Relationship between the Coil-Globule Transition of an Aqueous Poly(*N*-isopropylacrylamide) Solution and Structural Changes in Local Conformations of the Polymer

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Summary: Structural changes in the local conformation of poly(*N*-isopropylacrylamide) (PNiPA) during the thermally and solvent-induced coil-globule transitions in an aqueous solution were studied by using attenuated total reflection / infrared (ATR/IR) spectroscopy combined with density functional theory (DFT) calculation. DFT calculation makes it possible to connect the spectral changes observed during the transitions with the structural changes of the local conformation of polymer chains. The results suggest that some of the intramolecular C=O···H-N hydrogen bonds of amide groups are broken, and the changes in local conformations occur during the coil-globule transitions of PNiPA. In this paper, an overview of our recent studies on the coil-globule transitions of PNiPA is given for introducing a new idea that may explain the stimulus sensitivities of PNiPA in solutions; the solubility of segments concerning with the local conformation of repeating monomer units is changed by an external perturbation, and then the polymer system shows the coil-globule transition.

Keywords: amide groups; density functional theory calculations; hydrogen bond; infrared spectroscopy; phase behavior; poly(*N*-isopropylacrylamide)

Introduction

To understand the transition phenomena of polymer systems based on the inter- and intra-molecular interactions, a more concrete illustration for the "segment" of the polymer systems must be required. Generally the segment has been defined as a repeated unit for a polymer chain in terms of the statistical physics [1-3]. However, to investigate the inter- and

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intra-molecular interactions in a real polymer system, it is necessary to consider that a real segment is constituted of a few repeating monomer units. In other words, the chemical features of the segment are expected to give more realistic pictures on the interactive forces of molecules. Of course, in some polymer systems such as cyclohexane-polystyrene system, the phase behavior can be explained qualitatively without considering explicitly any chemical features of the monomer [1-3]. On the other hands, the phase behavior of some other systems, such as those in which a strong hydrogen bonding between solvent and a polymer exists, show large deviations from that theoretically predicted from a simple lattice model [1].

As such a system, aqueous solutions of poly(*N*-isopropylacrylamide) (PNiPA) have been received great interest and been investigated by use of several experimental techniques, *e.g.* turbidity [4-6], light scattering [4,7,8], calorimetry [9,10], fluorescence [11,12], nuclear magnetic resonance [13], and infrared (IR) spectroscopy [14-16]. In general, it has been believed that the thermo-responsive behavior of PNiPA/water system is responsible for lower critical solution temperature (LCST) [4]. However, its phase diagram is still controversial. While Heskins and Guillet reported that PNiPA/water system has a normal phase diagram with lower critical solution temperature (LCST) [4], Fujishige *et al.* suggested that the cloud point of a PNiPA aqueous solution is concerned neither with the molecular weight of the polymer (from 5×10^4 to 840×10^4) nor with its concentration (from 0.01 to 1 wt%) [5]. Tong *et al.* described that the cloud point temperature monotonically decreases with the increase in the polymer concentration from 0.58 to 70 wt% and LCST can not be determined [6]. Many researchers have presumed that these unusual transition behavior of PNiPA/water system is caused by a strong and characteristic interaction between the polymer and water molecules. Therefore, it may be natural to consider the segments of PNiPA as a realistic chemical substance.

Recently, we have been investigating the coil-globule transition of PNiPA in an aqueous solution by the use of IR spectroscopy combined with density functional theory (DFT) calculation [17,18]. That is to say, we have tried to clarify the relationship between the

spectral changes observed during the coil-globule transition of PNiPA and the changes in the local structure of the polymer.

Experimental Section

Sample **:** PNiPA and poly(*N,N*-dimethylacrylamide) (PNdMA) were synthesized by radical polymerization of *N*-isopropylacrylamide (Tokyo Chemical Industry, Tokyo) and *N,N*-dimethylacrylamide (Wako, Osaka), respectively. The details of polymerization are described in our previous papers [17,18]. *N*-methylacetamide (NMA), *N,N*-dimethylacetamide (NdMA), and perdeuterated methanol (CD_3OD) were purchased from Wako Pure Chemicals and used without further purification. The infinity pure grade of methanol (CH_3OH) was obtained from Wako and was used as received. Figure 1 shows the chemical structures of PNiPA, PNdMA, NMA and NdMA. The resistance of the finally prepared water used was greater than 18.1 MΩ. The concentrations of PNiPA, PNdMA, NMA and NdMA are about 20g/L.

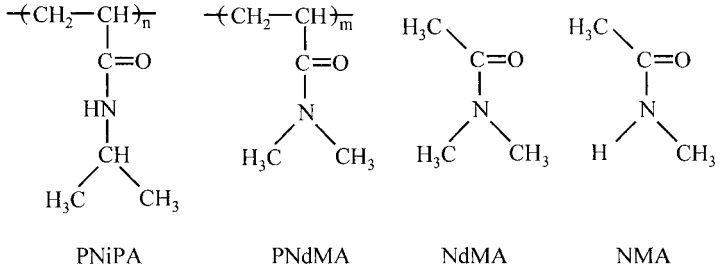

Fig.1. Chemical structures of PNiPA, PNdMA, NdMA, and NMA

IR Spectroscopy : The attenuated total reflection (ATR) / IR spectra were measured with a 4 cm^{-1} resolution using a Nicolet Magna 760 Fourier-transform IR spectrometer with a liquid-nitrogen cooled mercury-cadmium-telluride detector. The ATR cell was made of a horizontal ZnSe crystal (the refractive index is 2.403) with an incidence angle of 45° (Thermal A.R.K, Spectra-Tech, Inc.). A total of 512 scans was co-added for each spectrum. The temperature of the ATR cell was controlled by use of a home-made thermoelectric device with

an accuracy of ±0.1°C. The ATR cell was covered by a toggle-clamp type sealing to prevent the evaporation of solvent.

Data processing **:** Data processing, such as the subtraction of spectra and the calculation of a second derivative, was performed by a software written in C++ language (Visual C++ 6.0, Microsoft), which is composed by one of us (YK). The detailed algorithm for the data processing was described in the previous paper [17,18]. In this paper, all IR spectra of PNiPA are presented after the subtraction of the solvent spectrum.

DFT Calculations **:** All DFT calculations were performed using the B3LYP functional and the 6-31G(d) basis set [19]. The computations were carried out with GAUSSIAN 98 program (Gaussian Inc.) at the Information Processing Center of Kobe University. The single scale factor, 0.9613, was multiplied to the calculated frequencies [19]. In order intuitively to compare the calculated frequencies and intensities with the observed ones, IR spectra were simulated from the frequencies and intensities of the DFT calculations assuming the Lorentzian band shapes having the bandwidth of 7 cm^{-1}. The vibrational assignments of the dimer models for PNiPA were carried out based on Cartesian normal coordinates by DFT calculation.

Results and Discussion

Thermally induced coil-globule transition of PNiPA. PNiPA undergoes the coil-globule transition at *ca.* 32°C in an aqueous solution [4,5]. The polymer chain has an extended coil conformation below the coil-globule transition temperature (T_θ), and collapses to a globule state above T_θ.[7,8] The temperature-dependent IR spectra have revealed that the microenvironment around the amide groups changes dramatically in the vicinity of T_θ.[17] Figure 2 shows typical IR spectra of PNiPA at 23.8°C (below T_θ) and 38.2°C (above T_θ). Below T_θ, a unimodal peak is observed at 1624 cm^{-1} in the amide I region of the IR spectra, while above the θ temperature, a new peak appears at 1653 cm^{-1}. The amide II band near 1560 cm^{-1} shows a gradual upward shift by *ca.* 8 cm^{-1} as temperature increases from 23.8 to 38.2°C.

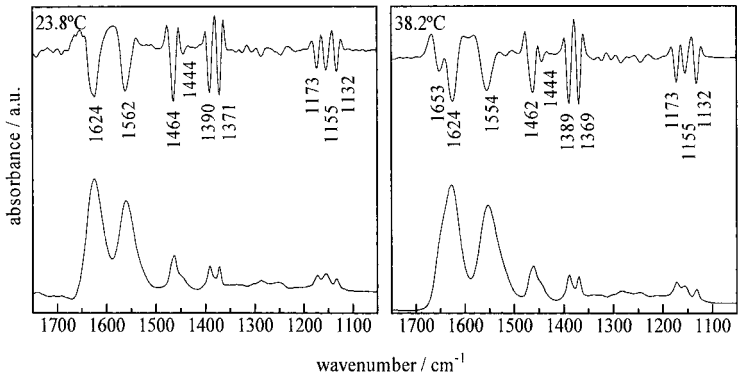

Fig.2. Typical IR spectra of PNiPA and their second derivatives observed below T_θ (left) and above T_θ (right)

The relative intensity of the band at 1173 cm^{-1} is weaker than that of the band at 1155 cm^{-1} at lower temperatures, but the former it becomes stronger during the coil-globule transition of PNiPA. Two possibilities may be considered to interpret the observed changes in the amide bands; (1) the changes in the interaction between the amide groups and water molecules (*i.e.* the hydration of the amide groups), and (2) the changes in the C=O···H-N hydrogen bond between the neighboring amide groups.

Solvent-induced coil-globule transition of PNiPA. It is also well known that the addition of certain solvent such as methanol, ethanol, acetone, and tetrahydrofuran results in a soluble-precipitation-soluble process of PNiPA in a mixed solvent system [20,21]. Recently, Zhang and Wu [21] revealed by using the light scattering technique that a single PNiPA chain undergoes a reentrant coil-globule transition in water-methanol mixtures. That is to say,

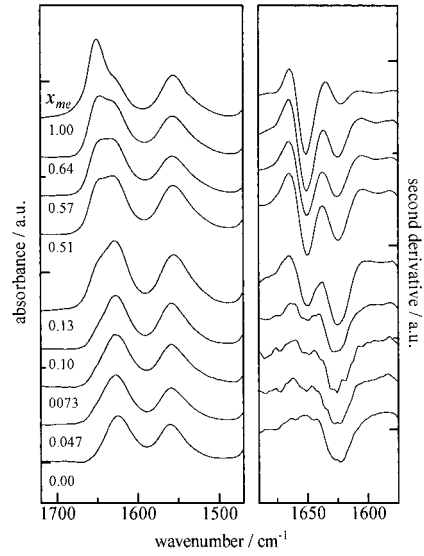

Fig.3. IR spectra of PNiPA (left) and their second derivatives (right) in the water-methanol mixtures at the various mol fractions of methanol (x_{me})

although both water and methanol are good solvents for PNiPA at room temperature, their mixtures are not good solvents. IR spectra of PNiPA in water-methanol mixtures are very informative for understanding the changes in the microenvironment around the amide groups [18]. Figure 3 shows IR spectra of PNiPA in the 1720-1450 cm^{-1} region at the various mol fraction of methanol (x_{me}). An IR spectrum of PNiPA in an aqueous solution shows only one band at 1624 cm^{-1} in the amide I region. In the mixture of x_{me}=0.13, a new band is observed at 1651 cm^{-1}. The relative intensity of this band to that at 1624 cm^{-1} increases with increasing x_{me}, and then the band at 1651 cm^{-1} becomes dominant at $x_{me}\geq 0.64$. No remarkable wavenumber

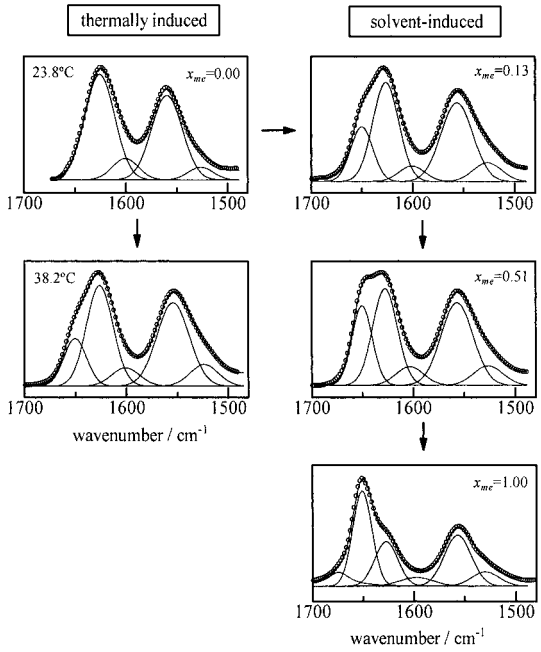

Fig.4. Curve fitting results for the spectra shown in Fig.2 and 3

shifts of the amide bands are observed in the whole range of x_{me}.

According to Zhang and Wu[21], PNiPA undergoes the following process: (1) the polymer chain is in an extended coil state in bulk water, and collapses into a globular state at $x_{me} \sim 0.18$. (2) addition of methanol in the range of $0.2< x_{me}<0.4$ results in a slight swelling of the globule, and then the globule-to-coil transition occurs in the vicinity of x_{me}~0.4. (3) the polymer

recovers to an extended coil conformation in the range of x_{me}>0.5 and bulk methanol. Winnik and co-workers reported the local polarity in the vicinity of the PNiPA chain by measuring the electronic paramagnetic resonance spectra of a probe molecule attached to the polymer chain[20]. According to them, the local polarity estimated by the hyperfine coupling constant varies together with the macroscopically observed coil-globule-coil process of PNiPA in water-methanol mixtures.

The spectral changes observed in Figure 3 seem to be in good agreement with their observations for the macroscopic phenomena and the local polarity in the range of $0.0 \leq x_{me} \leq 0.13$, *i.e.* the appearance of the band at 1651 cm^{-1} represents the macroscopic polymer conformation changes from the coil state to the globule state. In the $0.51 \leq x_{me} \leq 1.00$ range, however, the changes in the amide bands of PNiPA are not in accord with the results of references 20 and 21. According to reference 20 and 21, the polymer recovers to an extended coil in methanol but the IR spectrum of PNiPA for the methanol solution is completely different from that for water, in which PNiPA also assumes an extended coil conformation. Thus, we have to consider that the IR spectra of PNiPA in solutions do not reflect only the macroscopic phase transition or the local polarity around the chain.

What is the dominant factor for the changes in the amide I bands? Figure 4 illustrates the results of curve fitting for the spectra shown in Fig. 2 and 3. It can be seen from Figure 4 that the spectral changes in the 1700-1600 cm^{-1} region (amide I) observed during both thermally and solvent-induced coil-globule transition of PNiPA are mainly due to the variation of the intensity ratio of two components (the bands at *ca.* 1651 and 1624 cm^{-1}) without a significant wavenumber shift of the bands. It is very likely that each band arises from the same origin through all the spectra observed during the thermally and solvent-induced coil-globule transitions. Several research groups concluded that the band at *ca.* 1624 cm^{-1} is due to the C=O group that form a hydrogen bond with water molecules, and the band at ca. 1651 cm^{-1} is attributed to an intramolecular hydrogen bonding within the polymer chain [15,16]. Maeda and co-workers [16] proposed the following phenomenological scheme for the spectral

changes in the amide I region during the thermally induced transition; (1) Below T_θ, the most of C=O groups forms a hydrogen bond with water and the polymer keeps an extended coil conformation. (2) Some of them are broken during the transition. (3)The band at 1651 cm^{-1} appears when intra- or inter-chain cross-linkages are formed above T_θ. This scheme cannot explain our experimental results obtained for the solvent-induced transition process. For example, the band at 1651 cm^{-1} is still dominant in the $0.51 \leq x_{me} \leq 1.00$ range where the polymer becomes an extended coil.

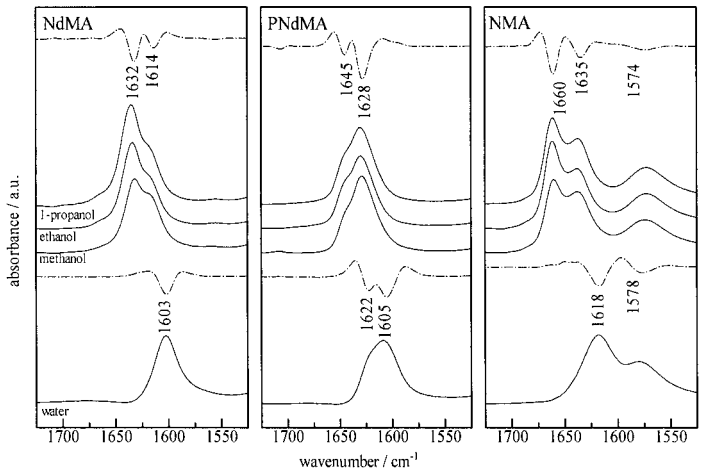

Fig.5. IR spectra of NdMA, PNdMA, and NMA for aqueous, methanol, ethanol, and 1-propanol solutions (solid lines), and their second derivatives for aqueous and methanol solutions (broken lines)

To examine the effect of the hydration on the spectral changes in the C=O stretching vibration, IR spectra of three model compounds, NdMA, PNdMA, and NMA were investigated. Figure 5 shows the IR spectra of these model compounds in aqueous and alcohol solutions. It is noted that the IR spectra of each model compounds changes a little with the alcohols. Therefore, it seems that the feature of the C=O stretching bands (NdMA, PNdMA) or the amide I band (NMA) of these compounds is not influenced significantly by the polarities of the solvents (the polarities of methanol, ethanol, and 1-propanol are 32.6, 24.3, and 20.1 at 25°C, respectively [22]). Thus, the wavenumbers of the C=O stretching bands are affected by

the hydrogen bondings with O-H groups of alcohol molecules. On the other hand, the C=O bands of NdMA and PNdMA, and the amide I band of NMA show a large downward shift in the spectra of the aqueous solutions. Although the NMA may form the self-associated complexes via an intermolecular C=O···H-N hydrogen bond in the aqueous solution, this tendency is the same. For all the model compounds, the IR spectra of aqueous solutions are largely different from those of the alcohol solutions. The bands observed in the IR spectra of the aqueous solutions do not have counter parts in the spectra of the alcohol solutions.

The above-mentioned results for the solutions of model compounds are discordance with those for the aqueous and methanol solutions of PNiPA. That is, when we consider the results

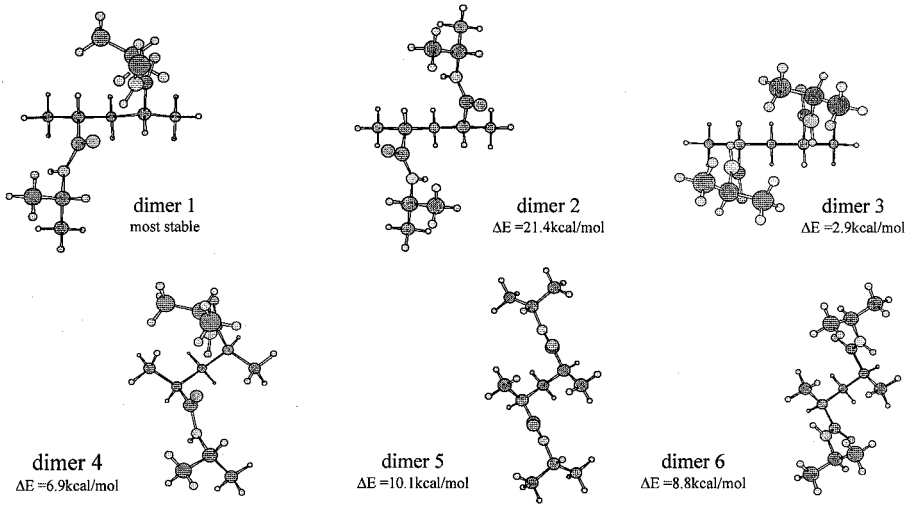

Fig.6. Conformations of dimer models of PNiPA optimized by DFT calculation at B3LYP/6-31G(d) level

for the model compounds, the amide I band of PNiPA in the aqueous solution should be at a lower wavenumber than 1624 cm^{-1}. However, the frequencies of the amide I of PNiPA bands are the same for both aqueous and methanol solutions. This shows that the solvation effect is not dominant for the spectral changes of PNiPA observed during the coil-globule transition. Thus, we have to consider conformational changes of PNiPA as a dominant factor for spectral variations observed during the transitions.

DFT calculation for dimer models of PNiPA. To correlate the observed spectral changes with the conformational changes, the spectral simulation for dimer models of PNiPA based on DFT calculation was carried out [17,18]. The structures of the dimer models for PNiPA were optimized at B3LYP/6-31G(d) level and their IR spectra were simulated using the DFT force fields. Six optimized conformations of the dimer models for PNiPA are illustrated in Figure 6 [17]. The main chains of dimer 1, 2, and 3 models assume a trans conformation, while those of dimer 4, 5 and 6 models take a gauche conformation. The tacticity of these dimer models is syndiotactic. In dimer 2 and 5 models, the neighboring C=O groups are close to each other, while in dimer 3 and 6 models the neighboring N-H groups face to face each other. Dimer 1 and 4 have a hydrogen bond between the neighboring amide groups (C=O ··· H-N). The single point energy calculation for the optimized structures shows that, dimer 1 has the most stable structure. The difference energy (ΔE) between dimer 1 and the other dimers is in Figure 6 [17]. Figure 7 compares the simulated IR spectra for the six models. The Lorentz type with a bandwidth, full width at the half height, of 7 cm^{-1} was assumed for each band in the simulated spectra. The simulated spectra show marked dependences on the conformations of dimer models. Note that the amide I band of dimer 1 and 4 splits into two bands. The band with the lower frequency arises from a C=O ··· H-N hydrogen bond, while that with the higher

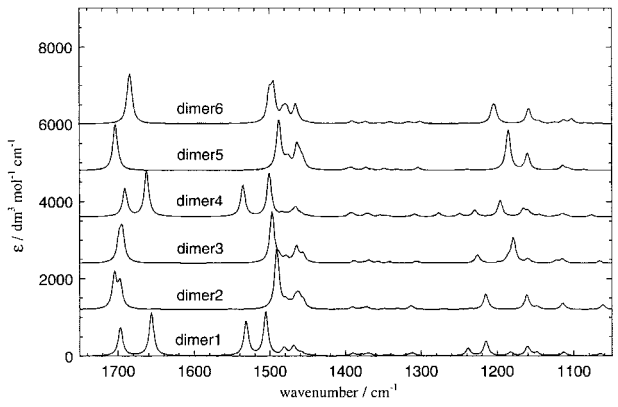

Fig.7. Simulated IR spectra for the six dimer models displayed in Figure 6

frequency is due to the "free" C=O group. Two corresponding bands are observed in the amide II region. When a C=O group is not involved in an intramolecular C=O ··· H-N hydrogen bond, an amide I band appears at a higher wavenumber than 1680 cm^{-1}, and conformation dependent shift of the amide I band is *ca.* 20 cm^{-1}. On the other hand, an amide I band arising from a C=O ··· H-N hydrogen bond is located around 1660 cm^{-1}. The shift caused by the intramolecular hydrogen bond is more than 30 cm^{-1}. As shown Figures 2, 3 and 4, the two amide I bands are observed at 1651 and 1624 cm^{-1}. The difference between the two bands is 27 cm^{-1}. Thus, one can conclude that the dimer 1 and 4 are feasible models for explaining the experimental results. In other words, only dimer modes that form an intramolecular C=O ··· H-N hydrogen bond can reproduce the band shift about 30 cm^{-1}, which is experimentally observed during the coil-globule transitions of PNiPA.

The incompatibility in the peak positions of the amide I and II bands between the simulation and experimental IR spectra may be attributed to the solvation of the C=O groups. Compared with the experimental spectra, both of the amide I bands due to the free C=O group (near 1690 cm^{-1}) and the C=O··· H-N hydrogen bond (near 1660 cm^{-1}) shift to a lower frequency, while the corresponding amide II bands show an upward shift. Note that the dependence of simulation spectra on basis sets and the solvation model are described in ref.17 and 23, respectively. Based on the detailed analysis of the experimental and simulated IR spectra, we have proposed the following band assignments for PNiPA in the aqueous and methanol solutions [17,18]; the lower frequency band (1624 cm^{-1}) arises from the intramolecular C=O···H-N hydrogen bond between the neighboring side chains of PNiPA, and the higher frequency band (1651 cm^{-1}) is assigned to the C=O stretching vibration that is not involved in the intramolecular hydrogen bond. The amide III bands of PNiPA provide the information about conformation changes of the main chain. Please see ref.17.

Experimental evidence for the existence of a C=O ··· H-N hydrogen bond in PNiPA solutions. We have proposed that the band at 1624 cm^{-1} arises from the intramolecular C=O···H-N hydrogen bonds between the neighboring side chains of PNiPA. Scarpa *et al.* [24]

has suggested that PNiPA has an intramolecular C=O···H-N hydrogen bond in an aqueous solution at 15°C (below T_θ) by analyzing the overtone bands (6800-6500 cm^{-1}) originating from the N-H stretching vibrations. On the contrary, several research groups have concluded that the intramolecular C=O···H-N hydrogen bond is formed exclusively above T_θ, and that the amide I band at *ca.* 1624 cm^{-1} is due to the hydrated C=O group [15,16]. This disagreement may come from ambiguous assignment for the C=O and/or N-H bands. For example, Scarpa *et al.* did not take account of the hydration of the N-H groups [24], and Maeda *et al.* made the assignment of the band at *ca.* 1624 cm^{-1} by means of phenomenological discussion [16]. To explore the local environment around the amide group of PNiPA, we investigated that the hydrogen-deuterium (H-D) exchange of amide protons of PNiPA side chains.[18] Since the H-D exchange of an aqueous PNiPA solution was also investigated by Scarpa *et al.* [24], we have used the perdeuterated methanol (CD_3OD) solution. The methanol dissolves PNiPA more easily than water, and IR bands of methanol less severely overlap with IR bands of PNiPA than those of water. Figure 8 shows the intensity variations of the amide II bands of PNiPA and NMA in CD_3OD caused by the H-D

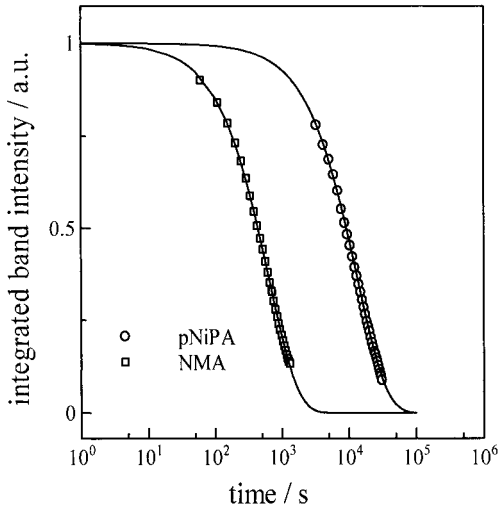

Fig.8. Intensity variations of the amide II bands of PNiPA (circle) and NMA (square) in a CD_3OD solution as a function of exposure time at 25°C

exchange of amide protons [18]. The concentration of PNiPA and NMA in the solution is about 2 % in weight. The H-D exchange rate of the amide proton for PNiPA and NMA were estimated to be 6.82×10^{-5} s^{-1} and 1.59×10^{-3} s^{-1}, respectively [18]. It is noted that the H-D exchange rates for the PNiPA and NMA show the differences of the order of 10^2. Although NMA may form an intermolecular C=O···H-N hydrogen bond [25,26], the observed exchange rate for NMA was much faster than that for PNiPA. The obtained slow rate for the PNiPA / CD_3OD system suggests that the side chain amide groups are involved in the internal hydrogen bonding.

The inaccessibility of the solvent molecules due to steric hindrance is rather unlikely in our system, because PNiPA is a homopolymer and has a fairly flexible random coil structure in methanol [21]. This means that the perdeuterated methanol molecules should have high accessibility to the side chains of PNiPA. As another possible interpretation, Scarpa and co-workers reported that a slow H-D exchange rate is attributed to a change in the self-dissociation constant of water in the neighborhood of the polymer chain [24]. However, their interpretation is not dependable, because it was derived from unclear assignments for the N-H bands. It is found from analysis of the N-H stretching bands in the 3600-3100 cm^{-1} region of PNiPA in the CD_3OD solution that a band due to a free N-H group was not observed [18]. This implies that on the contrary to the conclusion by Scarpa and co-workers the free N-H group hardly exists in solutions whose the solvent molecules have an O-H group.

If the solvent accessibility to N-H groups of PNiPA and NMA is similar, the existence of the intramolecular C=O···H-N hydrogen bond should be a main factor for the difference of the H-D exchange rate between PNiPA and NMA. The detailed analysis of the amide II' bands also supported the interpretation [18]. It was concluded therefore that the band at 1624 cm^{-1} is due to the C=O groups that forms an intramolecular C=O···H-N hydrogen bond.

Changes in local conformation during coil-globule transition of PNiPA. The IR study combined with the DFT calculations revealed that PNiPA has the intramolecular C=O ··· H-N hydrogen bond in the coil-state and that its amide band is observed at *ca.* 1624 cm^{-1}. The band

at 1651 cm^{-1} appears because some of the intramolecular hydrogen bonds of neighboring amide groups are broken during the coil-globule transition. The conformation of the main chain of PNiPA also changes during the transition as we reported previously [17,18]. The spectral changes observed during the solvent induced reentrant coil-globule transition in the $0 \leq x_{me} \leq 0.13$ region are very similar to those during the thermally induced coil-globule transition. Note that similar spectral variations were observed during the coil-globule transition of PNiPA induced by the addition of salts [16]. These imply that the local structure of PNiPA undergoes a similar conformational change during the coil-globule transitions with different perturbation. Another important conclusion reached was that the local conformations of PNiPA in the methanol solutions are completely different from that in the aqueous solution, although the polymer has an extended coil conformation in both solutions. That is to say, the local conformation of PNiPA changes depending upon water or methanol. We supposed therefore that the origin of the solvent-induced reentrant coil-globule transition in the water-methanol mixtures lies in the changes in the local conformation of PNiPA; when the methanol is added to the aqueous solution of PNiPA or water is added to the methanol solution, the local conformation starts changing. An intermediate conformer is realized in the $0.15 < x_{me} < 0.45$ region, and then PNiPA hardly dissolves.

Although, in general, it is believed that the PNiPA/water system has LCST, the information about the phase diagram is still confused. As mentioned in Introduction, this system shows an unusual phase behavior that deviates largely from the prediction of the Flory-Huggins theory [1-3]. Our recent IR studies suggested that for a fundamental understanding of the phase behavior of PNiPA/water system, one should consider not only the interaction between water and the monomer unit of PNiPA but also the effects of the local structure of PNiPA on the solubility of the polymer. This point of view may provide new physical insight into the segment-solvent interaction in a polymer system.

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