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# N.m.r. investigation of phase separation in poly(N-isopropyl acrylamide)/water solutions

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$^1$H and $^{13}$C n.m.r. spectra of poly(N-isopropyl acrylamide) (PNIPA) in $D_2O$ and $CDCl_3$ were measured at several temperatures encompassing the lower critical solution temperature (LCST) about 32°C of the PNIPA/water solution, using a high resolution n.m.r. spectrometer (500 MHz for proton). The PNIPA/$CDCl_3$ is homogeneous in the temperature ranging from 16 to 36°C and the hydrogen bonds of the amide groups are weakened by the solvation of $CDCl_3$ and broken by heating. In the PNIPA/$D_2O$ solution, the proton and $^{13}$C spectra are well resolved below the LCST. Whereas at temperatures above the LCST, all the resonance peaks except that for water proton became broad and the spectra lost their fine structure. The integral intensity of the water proton relative to that of the lone proton in the isopropyl group increases with increasing temperature, suggesting that some water molecules appear to be released out of the hydrated shells around the polymer chains. When the solution was heated from 22 to 35°C, the spin–lattice relaxation time $T_1$ for the proton of the methyl group in the isopropyl residue increased, while that for the protons of the methylene and methyne groups of the backbone chain decreased. This indicates that during heating the relaxation of the isopropyl side chain slows down and that of the main chain speeds up. The phase separation was qualitatively interpreted with the Nemethy–Scheraga model for the hydrophobic bonding.


**(Keywords: poly(N-isopropyl acrylamide); phase transition; hydrophobic interaction)**

## INTRODUCTION

The feature that poly(N-isopropyl acrylamide) (PNIPA) contains hydrophilic amide and hydrophobic isopropyl groups in its side chain renders this polymer soluble in water and in low polarity solvents such as tetrahydrofuran[1]. A slightly crosslinked PNIPA forms a soft gel in water, which undergoes a discontinuous and reversible volume change in response to changes in temperature, solvent composition, etc.[2,3]. With these characteristics PNIPA is counted as an inviting polymeric material both academically and industrially.

It is known that the PNIPA/water solution has a lower critical solution temperature (LCST) at about 32°C[4]. Its phase separation process has, however, not been fully clarified[1], though many methods including cloud point measurement[5–7], light scattering[4–6,8,9], differential scanning calorimetry (d.s.c.)[5,7,10], viscometry[5,11], and fluorescence[12–21], have been used. A two-step process has been proposed[9], in which collapse of single chains is followed by their aggregation into larger particles. The first step, i.e. the coil-to-globule transition, was studied by Fujishige *et al.*[4,6], who measured the radius of gyration and the Stokes radius on a PNIPA with a narrow molecular weight distribution and concluded that the collapse is completed before the system becomes thermodynamically unstable. Recently, Wu and Zhou[22,23] carried out light scattering measurements on a narrow distribution PNIPA of high molecular weight in water at extremely low polymer concentrations and found that thermodynamically stable globules existed up to about 32°C.

The aggregation of collapsed chains can be detected by the nonradiative energy transfer (NRET). Using PNIPA doubly labelled with a naphthalene donor and a pyrene acceptor, Winnik[14] observed that the aggregation took place after the chain collapse was completed. Below the LCST donor and acceptor labelled PNIPA exhibited no NRET, which indicates a lack of interchain interactions. Further evidence for this indication was obtained from the observation that no NRET occurred between fluorene-labelled PNIPA and free pyrene below the LCST[24].

Information about the phase diagram for aqueous solutions of PNIPA is still confused. By visible observation of the phase separation upon heating Heskins and Guillet[5] determined the cloud point as a function of the polymer concentration. From optical transmittance measurements Fujishige *et al.*[6] showed that the cloud point curves for PNIPA ranging in molecular weight

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from 50 000 to 8 400 000 were superimposable. The curve for the highest molecular weight was almost flat, i.e. parallel to the concentration axis. By contrast, Schild and Tirrell[7] argued that the cloud point for PNIPA in water depends on polymer molecular weight and concentration. To be more serious, neither the concentration of the lower critical point nor binodals for this system is available as yet.

D.s.c. measurements[5] upon heating of the PNIPA/water solution at several concentrations exhibited endotherms, which give similar enthalpies of about 6.3 kJ mol$^{-1}$ during the phase separation[7,10]. This heat absorption indicates the elimination of polymer–water contacts with increasing temperature.

Tokuhiro *et al.*[25] applied proton n.m.r. technique to PNIPA hydrogels, compared the results with the spectra for linear PNIPA chains in $D_2O$ during the phase separation. According to them, the line shapes for the linear chains underwent no change until the temperature reached the LCST and the isopropyl groups in the side chains were much more mobile than the main chain. Ohta *et al.*[26] determined the spin–lattice relaxation time $T_1$ and the spin–spin relaxation time $T_2$ for PNIPA in water by a 20 MHz spectrometer. Since this apparatus was not capable of examining the relaxation of various protons individually, they determined by curve-fitting the values of $T_2$ for the protons in water and those in both main and side chains of the polymer and found that all $T_2$ exhibited a sudden change around the LCST.

This paper reports a study on proton and $^{13}C$ n.m.r. resonance of PNIPA in water and chloroform using a high-resolution 500 MHz spectrometer in the temperature range encompassing the LCST of the PNIPA/water system. Thus, we monitored $T_1$ and $T_2$ of specific protons individually.

## EXPERIMENTAL

### *Sample preparation*

PNIPA was obtained by free radial polymerization in a benzene/acetone mixture at 60°C (we thank Kohjin Co., Japan for the monomer)[11]. The product was precipitated into benzene, and the reprecipitation from acetone into benzene was repeated four times, and the polymer was dried *in vacuo*. All solvents used were analytically pure reagents.

Gel permeation chromatography of the final PNIPA sample, obtained by a Waters-150C instrument with tetrahydrofuran as the solvent, yielded a weight-average molecular weight $M_w$ of 65 000 and a polydispersity index $M_w/M_n$ of 1.9. The calibration curve was constructed using five narrow-distribution polystyrene samples.

### *N.m.r. measurements*

$^1H$ and $^{13}C$ n.m.r. spectra were obtained on a Bruker ARX-500 superconducting Fourier transform n.m.r spectrometer operating at 500.13 MHz for proton and 125.76 MHz for $^{13}C$. For the $^1H$ spectrum a 90° pulse width of 8.1 $\mu$s and a repetition time of 2 s were used to accumulate 32 transits, and the corresponding figures for the $^{13}C$ spectrum were 10 $\mu$s, 2 s, and 2048 transits. $^1H$ decoupling was effected by using the Waltz 16 point sequence.

For the assignment of each resonance peak, heteronuclear $^1H$–$^{13}C$ correlation spectroscopy (HETCOR) was determined for PNIPA in $CDCl_3$ by multi-quantum n.m.r. technique with 512 × 256 data points. The spectra were processed with a base-line correction and zero filling to obtain a final matrix of 512 × 512 real points. The spin–lattice relaxation $T_1$ was evaluated by the inversion recovery method with a pulse of about $5T_1$, and $T_2$ by the spin-echo CPMG method.

N.m.r. data on the PNIPA sample were taken at a polymer concentration of 30 mg ml$^{-1}$ in $D_2O$ and 50 mg ml$^{-1}$ in $CDCl_3$ in the temperature range from 16 to 36°C controlled to ±0.1°C, which encompasses the LCST. The measuring concentrations were chosen to obtain maximal accuracy in both proton and carbon n.m.r. measurements. The $^1H$ chemical shifts were scaled by the proton signals left at 4.82 ppm in $D_2O$ and 7.28 ppm in $CDCl_3$, while the $^{13}C$ chemical shifts were scaled with the $^{13}C$ resonance at 77.7 ppm in $CDCl_3$ taken as the reference.

## RESULTS AND DISCUSSION

### *PNIPA in $CDCl_3$*

*Figures 1* and *2* show $^1H$ and $^{13}C$ n.m.r. spectra, respectively, for PNIPA in $CDCl_3$ at the four temperatures indicated. The assignment of the chemical species to the respective resonance peaks followed the cross-peaks of the $^1H$–$^{13}C$ HETCOR shown in *Figure 3*. As the temperature is raised, all peaks in *Figures 1* and *2* gradually become sharper, but the chemical shifts remain unchanged except that for the amide proton (NH). These features can be attributed to the increasing mobility of the molecules with increasing temperature. In *Figure 1*, the proton signal for the hydrogen bonded NH at 16°C overlaps that at 3.85 ppm for the lone proton in the isopropyl group. Its shift to 3.28 ppm upon heating to 30°C indicates that some of the hydrogen bonds between the amide groups are broken at higher temperature, thus showing the free proton resonance of NH at high field.

*Figure 1* also reveals two broad signals for the methylene proton and one for methyne proton in the

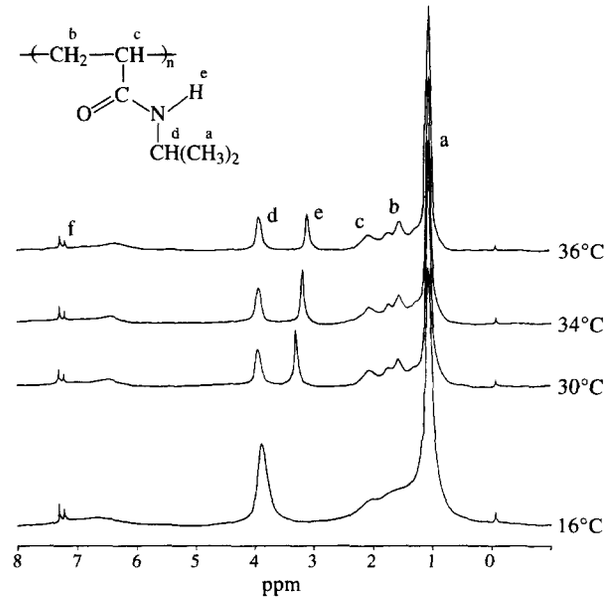


**Figure 1** Proton n.m.r. spectra of poly(N-isopropyl acrylamide) (PNIPA) in $CDCl_3$ at indicated temperatures. (a) Methyl proton of the isopropyl group; (b) methylene proton; (c) methyne proton; (d) lone proton of the N-isopropyl group; (e) proton of NH; (f) remaining proton in the solvent

vicinity of the strong methyl signals at 1.06 ppm. This broadening of $^1H$ signals can be attributed to a distribution of PNIPA chain conformations which are somewhat fixed due to a lack of mobility.

*Figure 4* shows that the two peaks (at 41.76 and 42.71 ppm) of the methyne carbon resonance at 16 and 30°C are split into four peaks (at 41.13, 41.61, 42.24 and 42.72 ppm) at 34 and 36°C. This could be due to both the different tacticities of the side chain onto the backbone methyne carbon and the environment change around the methyne with increasing temperature.

The above n.m.r. data indicate that the PNIPA/$CDCl_3$ solution is homogeneous in the temperature range studied and that the hydrogen bonds between the side chain amide groups are weakened by solvation of the hydrophobic chain backbone and side chain isopropyl groups with the low polarity solvent $CDCl_3$ and easily broken by heating.

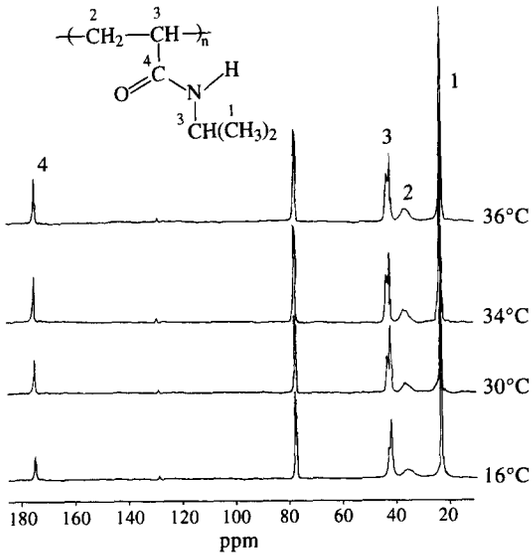


**Figure 2** $^{13}C$ n.m.r. spectra of PNIPA in $CDCl_3$ at indicated temperatures. (1) Methyl carbon; (2) methylene carbon; (3) methyne carbons in the polymer backbone and the isopropyl group; (4) carboxyl carbon

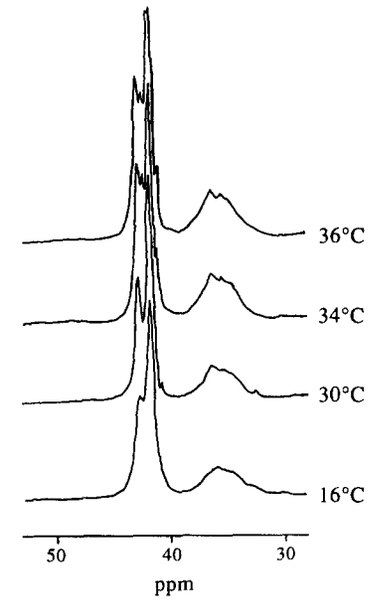


**Figure 4** Spectral signals of methyne carbons splitting from two into four with increasing temperature

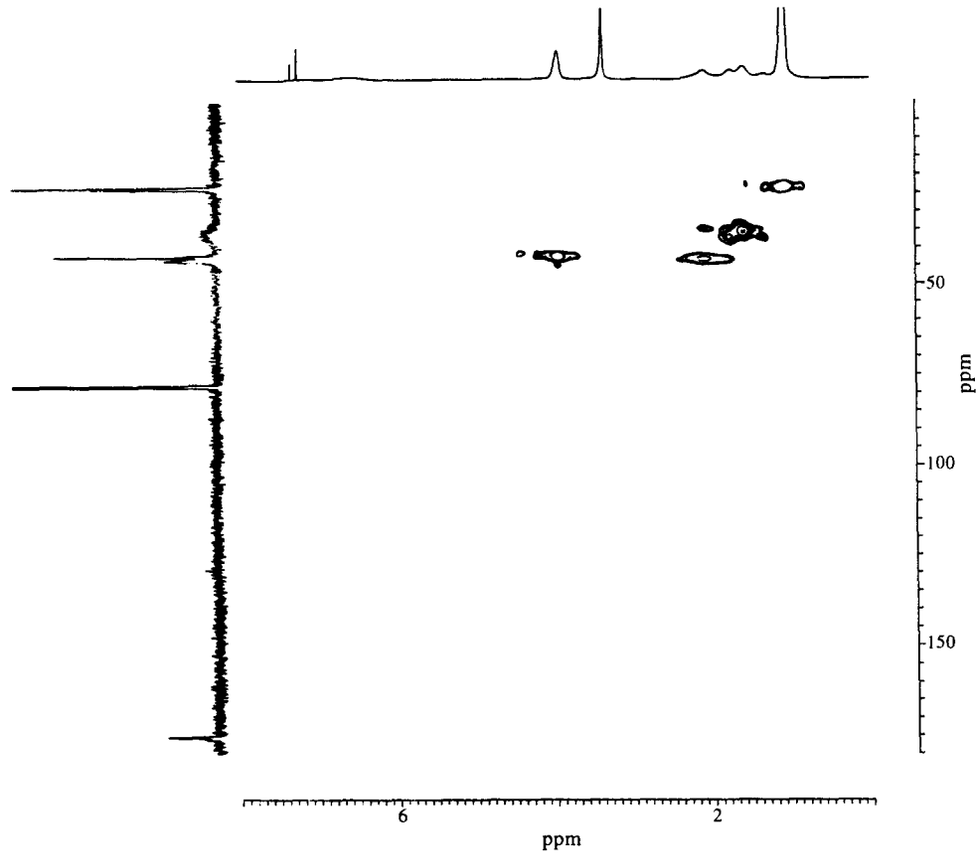


**Figure 3** 2D $^1H$–$^{13}C$ HETCOR spectrum of PNIPA in $CDCl_3$ at room temperature

*PNIPA in water*

*Figure 5* depicts the $^{13}C$ n.m.r. spectra of the PNIPA/$D_2O$ system at different temperatures below and above the LCST. The corresponding proton n.m.r. spectra are presented in *Figure 6*. The assignment of characteristic peaks is the same as in *Figures 1* and *2*. Note that the NH proton signal at about 3.2 ppm in *Figure 1* is absent in *Figure 6*, owing to deuterium exchange with the solvent.

As the temperature is increased from 25 to 29°C, so that it is still below the LCST, all the peaks in *Figure 5* shift slightly towards lower field, e.g. the peak for the methyl carbon from 21.05 to 21.26 ppm. The signal at about 42 ppm for the methyne carbon consists of a triplet, and the signal for the methylene carbon is single-peaked and broad. With increasing temperature beyond the LCST, the sharp signal for the methyl carbon at 21.26 ppm is markedly broadened. It is reasonable to ascribe this to intra and interchain associations formed during the phase separation which hinder the internal rotations of the polymer chains.

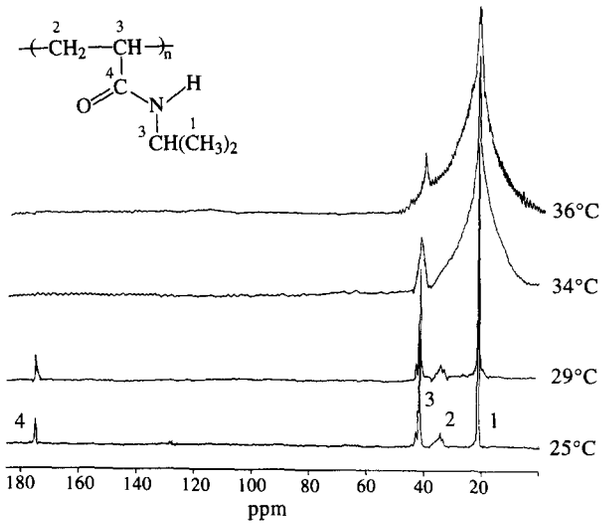


**Figure 5** $^{13}C$ n.m.r. spectra of PNIPA in $D_2O$ at indicated temperatures, with the same assignment as in *Figure 2*

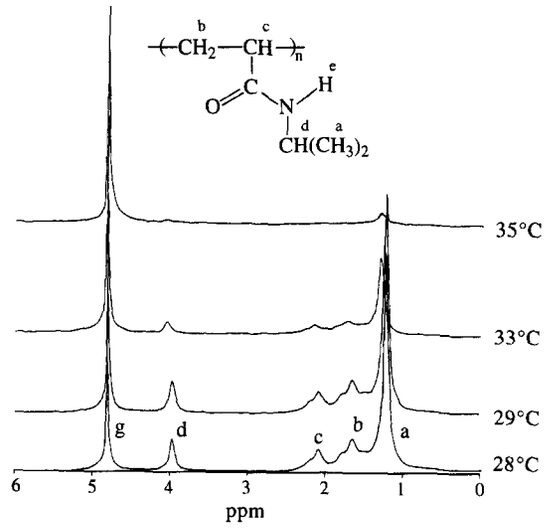


**Figure 6** Proton n.m.r. spectra of PNIPA in deuterated water ($D_2O$) at different temperatures. The assignment is the same as that in *Figure 1*, except the presence of (g) for water proton and the absence of (e) for NH proton

It can be seen from *Figure 6* that when temperature is lower than the LCST, all proton spectra are well resolved. The spin–spin relaxation time $T_2$ given in *Table 1* slightly increases with raising temperature for the lone and methyl protons in isopropyl groups. However, as the temperature is above the LCST, all resonance peaks shift towards lower field and are broadened except that for the water proton at 4.82 ppm. Signals for the methylene and methyne protons on the chain backbone are masked by the large methyl proton peak. As pointed by Tokuhiro *et al.*[25], the larger changes in the line width of the methyl proton and carbon implies that conformational change in the side chain isopropyl groups is more significant than that in the backbone groups during the phase separation.

*Figure 7* shows the integral intensity for water protons at 4.82 ppm, $I_w$ and for all protons in one repeat unit of PNIPA, $I_t$ relative to that for the lone proton in the isopropyl group, $I_d$ as functions of temperature below the LCST. $I_t/I_d$ remains constant at about 10.5, which is fairly equal to the number of protons in one repeat unit of PNIPA, implying that the protons other than the amide proton are not deuterated during the n.m.r. measurements. On the other hand, $I_w/I_d$ increases with temperature and the observed $I_w$ value can be reversibly reduced as temperature is decreased again[27]. There are two causes responsible for this phenomenon, i.e. the decrease in $I_d$ owing to the broadening of the peak and the release of water from the hydrated shell around the PNIPA chain upon heating. The share of the former should be smaller since the proton spectra are well resolved at these temperatures and the $T_2$ for the lone proton in isopropyl groups even increases as temperature rose from 20 to 30°C. The light scattering results on dilute aqueous PNIPA solutions also emphasize that the collapse of PNIPA chains occurs at about 31°C, below which the chain behaves like a random coil in a good solvent[23].

**Table 1** Proton n.m.r. spin–spin relaxation time $T_2$ of PNIPA/$D_2O$ solution

| | $T_2$(mS) | |
|---|---|---|
| $T$(°C) | Lone proton in ispropyl group | Methyl proton in isopropyl group |
| 20.0 | 139.6 | 52.42 |
| 30.0 | 150.9 | 61.41 |

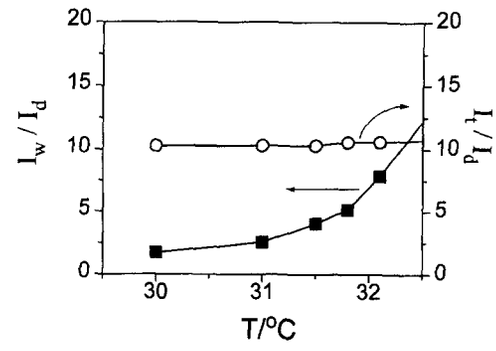


**Figure 7** Temperature dependence of the intensity of water proton relative to the lone proton in the isopropyl group, $I_w/I_d$ (squares), and that of the total proton in one repeat unit of PNIPA relative to the lone proton in the isopropyl group, $I_t/I_d$ (circles)

It is estimated from the above data that about one proton water molecule is released from one repeat unit of PNIPA at 31°C. This normal water will be the residue of the heavy water and/or polymer sample, which seems to preferentially exist in the solvated shell of the PNIPA below the LCST due to the difference in hydrogen bonding affinities of $H_2O$ and $D_2O$[28]. The n.m.r. resonance of the normal water proton may be covered by other proton signals, giving the $I_t/I_d$ larger than the exact value of 10.

*Dynamic behaviour of PNIPA in water*

*Figure 8* shows the temperature dependence of the spin–lattice relaxation times $T_1$ for the protons of the main chain methylene and methyne and those of the side chain methyl and methyne in the PNIPA/$D_2O$ solution. The accuracy of $T_1$ is low above the LCST where the resolution of proton signals decreases. Interestingly, with increasing temperature, $T_1$ for the methyl proton in the isopropyl groups increases, while those for the methylene and methyne protons in the backbone decrease. Though the data are quite scattered, the temperature dependence of $T_1$ for the lone proton in the isopropyl group appears to follow a curve that is convex upwards.

Instead of applying a rigorous model for the spin–lattice relaxation, we try to understand the general nature of molecular motions in view of the general behaviour of the temperature dependence of $T_1$. For this purpose, the BPP theory[29] can be sufficiently adopted to relate $T_1$ with the correlation time $\tau$ and the temperature dependence of $\tau$ is described by the Arrhenius expression, similar to the discussion of Tokuhiro *et al.*[25]. For a specific proton, there is a minimum in its curve of $T_1$ against temperature $T$ dividing the curve into high- and low-temperature sides[30]. In the observed temperature range, the experimental $T_1$ vs. $T$ curve usually locates on either side depending on the product of the Larmor frequency and correlation time. With increasing temperature and relaxation for the methyl proton in the isopropyl group follows the $T_1$ curve on the high-temperature side of the $T_1$ minimum, whereas the $T_1$ behaviour of the backbone protons follows the $T_1$ curve on the low-temperature side.

The above temperature dependencies of $T_1$ suggest that as temperature increases the relaxation of the side chain isopropyl group is slowed down while that of the backbone methylene and methyne groups is speeded up. Probably it is more significant to see that all $T_1$ data for various protons show change smoothly in crossing the LCST.

*Interpretation of phase separation*

Finally, we consider in qualitative terms why the PNIPA/water system has an LCST with the help of the Nemethy–Scheraga model for the hydrophobic bonding[31–33]. The backbone of PNIPA and its side chain isopropyl groups are hydrophobic. Therefore, it is reasonable to assume that this polymer is made water-soluble by the formation of hydrogen bonds between the side chain amide groups and water. The water molecules trapped by these bonds form a thin shell of ordered structure around the hydrophilic part of the polymer. At the same time, water molecules also form a hydrated shell of ordered icelike structure upon the hydrogen bonds between water molecules themselves around the hydrophobic part of the polymer[34]. Formation of these two hydrated shells gives a negative enthalpy for the solution process $\Delta H(T_0)$ at a lower temperature $T_0$, at which the hydrogen bonds stay substantially unbroken. However, the same process involves a larger negative entropy change $\Delta S(T_0)$ owing to the formation of icelike cages of water molecules around the solutes[32].

Increasing temperature tends to break the hydrogen bonds, and this increases $\Delta H(T_0)$ by $\delta H_w$. Some of the water molecules are released out of the hydrated shell as a result of hydrogen bond breaking, so the structure of the hydrated shell is partially destroyed. Then, it becomes possible for the side chain isopropyl groups to approach within their van der Waals radii and thus to form so-called hydrophobic bonding[33]. The formation of such bonds lowers $\Delta H(T_0)$ by $\delta H_h$. Hence, $\Delta H(T_0)$ increases by $\delta H = \delta H_w - \delta H_h$ as a result of hydrogen bond breaking and hydrophobic bonding.

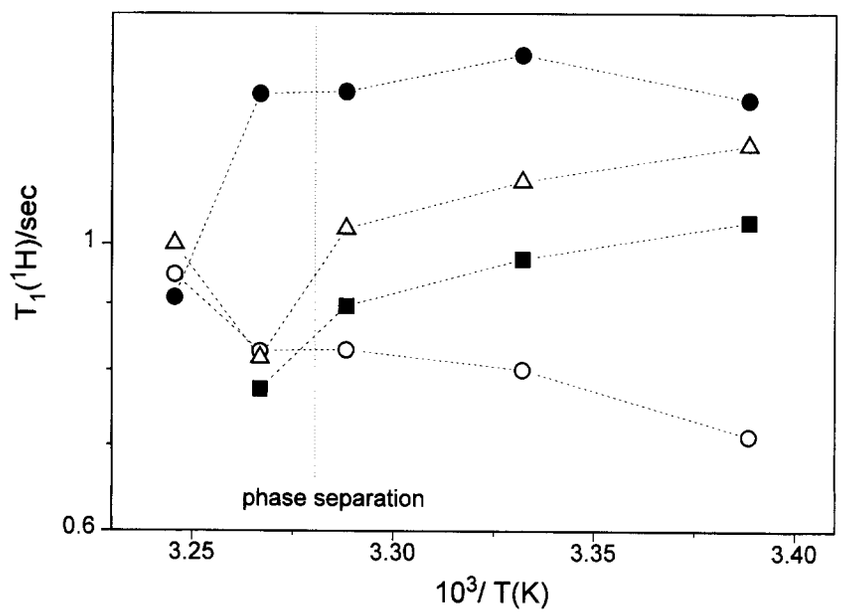


**Figure 8** Proton spin–lattice relaxation times $T_1$ of PNIPA in $D_2O$ at different temperatures. (○) Methyl proton; (■) methylene proton; (△) methyne proton of the main chain backbone; (●) the lone proton of the isopropyl group

Hydrophobic bonding can be formed between the same and different polymer chains, and this process is manifested as single chain collapse and intermolecular aggregation. Which of these processes occurs preferentially depends on the concentration of the solution. It suppresses conformation changes of the polymer, and hence decreases $\Delta S(T_0)$ by $\delta S_h$. On the other hand, as the hydrated shells of the polymers are disordered and water molecules are excluded into the bulk, $\Delta S(T_0)$ is increased by $\delta S_w$. Therefore, the hydrophobic bonding leads to an increase in $\Delta S(T_0)$ given by $\delta S = -\delta S_h + \delta S_w$.

Then, the above considerations allow the Gibbs free energy $\Delta G(T) = \Delta H(T) - T\Delta S(T)$ for the solution process at temperature $T$ to be expressed by

$$\Delta G(T) = \Delta H(T_0) + \delta H(T) - T[\Delta S(T_0) + \delta S(T)] \quad (1)$$

where

$$\delta H(T) = \delta H_w(T) - \delta H_h(T) \quad (2)$$

$$\delta S(T) = -\delta S_h(T) + \delta S_w(T) \quad (3)$$

As mentioned earlier, d.s.c. measurements indicate that heat is absorbed during the phase separation of PNIPA in water[7,10]. This implies that $\delta H(T)$ should be taken as positive and increase with $T$ to make $\Delta H(T) = \Delta H(T_0) + \delta H(T)$ positive at the phase separation. As evaluated by Nemethy and Scheraga[33], the entropy change $\delta S(T)$ for hydrophobic bonding between isolated pairs of isopropyl side chains is positive, decreases with $T$, and is smaller than the absolute value of $\Delta S(T_0)$ in the temperature range studied. So that the term $-T[\Delta S(T_0) + \delta S(T)]$ is also positive. Therefore, it follows that the sum of the second and third terms on the right-hand-side of equation (1) increases monotonically with $T$, but the increase is offset by the first term at lower temperatures, keeping the solution homogeneous. With increasing $T$, however, the magnitude of negative $\Delta H(T_0)$ is exceeded progressively by the sum of the last two terms resulting in a positive $\Delta G(T)$. This predicts that, as the temperature is raised, the system becomes increasingly unstable and phase-separated.

Typical theories[35,36] for the phase separation with an LCST take into account a volume contraction increasingly at high temperature due to the equation-of-state contributions, which lowers both $\Delta H$ and $\Delta S$ of the solution process. This idea does not seem to be needed for explaining the phase separation of the PNIPA/water system. In this system, the increase in $\Delta H$ due to hydrogen bond breaking makes the solution unstable even more rapidly with the slight increase in $\Delta S$ for the solution process owing to the hydrophobic bonding.

The basic idea that more hydrogen bonds are broken and some of the bound water is released out of the hydrated shells with increasing temperature is consistent with the temperature dependence of $I_w/I_d$ shown in *Figure 7*. For isolated side groups in a series of polypeptides, Nemethy and Scheraga[33] estimated the number of water molecules that are excluded to form the strongest hydrophobic bond between a pair of them. As hydrophobic bonding becomes stronger between the isopropyl groups, the microenvironment around PNIPA should become less polar. Winnik *et al.*[12] have shown with fluorescence techniques that the polarity is lowered to that of organic liquids such as methanol and tetrahydrofuran.

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## REFERENCES

1. Schild, H. G., *Prog. Polym. Sci.*, 1992, **17**, 163.
2. Hirokawa, Y. and Tanaka, T., *J. Chem. Phys.*, 1984, **81**, 6379.
3. Shibayama, M. and Tanaka, T., *Adv. Polym. Sci.*, 1993, **109**, 1.
4. Kubota, K., Fujishige, S. and Ando, I., *J. Phys. Chem.*, 1990, **94**, 5154.
5. Heskins, M. and Guillet, J. E., *J. Macromol. Sci. Chem.*, 1968, **A2**, 1441.
6. Fujishige, S., Kubota, K. and Ando, I., *J. Phys. Chem.*, 1989, **93**, 3311.
7. Schild, H. G. and Tirrell, D. A., *J. Phys. Chem.*, 1990, **94**, 4352.
8. Kubota, K., Fujishige, S. and Ando, I., *Polym. J.*, 1990, **22**, 15.
9. Yamamoto, I., Iwasaki, K. and Hirotsu, S., *J. Phys. Soc. Jpn.*, 1989, **58**, 210.
10. Otake, K., Inomata, H., Konno, M. and Saito, S., *Macromolecules*, 1990, **23**, 283.
11. Fujishige, S., *Polym. J.*, 1987, **19**, 297.
12. Winnik, F. M., *Macromolecules*, 1990, **23**, 233.
13. Winnik, F. M., *Macromolecules*, 1990, **23**, 1647.
14. Winnik, F. M., *Polymer*, 1990, **31**, 2125.
15. Winnik, F. M., Ringsdrof, H. and Venzmer, J., *Macromolecules*, 1991, **24**, 1678.
16. Winnik, F. M., Winnik, M. A., Ringsdrof, H. and Venzmer, J., *J. Phys. Chem.*, 1991, **95**, 2583.
17. Winnik, F. M., Ringsdrof, H. and Venzmer, J., *Langmuir*, 1991, **7**, 905.
18. Winnik, F. M., Ringsdrof, H. and Venzmer, J., *Langmuir*, 1991, **7**, 912.
19. Schild, H. G. and Tirrell, D. A., *Langmuir*, 1990, **6**, 1676.
20. Schild, H. G. and Tirrell, D. A., *Langmuir*, 1991, **7**, 665.
21. Schild, H. G. and Tirrell, D. A., *Langmuir*, 1991, **7**, 1319.
22. Wu, C. and Zhou, S., *Macromolecules*, 1995, **28**, 5388.
23. Wu, C. and Zhou, S., *Macromolecules*, 1995, **28**, 8381.
24. Schild, H. G. and Tirrell, D. A., *Macromolecules*, 1992, **25**, 4553.
25. Tokuhiro, T., Amiya, T., Mamada, A. and Tanaka, T., *Macromolecules*, 1991, **24**, 2936.
26. Ohta, H., Ando, I., Fujishige, S. and Kubota, K., *J. Polym. Sci., Polym. Phys.*, 1991, **29**, 963.
27. Feng, H., Unpublished results.
28. Chu, E. Y., Xu, Z. S., Lee, C. M., Sek, C. K., F., Okamoto, Y., Pearce, E. M. and Kwei, T. K., *J. Polym. Sci., Polym. Phys.* 1995, **33**, 71.
29. Bloembergen, N., Purcell, E. M. and Pound, R. V., *Phys. Rev.*, 1948, **73**, 679.
30. Howarth, O. H., in *NMR Spectroscopy of Polymers*, ed. R. N. Ibbett, Chapter 4. Blackie Academic & Professional, Glasgow, 1993.
31. Nemethy, G. and Scheraga, H. A., *J. Chem. Phys.*, 1962, **36**, 3382.
32. Nemethy, G. and Scheraga, H. A., *J. Chem. Phys.*, 1962, **36**, 3401.
33. Nemethy, G. and Scheraga, H. A., *J. Chem. Phys.*, 1962, **66**, 1773.
34. Horne, R. A., Alneida, J. P., Day, A. F. and Yu, N.-T., *J. Colloid Inter. Sci.*, 1971, **35**, 77.
35. Flory, P. J., *J. Am. Chem. Soc.*, 1965, **87**, 1833.
36. Patterson, D., *Macromolecules*, 1969, **2**, 672.