was occurred the cononsolvency phenomenon has been reported in recent.[14,16–18] Cononsolvency was an extraordinary phenomenon, which described the situation of polymers soluble in two pure solvents but insoluble in their mixtures. In a ternary solution system, the affinity between the polymer and cononsolvents must directly affect the composition and density fluctuation of the solutions. Therefore, the chemical structure of solvent, the dipole moment, and the donor–acceptor electron property of each solvent should be primarily considered to impact the affinity between the polymer and cononsolvent. Recently, Hong and Huang reported the effect of cosolvent complex on preferential adsorption phenomenon in PVA/NMP/water ternary solutions.[19] They indicated that the cosolvents from the NMP and water mixtures were used to dissolve PVA chain. In the ternary system, the NMP molecule, which was a typical dipolar solvent, could particularly bound with two water molecules to form a $NMP(H_2O)_2$ complex. Therefore, the formation of $NMP(H_2O)_2$ complex may affect the preferential adsorption phenomenon and the thermodynamic properties of PVA solutions.

According to the aforementioned discussion, in the PNIPAM ternary solution system, the mixed cosolvent was complicated by the possibility that one or other of the liquid components may be preferentially adsorbed by the PNIPAM molecules. The preferentially adsorbed parameter, α_a, in ternary solution system can be predicted from Read theory.[20] This expression has been derived from the Flory–Huggins and Flory–Patterson–Prigogine theories. In these theories, the preferential adsorption of solvents on polymer chains in solution state is fundamentally dominated by many parameters,[21–30] such as the binary interaction parameters χ_{ij}, the ternary interaction parameter χ_T, the molar volumes of two solvents,[21,22] the molar volume and structure of the side group of polymer,[22] the molecular weight of polymer,[23] and temperature.[24–26] Katime has already verified that the increase in the molecular weight of polymer resulted in the decrease of the preferential adsorption coefficient.[22] Horta also pointed out that the solvent with small molecular volume was preferentially adsorbed because the combinatorial entropy is favorable to the entrance of small molecules into the polymer domain.[27] Generally, the theoretical α_a values could be evaluated from Read formalisms,

considering χ_{ij}, χ_T, and the effect of solvent volume,[20,28–29] according to the Gibbs free energy of mixing in the ternary system. The Gibbs free energy of mixing in the ternary system, ΔG_T^m, could be generally expressed as follows.

$$\Delta G_T^m / RT = n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_3 \ln\phi_3 + g_{12}(u_1)n_1\phi_2$$
$$+ g_{13}(\phi_3)n_1\phi_3 + g_{23}(\phi_3)n_2\phi_3 + g_T n_1\phi_2\phi_3 \quad (1)$$

where n_i is the number of moles of the ith component, g_{ij} the binary interaction potentials, g_T the ternary interaction potential, and $u_1 = \phi_1/(\phi_1 + \phi_2)$. Then, the preferential adsorption coefficient α_a was derived from the second derivation of ΔG_T^m, $(\partial\mu_i/\partial m_j)_{P,T}, m_{k \neq j}$, as given below.

$$\alpha_a = \frac{V_2 \bar{v}_3 \phi_1}{V_3} \frac{(\partial\mu_2/\partial m_3)_{m_2 m_3 \to 0}}{(\partial\mu_2/\partial m_2)_{m_3 \to 0}} \quad (2)$$

where $\bar{v}_3$ is the partial specific volume of polymer that could be derived from eq. (3), V_i is the molar volume of the ith component, μ_i the chemical potential of the ith component, and m_i the molality of the ith component.[30] The second derivations of ΔG_T^m and $(\partial\mu_i/\partial m_j)_{P,T}, m_{k \neq j} = a_{ij}$ could be derived in eq. (4) as follows:

$$\bar{v}_3 = [1 - (\rho - \rho_s)/C]/\rho_s \quad (3)$$

$$a_{22} = \frac{n_1}{n_2} \frac{V_2 RT}{V_m} b_{22} \quad \left(or \quad a_{23} = \frac{n_1 V_2 V_3 RT}{V_m^2} b_{23} \right) \quad (4)$$

where V_m is total volume and l is the ratio of molar volumes V_1/V_2.

Here,

$$b_{22} = \phi_1 l + \phi_2 - \phi_1\phi_2 \left\{ 2\left[g_{12} + (\phi_1 - \phi_2)\frac{\partial g_{12}}{\partial u_1} \right] \right.$$
$$\left. - \phi_1\phi_2 \frac{\partial^2 g_{12}}{\partial u_1^2} \right\} \quad (5)$$

$$b_{23} = g_{23}l - g_{13} + 1 - l - (\phi_1 - \phi_2)(g_{12} - g_T)$$
$$+ \phi_1\phi_2 \left(\frac{\partial g_{12}}{\partial u_1} - \frac{\partial g_T}{\partial u_1} \right) \quad (6)$$

The binary interaction parameters χ_{i3} and the ternary interaction parameter χ_T, respectively, relate to the g_{i3} and g_T values, as given in eqs. (7) and (8).

$$\chi_{i3} = g_{i3} - (\partial g_{i3}/\partial\phi_3) \quad (7)$$

$$\chi_T = g_T - (\partial g_T/\partial\phi_3) \quad (8)$$

Read[20] has derived a formalism for determining the theoretical α_a value for a special case in eq. (1),

where all g_{ij} values are independent of composition (i.e., $g_{ij} = \chi_{ij}$) and the g_T value is equal to zero, as shown in eq. (9).

$$\alpha_a = -\bar{v}_3 \phi_1 \phi_2 \frac{l - 1 + \chi_{13} - l\chi_{23} + \chi_{12}(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2} \quad (9)$$

On the other hand, Chu et al.[31] and Aminabhavi et al.[32] also developed a more complete formalism, as presented in eq. (10), to derive α_a by considering the χ_T parameter that could be calculated through eqs. (11) and (12).

$$\alpha_a = -\bar{v}_3 \phi_1 \phi_2 \frac{l - 1 + \chi_{13} - l\chi_{23} + (\chi_{12} - \chi_T)(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2}$$
$$(10)$$

$$\chi_T(\phi_1) = -\frac{1}{\phi_2} \int_{\phi_1}^{1} L(\phi_1) b_{22} d\phi_1$$
$$+ \frac{1}{\phi_1} \int_{0}^{\phi_1} L(\phi_1) b_{22} d\phi_1 + \frac{0.5 - \chi_{13}}{\phi_2}$$
$$+ \frac{l(0.5 - \chi_{23})}{\phi_1} - \frac{V_1 A_2}{\bar{v}_3 \phi_1 \phi_2} - \frac{L^2 b_{22}}{2} \quad (11)$$

$$L(\phi_1) = \frac{\alpha_a}{\phi_1 \phi_2 \bar{v}_3} \quad (12)$$

The χ_{13} and χ_{23} values in this system, respectively, could be actually calculated from the A_{2i} values with SLS measurement in this study.

$$\chi_{i3} = \frac{1}{2} - \frac{A_{2i} V_i}{\bar{v}_3^2} \quad (13)$$

Regarding the thermodynamic properties of the water/methanol cononsolvent system, the activity coefficients of water and methanol, γ_1 and γ_2, for water/methanol mixtures through the vapor–liquid phase equilibrium method at various pressures and temperatures[33] indicate $\gamma_1 = P_1/P_1^0$ and $\gamma_2 = P_2/P_2^0$. Here, the P_i^0 is the equilibrium vapor pressure of pure solvents. Using a well-known equation, $(d \ln \gamma_i/d(1/T)) = $ constant, the γ_1 and γ_2 values at 25°C could be achieved by extrapolating from the results. Then, the Gibbs free energy of mixing of the cononsolvents, ΔG^m, directly relates to the activity coefficients of two solvents, γ_1 and γ_2, as represented in eq. (14).

$$\Delta G^m = RT(x_1 \ln x_1 \gamma_1 + x_2 \ln x_2 \gamma_2) \quad (14)$$

The excess volumes, $\Delta \bar{V}^E$, and the interaction parameter, γ_{12}, of cononsolvent (methanol/water) could be subsequently obtained using eqs. (15) and (16). The values of ρ_S, ρ, $\Delta \bar{V}^E$, and $\bar{v}_3$ at a given ϕ_2 are presented in Table I.

$$\Delta \bar{V}^E = \frac{x_1 M_1 + x_2 M_2}{\rho_s} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (15)$$

$$\chi_{12} = \frac{(\Delta G^m/RT) - (x_1 \ln\phi_1 + x_2 \ln\phi_2)}{x_1 \phi_2} \quad (16)$$

In this study, the apparent affinity between the PNIPAM and cononsolvent system (methanol/water) at a particular composition of cononsolvent mixture is quite different from the average affinity of the two pure solvent components. This may be mainly because of the formation of a third component, which is complex or hydrate, resulting in the various phenomena of preferential adsorption for PNIPAM chains. In addition, the phase transition and the LCST behaviors of PNIPAM molecule in ternary solutions are also discussed in this work.

EXPERIMEMTAL

Materials and preparation

The PNIPAM powder used in this work was purchased from Polymer Sciences Chemical, USA. The average molecular weight was 4×10^4 g mol^{-1}. All samples were used as received without any additional purification. The deionized water and HPLC grade methanol were repeatedly filtered using a 0.02-μm Teflon filter for removing dust. The PNIPAM ternary solutions were prepared in a precleaned wide-mouth bottle, with stirring at 7 ± 0.2 °C for 2 h until they dissolved into homogeneous solutions. The concentration of the PNIPAM ternary solutions studied was from 0.01 to 1.0 g L^{-1}; the solution was filtered using a 0.45-μm Teflon filter, and then cooled in a thermostat oven at constant temperature of 7°C for 1 week to stabilize the solutions before the measurements.

Phase transition of PNIPAM solutions

Light scattering measurement were studied by using a commercial light scattering spectrometer as the light source (ALV/CGS-3 with an ALV/LSE-5003 light scattering electronics and multiple-tau digital correlator), with a JDS-Uniphase solid-state He-Ne laser output power ca. 22 mW and wavelength 632.8 nm. About 2 mL of PNINAM ternary solution was directed into sealed glass tube; initially, the solutions were immersed in a thermostatic equipped for 20 min at a temperature of 7°C. The temperature dependence of scattering intensity during the phase separation was measured using the step scattering measurement, with 240 s measurement time, scattering angle at 90°, heating rate around 0.25°C/min, and the temperature at which the solution started to

TABLE I
Thermodynamic Properties of the Composition of Mixture Solvents

$\phi_{2\text{MeOH}}$[a]	x_{MeOH}[b]	ρ_S (g cm^{-3})	ρ (g cm^{-3})	$\bar{v}_3$ (g cm^{-3})	η_s (mPa s^{-1})	$\Delta\bar{V}^E$ (cm^3 mol^{-1})	$\Delta\bar{G}^M$ (J mol^{-1})	χ_{12}
0	0.000	0.9948	0.9964	0.8443	0.89	0	0	–
0.1	0.047	0.9826	0.9842	0.8549	1.16	−0.128	−760	1.128
0.2	0.100	0.9693	0.9709	0.8666	1.38	−0.315	−1021	1.203
0.3	0.160	0.9548	0.9564	0.8798	1.46	−0.509	−1199	1.284
0.4	0.229	0.9388	0.9403	0.9054	1.52	−0.702	−1347	1.313
0.5	0.308	0.9209	0.9224	0.9230	1.58	−0.856	−1377	1.358
0.6	0.400	0.9008	0.9023	0.9436	1.56	−0.973	−1393	1.408
0.7	0.509	0.8780	0.8795	0.9681	1.34	−0.988	−1271	1.430
0.8	0.640	0.8518	0.8532	1.0096	1.12	−0.887	−1063	1.417
0.9	0.800	0.8216	0.8230	1.0467	0.84	−0.621	−902	1.392
1.0	1.000	0.7870	0.7885	1.0801	0.55	0	0	–

[a] All percentage in volume.
[b] Partial molar volume of methanol calculated by $x_{\text{MeOH}} = \phi_{2\text{MeOH}}/[\phi_{2\text{MeOH}} + 2.25(1.0 - \phi_{2\text{MeOH}})]$.

change the intensity. This was defined as the phase transition of PNINAAM solutions.

Viscosity of PNIPAM solutions

Intrinsic viscosity, $[\eta]$, and Huggins constant, k', of PNIPAM dilute ternary solutions were determined with an Ubbelohde viscometer immersed in a temperature-controlled water bath at 25°C, where temperature was controlled within ±0.2°C. The intrinsic viscosity, $[\eta]$, and Huggins constant, k', were obtained using Flory–Huggins equation:[34]

$$(t - t_o/t_o)/c = (\eta_{\text{sp}}/c) = [\eta] + k'[\eta]^2 c \qquad (17)$$

where t is the time of flow of the dilute solution, t_0 is the time of flow of the pure solvent, c is the concentration of polymer, η_{sp} is specific viscosity, and k' is the Huggins' constant.

Static light scattering of PNIPAM solutions

Static light scattering measurement was carried out by using a commercial light scattering spectrometer as the light source (ALV/CGS-3 with an ALV/LSE-5003 Light scattering electronics and multiple-tau digital correlator), with a JDS-Uniphase solid-state He-Ne laser output power ca. 22 mW and wavelength 632.8 nm. The reciprocal reduced scattering intensity, Kc/R_q was derived, where c is the concentration of polymer and R_q is the reduced intensity at scattering angle. The optical constant for vertically polarized light $K = 4\pi^2 n_0^2 (dn/dc)^2/N_A\lambda^4$ was derived, where n_0 is the refractive index of solvent, dn/dc is the rate of change of refractive index of the solution with concentration, λ is the wavelength of light in vacuum, N_A is the Avogadro's constant, and θ is the scattering angle. Thereafter, the second virial coefficient, A_2, the z-average radius of gyration, R_g, and the weight-average molecular weight, M_w could

be directly achieved using the well-known Zimm equation.[35,36]

$$\frac{Kc}{R_\theta} = \frac{1}{M_W}\left[1 + \frac{16}{3}\pi^2\frac{R_g^2}{\lambda^2}\sin^2(\theta/2) + \ldots\right] + 2A_2c + \ldots$$

$$(18)$$

The values of dn/dc for the PNIPAM/water and PNIPAM/methanol solutions at 20°C were 0.169 and 0.134 mL g^{-1}, respectively, which was obtained by operating the Optilab DSP interferometic refractometer with wavelength 632.8 nm (Wyatt Tech.).

RESULTS AND DISCUSSION

Figure 1(a,b) shows the phase transition of PNIPAAM/water/methanol ternary solutions as a function of composition of mixed cononsolvent at water-rich and methanol-rich regions, respectively. The composition of the mixed cononsolvent is reported as the volume fraction of methanol, ϕ_2, used for the preparation of the solvent mixtures. As demonstrated in Figure 1, the PNIPAM ternary solutions in the pure water show a phase transition/LCST at $\sim$ 34°C, and appearance of the LCST decreases remarkably with increasing composition of methanol at water-rich region. In the pure methanol and methanol-rich region, PNIPAM ternary solutions are transparent and the transition does not occur in the temperature range studied. The phase transition behavior is very sensitive to the composition of the mixed cononsolvent at water-rich region. The phase transition phenomenon of PNIPAM aqueous was earlier reported by Scarpa et al.[13] They have reported that the reversible behavior of soluble and precipitation of PNIPAM solution may be due to the PNIPAM chains collapsed to be a contracted globule at temperature higher than the LCST. The phase transition behavior of PNIPAM in aqueous solution
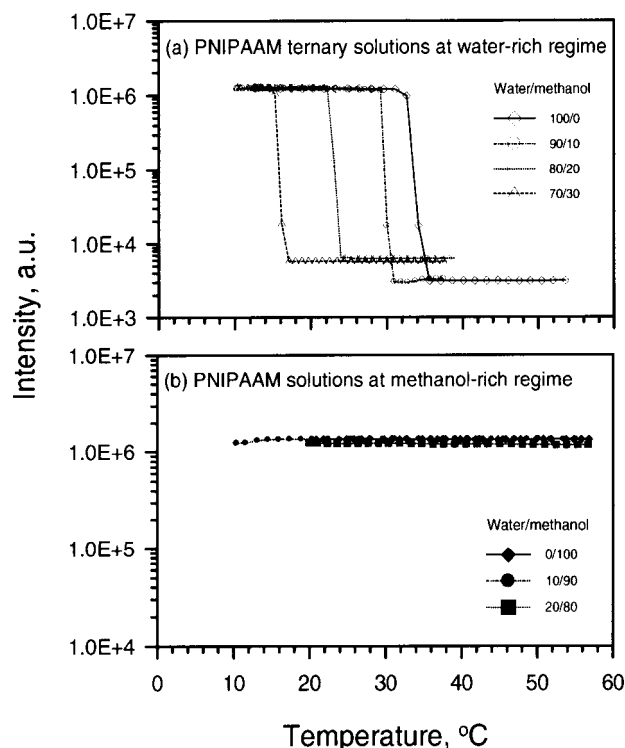
Figure 1 Plots of the phase separation/LCST transition of PNIPAAM ternary solutions as a function of composition of mixture solvent at concentration 1 g L^{-1}: (a) water-rich region; (b) methanol-rich region.

may lead to form a specific orientation required for hydrogen bonding with the arranged water molecules. This phase is especially important when water molecules must reorient around the hydrophobic isopropyl group of PNIPAM, being unable to hydrogen bond with them. This phenomenon has also been claimed to be a clathrate-like structure of water molecules around the hydrophobic group of PNIPAM as reported by Franks and Eagland.[37] The various behaviors of phase transition for PNIPAM molecules at water-rich and methanol-rich regions may be due to the different polymer–solvent interactions between PNIPAM and these solvents.

The phase transition of PNIPAM ternary solutions as a function of composition of mixed cosolvent is presented in Figure 2. However, for the PNIPAM ternary solutions, the phase transition phenomenon observed at water-rich region, while the transition does not occur at methanol-rich region as shown in Figure 1(b). This phase indicates that the PNIPAM ternary solution in composition of mixed cosolvent lower then 0.7 shows LCST phenomenon. Although PNIPAM ternary solutions are homogeneous and transparent at temperature lower than LCST, they undergo phase transition at temperature above LCST. This behavior is very sensitive to the composition of the mixed cosolvent as shown in Figure 2. Thus, it indicates that, as a small amount of metha-

nol added in pure water for ϕ_2 to be 0.2, the LCST/phase transition of the PNIPAM ternary solution decreases slightly from 34 to 24°C. On the contrary, an increase in the ϕ_2 from 0.2 to 0.55, the LCST/phase transition of the PNIPAM ternary solution decreases remarkably from 24 to −7°C. However, at ϕ_2 between 0.55 and 0.7, the LCST/phase transition of PNIPAM ternary solution increases remarkably from −7°C to over the measurement temperature. It is also noticed that water and methanol were the poorer and good solvents for PNIPAM molecules, respectively. Nevertheless, in the case of PNIPAM ternary solutions, a very wide quantity of water ($\phi_2 < 0.7$) suffices to turn the mixture solvent to a cononsolvent at a certain temperature. However, addition of dioxane solvent to a PNIPAM aqueous solution slightly influences the LCST of PNIPAM ternary solution. The addition of methanol to the PNIPAM aqueous solution leads to a remarkable depression of its LCST.

Additional information for effect the composition of mixed cosolvent on the polymer–solvent interaction of PNIPAM polymer ternary solution can be obtained with Huggins equation. Figure 3(a,b) shows the plot of the reduced viscosity, η_{sp}/c as a function of composition of mixed cosolvent for PNIPAM dilute ternary solutions at water-rich and methanol-rich regions at 25°C, respectively. From the linear relationship in Figure 3, the intrinsic viscosity, $[\eta]$, and the Huggins constants, k', could be estimated through Huggins equation. The values of k' and $[\eta]$, respectively, of PNIPAM dilute ternary solutions are shown in Figures 4 and 5. Generally, the k' value can
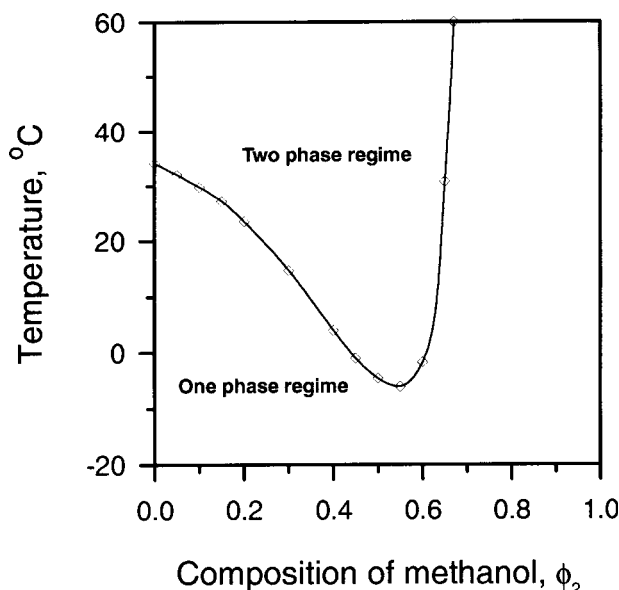

Figure 2 Plots of the LCST transition of PNIPAAM ternary solutions of various composition of methanol, ϕ_2, at concentration is 1 g L^{-1}.
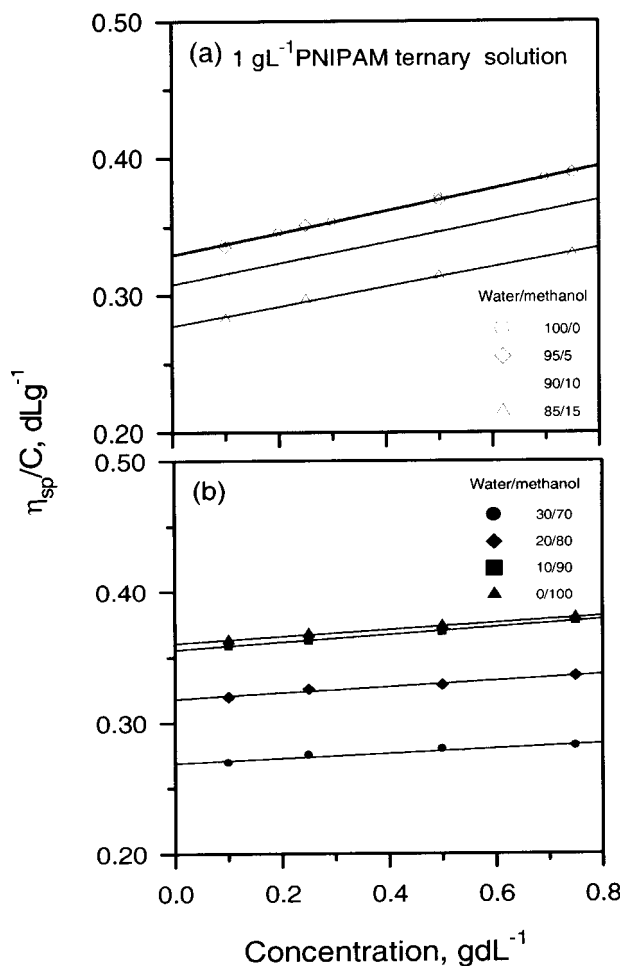
Figure 3 Plots of the η_{sp}/C versus C for PNIPAAM ternary solutions as a function of composition of mixture solvent: (a) water-rich region; (b) methanol-rich region at 25°C.

Figure 4 Plots of the Huggins constant, k' of PNIPAAM ternary solutions as a function of composition of methanol, ϕ_2 at 25°C.

be used to predict the degree of the polymer–solvent interaction in a polymer dilute solution. In a good solvent condition, $k' < 0.52$, the polymer chains exhibit relatively extended conformations. In a theta solvent condition, $k' = 0.52$, the polymer chains are unperturbed coils. In a poor solvent condition, $k' > 0.8$, the polymer chains collapsed and intramolecular aggregation occurred easily. However, Figure 4 shows that the k' value of PNIPAM ternary solutions at water-rich region is from 0.73 to 0.94; in contrary, at methanol-rich region, the k' value of PNIPAM ternary solutions is about 0.2. Therefore, this result proves that, at methanol-rich region, the mixed cosolvent presents a good solvent for PNIPAM molecule because the k' is about 0.2, while this is quite close to a poor solvent, at k' about 0.8, for PNIPAM at water-rich region and 25°C. Moreover, Figure 5 illustrates that the $[\eta]$ of PNIPAM dilute ternary solutions at methanol-rich region, ~ 0.36 dL g^{-1}, is larger than that at water-rich region, ~ 0.33 dL g^{-1}. The result also indicates that, at water-rich region,
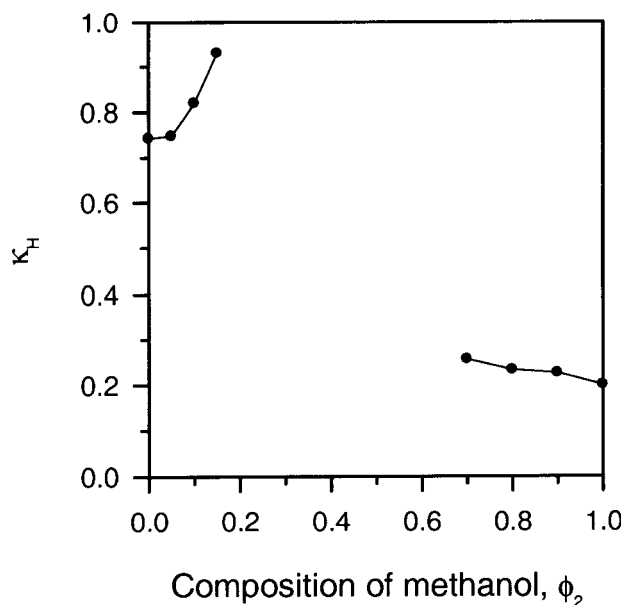
the $[\eta]$ of PNIPAM aqueous solution decreases, while that of PNIPAM decreases remarkably with composition of mixed solvent at methanol-rich region. Unfortunately, the intrinsic viscosity is decreased at the composition of mixed solvent between 0.2 and 0.7 at 25°C. In this state, however, the PNIPAM ternary solutions occur the serious phase separation at temperatures below 25°C. This indicates that the PNIPAM ternary solutions are in poor agreement with the viscometer experimental
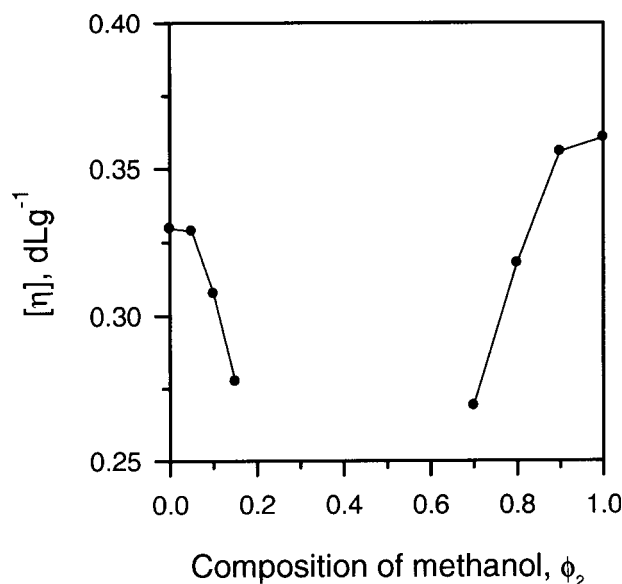

Figure 5 Plots of the intrinsic viscosity, $[\eta]$ of PNIPAAM ternary solutions as a function of composition of methanol, ϕ_2 at 25°C.

dates at the ϕ_2 between 0.2 and 0.7 at 25°C. These results indicate that the polymer–solvent interaction between PNIPAM and cosolvent decreases as the methanol was increased, implying that the conformation of PNIPAM chains in ternary solution constricts gradually with increasing methanol at water-rich region, whereas the polymer–solvent interaction between PNIPAM and cosolvent are almost the same at methanol-rich region, implying that the conformation of PNIPAM chains in ternary solution presents more extended conformation at this region. Figure 6(a,b) shows the Zimm plots of PNIPAM/water and PNIPAM/methanol solutions, respectively, at temperature is 20 ± 0.1°C. The result in Figure 6 shows the different Zimm plots that exhibit a linear-shaped Zimm plot for PNIPAM/water solution and a hook-shaped Zimm plot for PNIPAM/methanol solution, respectively. In our previous study, we discussed that the hook-shaped Zimm plot of dilute PNIPAM/methanol solutions might be due to the more extended conformation and lower thermodynamic properties in PNIPAM/methanol infinite dilute solutions, because the PNIPAM chains in a very good solvent, methanol must be more extended than those in a poor solvent.[15] However, a linear-shaped Zimm plot of PNIPAM/water diluted solutions was observed, that is, the PNIPAM chains are isolated random coils and larger thermodynamic properties in PNIPAM/water solutions at the same temperature. The A_2 values obtained from the Zimm plot could also be regarded as the degree of the polymer–solvent interaction. In PNIPAM/methanol solution, the large A_2 value, $\sim 1.13 \times 10^{-4} \, \text{mol} \, \text{cm}^3 \, \text{g}^{-2}$, was observed at 20°C. This indicates that there exists a strong attractive force between PNIPAM and methanol molecules. While a smaller A_2 value, $\sim 2.27 \times 10^{-5} \, \text{mol} \, \text{cm}^3 \, \text{g}^{-2}$, is observed in the PNIPAM/water solution at the same temperature. Moreover, the Zimm plots also show a larger R_g value, ~ 18.5 nm, in PNIPAM/methanol solution in comparison with that, ~ 15.6 nm, in PNIPAM/water solution at the same temperature. However, in the PNIPAM/water/methanol ternary solution, we should not only consider the properties of PNIPAM/water and PNIPAM/methanol solutions but also the property between methanol and water. In this system, the χ_{13} (water-PNIPAM) and χ_{23} (methanol-PNIPAM) values in the PNIPAM binary solution are about 0.499 and 0.496, respectively, calculated from eq. (13) in this work. The aforementioned results indicate that the interaction between PNIPAM and water is lower than that between PNIPAM and methanol. These facts let us to consider that the polymer–solvent interaction must play an important role on the thermodynamic behavior of PNIPAM chains in binary and also in ternary solutions. The apparent affinity between the PNIPAM and cosolvent system at a par-
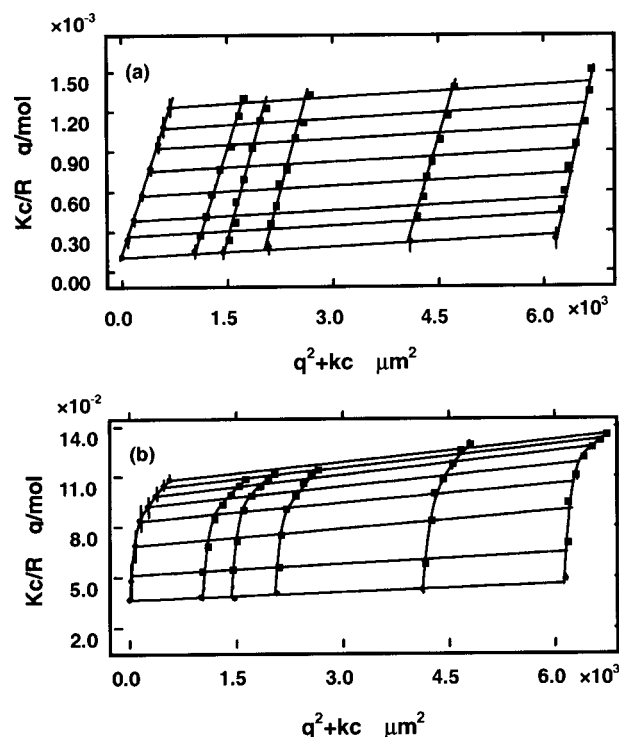

Figure 6 The Zimm plots of PNIPAM solutions at 20°C: (a) PNIPAM/water solutions; and (b) PNIPAM/methanol solutions.

ticular cononsolvent composition is quite different from the average affinity of the two pure solvent components. This may be mainly because of the formation of a third component, which is complex or hydration, resulting in the various phenomena of preferential adsorption for PNIPAM chains.

In the PNIPAM ternary solutions, we should not only consider the thermodynamic properties of PNIPAM/water and PNIPAM/methanol solutions but also consider the properties between water and methanol. The system is not really a binary system because the water and methanol interact by hydrogen bonding to form a complex structure, which is different structure for pure water or methanol. Therefore, this system must be considering a ternary solvent (pure water, pure methanol, and water-methanol complex). Figure 7 shows the viscosity values, η_s, of mixture cosolvent as a function of composition of mixed solvent at 25°C. It indicates that the η_s value expresses a nonlinear behavior and presents a maximum η_s value, ~ 1.58 mPa s^{-1}, at ϕ_2 around 0.5–0.6. A composition of methanol mixture, $\phi_2 = 0.65$, is quite particular where the mole ratio of water to methanol is about 1 : 1, indicating that one water molecule could directly bonded with one methanol molecule to from H_2O—MeOH complex structure as given in Table I. Recently, Bosch et al. reported an interaction model to interpret the water-methanol
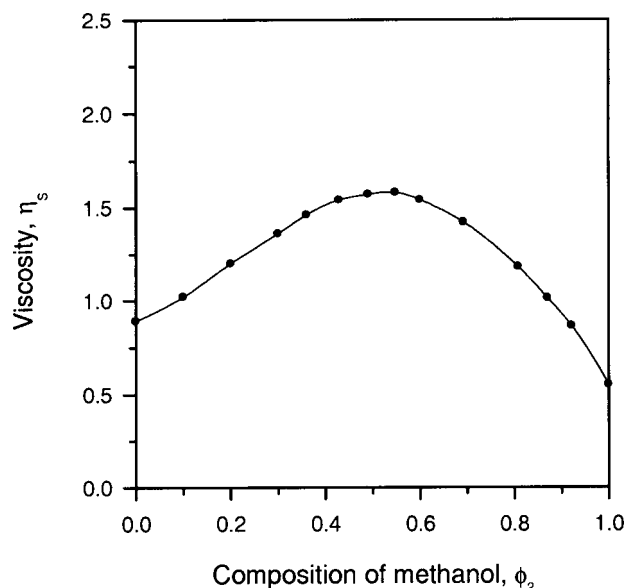
Figure 7 Plots of the viscosity, η_s of mixture cosolvent as a function of composition of methanol, ϕ_2 at 25°C.

mixtures cosolvent system.[38] They indicated that the water-methanol mixed solvent, represented by S_1 (water) and S_2 (methanol), interacted to form a complex structure S_{12} (water-methanol) and presented a maximum S_{12} (water-methanol) as methanol volume content was about 60%. Thus, the water-methanol mixed solvent is composed of clusters of water, methanol, and water-methanol complex in equilibrium state. The water and methanol clusters have molecular properties equal to those of pure water and methanol, respectively. But water interacted with methanol through the hydrogen bonding forming a new complex structure, S_{12}, which was different property from those of water or methanol. From the aforementioned discussion, the water/methanol mixed solvent system, one water molecule can directly bond with one methanol molecule to form the H_2O—MeOH complex structure. Moreover, Figure 8 shows the excess volumes, $\Delta \overline{V}^E$, excess enthalpies of mixing, $\Delta \overline{G}^m$, and the interaction parameter, χ_{12}, of the mixture cosolvent as a function of composition of mixed solvent at 25°C. The $\Delta \overline{V}^E$, $\Delta \overline{G}^m$, and χ_{12} values are calculated with eqs. (14)–(16), where the x_i and ϕ_i are molar fraction and volume fraction of the ith component, respectively, also listed in Table I. The result in Figure 8 shows that the $\Delta \overline{V}^E$, $\Delta \overline{G}^m$, and χ_{12} values express a nonlinear behavior, implying this system is a nonideal solution system. This phase indicates that a complex hydrate between water and methanol molecules must occur in the cononsolvent system. Therefore, the interaction force between water and methanol, χ_{12} increases slightly and then decreases with increasing ϕ_2, indicating that the content of complex hydrate (H_2O—MeOH

complex) increases slightly and then decreases; therefore, inducing the $\Delta \overline{V}^E$ and $\Delta \overline{G}^m$ decrease and then increase as ϕ_2 increased. The complex formation understandably induces the exothermic mixing process, decreases the bonding length of the solvent molecule and increases the friction force of flowing as reported by Bai et al.[39] From Figure 8, it is clear that the minimum values of $\Delta \overline{V}^E$ is ca. -0.99 cm^3 mol^{-1}, and $\Delta \overline{G}^m$ is ca. -1393 J mol^{-1}, while the maximum value of χ_{12} is ~ 1.43 at around 0.7. These facts indicate that one water molecule can directly bond with one methanol molecule to form the H_2O—MeOH complex as discussed earlier. This result indicates that the interaction force and structure of H_2O—MeOH complex slightly changes with composition of mixed solvent.

According aforementioned discussion, we elucidated the dynamic properties of PNIPAM chains in methanol/water cononsolvent system with adsorbed preferentially parameter, α_a, theory. Figure 9 shows the α_a values against various composition of mixed solvent, ϕ_2. The result in Figure 9 presents the negative α_a values at $\phi_2 < 0.4$, while the positive ϕ_a values at $\phi_2 > 0.4$ and $\phi_a = 0$ at $\phi_2 = 0.4$. These results illustrate that the water molecules are adsorbed preferentially by PNIPAM chains at $\phi_2 < 0.4$ whereas that the methanol molecules are adsorbed preferentially by PNIPAM chains at $\phi_2 > 0.4$. Particularly, we observe two inversion of the preferential adsorption coefficient at about $\phi_2 = 0.2$ and 0.55 in Figure 9. This result implies that the preferential adsorption parameter at ϕ_2 between 0.2 and 0.55 may be due to the PNIPAM molecules that not only adsorbed water and methanol molecules but also adsorbed large amount of H_2O—MeOH complexes, which remark-
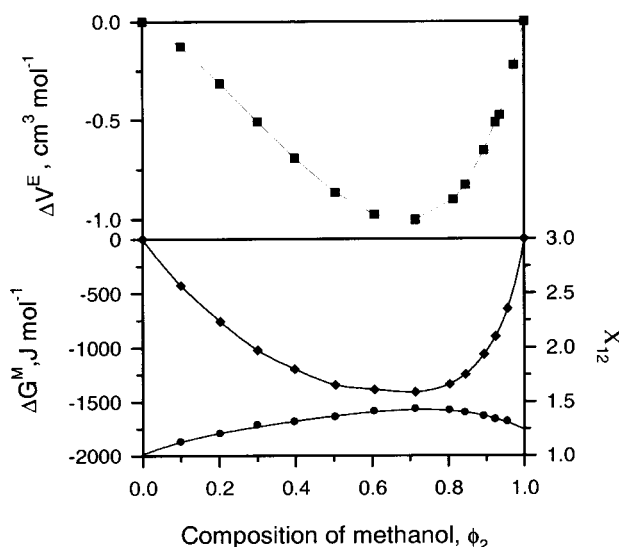

Figure 8 The $\Delta \overline{V}^E$, $\Delta \overline{G}^m$, and χ_{12} values of mixture cosolvent as a function of composition of methanol, ϕ_2 at 25°C.
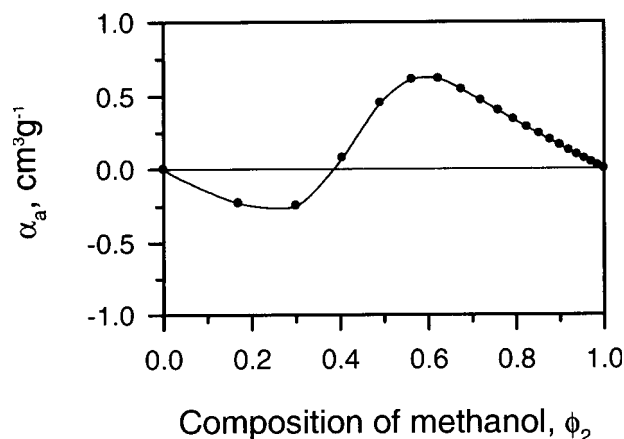
Figure 9 The adsorbed preferentially parameter, α_a values against various composition of methanol, ϕ_2.

ably changed the phase transition of PNIPAM ternary solution. The preferential adsorption phenomenon in this system is very special and dissimilar to other polymer ternary solutions. In several polymer/solvent/nonsolvent systems, one of the solvents can break down the association (cluster) of another solvent and the polymer chain, which preferentially adsorbs the broken solvent to form better affinity properties. However, in polystyrene/benzene/alcohol or paraffin systems, a good solvent, benzene, is always preferentially adsorbed as the precipitant was added.[24,40] In the polyvinyl pyrrolidone (PVP)/water/THF and PVP/ethanol/n-hexane systems, water and ethanol (good solvents) were always preferentially adsorbed, when THF and n-hexane were precipitated for PVP.[41] However, in the PNIPAM/water/methanol system, the formation of the H_2O—MeOH complex significantly affects the preferential adsorption phenomenon of PNIPAM chains in the cononsolvent ternary solution. At this cononsolvent system, the water is completely miscible with methanol to form the H_2O—MeOH complexes that reduce the interaction force between PNIPAM and the H_2O—MeOH complexes. Therefore, at $\phi_2 < 0.2$, it could be consider that almost whole methanol molecules should be associate with water molecules to form H_2O—MeOH complexes; therefore, the free water molecules are adsorbed preferentially by the PNIPAM chains. On the other hand, almost whole water molecules are suppose to form H_2O—MeOH complexes in the mixed cononsolvent; therefore, the free methanol molecules are preferentially adsorbed by the PNIPAM molecules at $\phi_2 > 0.55$. On the other hand, at $0.2 < \phi_2 < 0.4$, and $0.4 < \phi_2 < 0.55$ regimes, the PNIPAM molecules not only preferentially adsorb freely water and methanol molecules, respectively, but also adsorb large amount of H_2O—MeOH complexes structures. In these states, the clathrate-

like structure around the side chain of PNIPAM molecular become more defect due to the H_2O—MeOH complexes are unable to from an order structure and promote the phase transition of PNIPAM ternary solutions decreasing remarkable.

CONCLUSIONS

According to the aforementioned discussion, it is indicated that PNIPAM molecules undergone phase transition/LCST that may be due to the PNIPAM molecules adsorbed preferentially behavior as a function ϕ_2. Therefore, we combined the phase transition and the adsorbed preferred parameter, ϕ_a, of PNIPAM ternary solution with various ϕ_2 as shown in Figure 10. However, Figure 10 could be divided into five regions. At region (I), $\phi_2 < 0.2$, PNIPAM molecules may be preferentially adsorbed pure water molecules but decrease in the freely water molecules with ϕ_2; therefore, the phase transition decreases slightly ϕ_2 because of some the H_2O—MeOH complexes have be formed in the ternary solution. At region (II), $0.2 < \phi_2 < 0.4$, and the region (III), $0.4 < \phi_2 < 0.55$, the PNIPAM molecules not only preferentially adsorbed freely water and methanol molecules, respectively, but also adsorbed large amount of
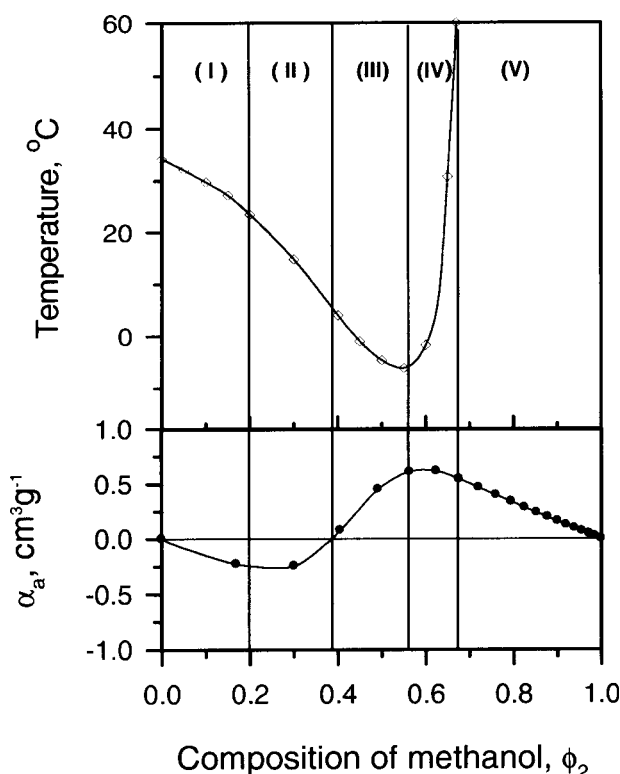

Figure 10 Combination the phase transition and α_a values of PNIPAM ternary solutions as a function of composition of methanol, ϕ_2 at 25°C.

H_2O—MeOH complexes structures. In these states, the clathrate-like structure around the side chain of PNIPAM molecular became more defect due to the H_2O—MeOH complexes were unable to from an ordered structure and promoted the phase transition of PNIPAM ternary solutions decreasing remarkable, whereas, the region (IV), the PNIPAM molecules preferentially adsorbed methanol molecules and decreasing adsorbed H_2O—MeOH complexes at ϕ_2 between 0.55 and 0.7. Thus, the interaction force between PNIPAM and H_2O—MeOH complexes gradually took place between PNIPAM and methanol; therefore, the phase transition of PNIPAM ternary solutions increased remarkably with ϕ_2. At $\phi_2 > 0.7$, the region (V), PNIPAM molecules preferentially adsorbed pure methanol molecules, which was a better solvent than water and H_2O—MeOH complex, inducing the PNIPAM ternary solutions appear transparent and not any transition occurred in this region.

From the viewpoint of the molecular structure of PNIPAM, it was interposed a hydrophilic group (CONH) between the hydrophobic backbone chain and isopropyl group of PNIPAM; therefore the hydrophilic and hydrophobic interactions between PNIPAM molecules and mixture cononsolvent (water, methanol, and H_2O—MeOH complex) may play a dominant role in the thermodynamic behavior of PNIPAM solutions. Water was a typical hydrophilic dipolar solvent, which is formed two strongly hydrogen bonding with hydrophilic group (CONH) of side chain of PNIPAM and other waters to form the clathrate-like structure around the side chain of PNIPAM. These clathrate-like structures/hydrophilic interactions promoted the PNIPAM chains soluble in aqueous solution at temperature below the LCST. When temperature at the LCST, the clathrate-like structure around the side chain of PNIPAM was collapsed, inducing the hydrophobic interactions between PNIPAM backbone chains and between hydrophobic groups and backbone chains of PNIPAM took place a primary role, thus the phase transition/LCST of PNIPAM was occurred in this state. On the other hand, methanol was an amphiphilic solvent that combines a hydrophilic group (hydroxide group) and a hydrophobic group (methyl group) together. The hydroxide group of methanol could build with a water molecule through hydrogen bonding to form the H_2O—MeOH complex. Therefore, PNIPAM molecules not only preferentially adsorbed water and methanol molecules, respectively, but also adsorbed the H_2O—MeOH complexes structures at $0.2 < \phi_2 < 0.4$ and $0.4 < \phi_2 < 0.55$ regions. In these states, the clathrate-like structure became more defected with increasing adsorbed content the H_2O—MeOH complex. Because of the H_2O—MeOH complex in the clathrate-like structure could not form the three dimensional ordered struc-

ture. The clathrate-like structure became more defected as PNIPAM molecules adsorbed larger amount of H_2O—MeOH complexes inducing the LCST of PNIPAM ternary solutions decreased remarkably. While PNIPAM molecules preferentially adsorbed pure methanol molecules at $\phi_2 > 0.7$. It indicates that the hydrogen bonding between hydroxide group of methanol and hydrophilic groups of PNIPAM was broken instantly and became a hydrophobic interaction between methyl group of methanol and isopropyl group and backbone of PNIPAM as temperature was increased. Therefore, the PNIPAM ternary solution without any transition occurred at PNIPAM molecules preferentially adsorbed pure methanol molecules region. Therefore, these results show that the various thermodynamic behaviors between PNIPAM and mixture solvents (water, methanol, and water-methanol complex) must be concerned with different preferential adsorption phenomenon, which was mainly related to different degrees of polymer–solvent interaction and structures of solvent used.

References

1. Hong, P. D.; Chen, J. H. Polymer 1998, 39, 711.
2. Hong, P. D.; Chen, J. H. Polymer 1998, 39, 5809.
3. Hong, P. D.; Chen, J. H. Polymer 1999, 40, 4077.
4. Hong, P. D.; Chen, J. H. Polymer 2000, 41, 5847.
5. Molyneux, P. Water-Soluble Polymers Properties and Behavior, Vol. 1; Florida: CRC Press, 1983.
6. Yamakawa, H. Macromolecules 1993, 26, 5061.
7. Tiktopulo, E. I.; Uversky, V. N.; Lushchik, V. B.; Klenin, S. I.; Bychkova, V. E.; Ptitsyn, O. B. Macromolecules 1995, 28, 7519.
8. Grosberg, A. Y.; Kuznetsov, D. V. Macromolecules 1993, 26, 4249.
9. Taylor, L. D.; Cerankowski, L. D. J Polym Sci Polym Chem Ed 1975, 13, 2551.
10. Winnik, F. M. Macromolecules 1990, 23, 233.
11. Winnik, F. M.; Ringsdorf, H.; Venzmer, J. Langmuir 1991, 7, 912.
12. Ben-Naim, A. Hydrophobic Interaction; Plenum: New York, 1980.
13. Scarpa, J. S.; Mueller, D. D.; Klotz, I. M. J Am Chem Soc 1967, 89, 6024.
14. Heskins, M.; Guillet, J. E. J Macromol Sci Chem 1968, 2, 1441.
15. Chen, J. H.; Lin, Y. L.; Zhang, Y. X.; Zhuang, P. Y. Polymer 2007, submitted.
16. Winnik, F. M.; Ringsdorf, H.; Venzmer, J. Macromolecules 1990, 23, 2415.
17. Schild, H. G.; Tirrell, D. A. Macromolecules 1991, 24, 948.
18. Ottaviani, M. F.; Winnik, F. M.; Bossmann, S. H.; Turro, N. J. Helv Chim Acta 2001, 84, 2476.
19. Hong, P. D.; Huang, H. T. Polymer 2000, 41, 6195.
20. Read, B. E. Trans Faraday Soc 1960, 56, 382.
21. Cowie, J. M. G.; Bywater, S. J Makromol Chem 1966, 1, 581.
22. Katime, I. A. Makromol Chem 1985, 186, 2125.
23. Katime, I.; Garro, P.; Teijon, J. M. Eur Polym J 1975, 11, 881.
24. Lange, H. Kolloid Z Z Polym 1964, 199, 128.
25. Lange, H. Kolloid Z Z Polym 1965, 201, 123.
26. Lange, H. Kolloid Z Z Polym 1966, 209, 26.

27. Horta, A. Macromolecules 1981, 14, 1519.
28. Schultz, A. R.; Flory, P. J. J Polym Sci 1955, 15, 231.
29. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1975.
30. Pouchĺy, J.; Živńy, A.; Šolc, K. J Polym Sci Part C: Polym Symp 1968, 23, 245.
31. Chu, S. G.; Munk, P. Macromolecules 1978, 11, 879.
32. Aminabhavi, T. M.; Munk, P. Macromolecules 1979, 12, 607.
33. Gmelting, J.; Onken, V. In Vapor-Liquid Equilibrium Data Collection, Vol. 1; Dechema: Frankfurt, 1977.
34. Huggins, M. L. J Polym Sci 1942, 64, 2716.
35. Zimm, B. H. J Chem Phys 1948, 16, 1093.
36. Zimm, B. H. J Chem Phys 1948, 16, 1099.
37. Franks, F.; Eagland, D. CRC Crit Rev Biochem 1985, 4, 165.
38. Bosch, E.; Bou, P.; Allemann, H.; Roses, M. Anal Chem 1996, 68, 3651.
39. Bai, T. C.; Yao, J.; Han, S. J. J Chem Eng Data 1999, 44, 491.
40. Lange, H. Makromol Chem 1965, 86, 192.
41. Nordmeier, E.; Lechner, M. D. Macromolecules 1991, 24, 2529.