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Polymer 43 (2002) 5607–5613

polymer

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Study of the volume phase transition of poly(*N*-isopropylacrylamide) gels in aqueous solutions of pyridine by depolarized Rayleigh and Raman scattering

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Received 25 April 2002; received in revised form 3 July 2002; accepted 15 July 2002

Abstract

The volume phase transition of neutral poly(*N*-isopropylacrylamide) gels in aqueous solutions of pyridine was studied by means of depolarized Rayleigh and Raman scattering. The Rayleigh reorientational relaxation time, τ_{Ray}, of pyridine, calculated from the half-width of the depolarized Rayleigh spectrum, attains a maximum at approximately $x = 0.2$ at which the gel undergoes the abrupt volume change. As the gel shrinks, the ratio, I_G/I_S, of the intensity of the spectrum of the gel to that of the aqueous solution abruptly decreases, reflecting the decrease in the number of free pyridine in the gel network. A new Raman band, which shifts by 130 cm^{-1}, appears for the shrunken gels. This new band is assigned to the C–H stretching vibrations of pyridine bound to the PNIPA chains by the hydrogen-bonding interaction. As the gel shrinks, the intensity, I_B, of the new Raman band abruptly increases, on the contrary, the intensity, I_F, of the free pyridine band decreases. The intensity ratio, $I_F/(I_F + I_B)$, which represents the number fraction of free pyridine in the network, excellently agrees with I_G/I_S. The results show that the hydrophilic solutes such as pyridine in PNIPA gels are bound by the hydrogen-bonding interaction between the solutes and the chains. © 2002 Published by Elsevier Science Ltd.

Keywords: Volume phase transition; Poly(*N*-isopropylacrylamide) gel; Depolarized Rayleigh and Raman scattering

1. Introduction

It has been known that poly(*N*-isopropylacrylamide) (PNIPA) gels undergo volume phase transitions in pure water in response to changes in temperature [1,2] or hydrostatic pressure [3]. The phase transitions in the gels are induced by competition between hydrophilic and hydrophobic natures of PNIPA chains. The gels also undergo the phase transition in aqueous solutions of methanol when the solvent composition is varied [4]. It has also been reported that polyacrylamide gels in aqueous solutions of acetone undergo the volume phase transition in response to a change in acetone concentration [5]. Recently, one of the authors reported that acrylamide gels in those solutions undergo the volume phase transition in response to the change of pressure as well as PNIPA gels [6]. Thermodynamically, the phase transitions of these hydrogels in such binary mixtures have been explained by considering the osmotic pressure of the gels derived from the mixing free energy. The free energy consists of the energies of the association between solute and polymer segment, solvent and polymer segment, and solute and solvent, which are derived from intermolecular interactions between them [7].

Aqueous solutions of non-elctrolytes such as alcohol and amine are known to show the peculiar concentration dependence in their physical properties such as acoustic and volumetric ones [8,9]. And the solutions of alcohol and pyridine are also known as the hydrogen-bonded systems which form complexes or local structures in the systems due to the hydrogen-bonding interaction between the solutes and water [10–13]. The experiments of depolarized Rayleigh and Raman scattering in the pyridine–water system had been done to study a complex formation in the system in terms of reorientational motions and a vibration spectrum of pyridine [11,12,14,15]. To examine the molecular motions of such hydrophilic substances in hydrogels is also important to the application of gels such as drug delivery systems [16].

The aim of the present study is to examine how local structure relates to the volume phase transition of the PNIPA gels from a viewpoint of intermolecular interaction

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0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00474-3

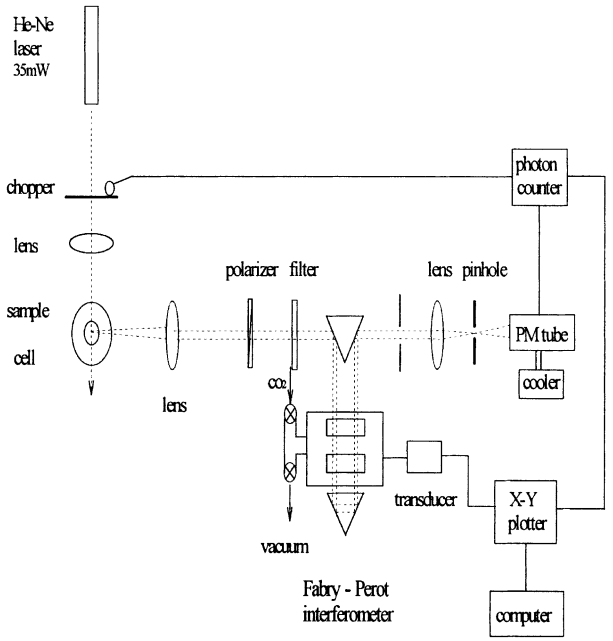

Fig. 1. Block diagram of the depolarized Rayleigh scattering apparatus.

between the solutes and the polymer chains. For this aim, we carried out the experiments of depolarized Rayleigh and Raman scattering of the gels immersed in the aqueous solutions of pyridine to examine how the reorientational motions and intramolecular vibrations of pyridine relate to the volume phase transition of the gels. We show that the pyridine causes the volume phase transition in PNIPA gels in the aqueous solutions of pyridine, and that the reorientational motions and C–H stretching vibrations of pyridine are restricted by the hydrogen-bonding interaction between the solute and PNIPA chains as the gels shrink.

2. Experimental

2.1. Sample preparation

Sample ionized PNIPA gels were prepared by a free radical copolymerization in water. 3.88 g of NIPA monomer, 0.067 g of *N*,*N*-methylenebisacrylamide as a cross-linker, and 0.064 g of sodium acrylate to ionize the network were dissolved in distilled water by bubbling with N_2 gas. The total volume of the solution was 50 ml. The mole ratio of NIPA monomer to sodium acrylate was 50:1. The substances which did not dissolve in water were removed by a filter of 1 μm pore size, and 20 mg of ammonium persulfate (initiator), and 120 μl of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (accelerator), were added to the solution. The glass tubes of 1.63 mm inner diameter were put in the glass vessel containing the solution. The solution was polymerized at 20 °C over night. The gels were taken out of the tubes and immersed in distilled water to remove residual substances. After this, the gels were immersed in aqueous solutions of pyridine.

2.2. Swelling curve

The sample PNIPA gel was put in a glass cell containing the aqueous solution of pyridine. The cell was suspended in the water bath and the temperature was kept constant within ±0.1 °C. The diameter, d, of the gel was measured with a microscope. The volume ratio, V/V_0, was obtained from the relation, $V/V_0 = (d/d_0)^3$, where V_0 and d_0 are the volume and diameter of the gel when it was prepared, respectively.

2.3. Depolarized Rayleigh and Raman scattering

The depolarized Rayleigh spectra were obtained by a conventional light scattering instrument as shown in Fig. 1. An He–Ne laser (632.8 nm) with an output power of 35 mW was used as an incident light and focused onto the sample gel in the scattering cell containing the solution. The light scattered at an angle of 90° is collimated by the lens and introduced into the double-pass pressure-scanning Fabry–Perot interferometer. To collect the depolarized scattering light (I_{HV}), a Glan Thompson prism is placed in front of the interferometer. The flatness and reflectivity of the mirrors making up the Fabry–Perot interferometer are $\lambda/175$ and 96%, respectively. The distance between mirrors is kept 0.33 mm by the spacers that gives the free spectra range of 454.5 GHz. The CO_2 gas was used to scan the spectrum. It needed to change the pressure of the gas from a vacuum to about 3 atm in order to scan one free spectral range and it took about 10 min. The light passing the interferometer was detected by a cooled photomultiplier operating on photoncounting.

Raman spectra were obtained by a simple light scattering instrument. A 50 mW argon-ion laser operating at 488 nm was used as the excitation source. It was focused onto the sample gel in a scattering cell containing the aqueous solution. The light scattered at an angle of 90° is collimated by the collecting lens and focused on the entrance slit of a spectrograph (300 g/mm grating) equipped with a cooled CCD camera by another lens. To cut the laser line due to elastic scattering, a holographic notch filter was placed between the two lenses.

3. Results and discussion

3.1. Swelling curves

The swelling ratio, V/V_0, of the present PNIPA gel immersed in the aqueous solution of pyridine is plotted as a function of pyridine concentration (vol% and mole fraction x) for various temperatures, 15, 30, and 40 °C, in Fig. 2. The overall behavior of the obtained swelling curves for the changes in concentration and temperature is almost the

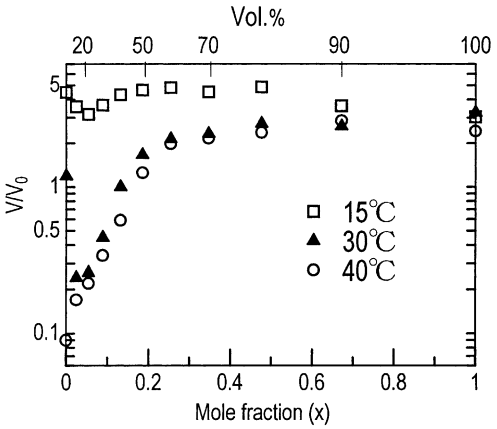

Fig. 2. The swelling ratio, V/V_0, of PNIPA gels in the aqueous solutions of pyridine as a function of pyridine concentration (vol% and mole fraction x) at 15, 30, and 40 °C.

same as that obtained when the gel is immersed in methanol [7]. Namely, for 30 °C, the reentrant volume transition is also observed in the present case. The gel swells at a higher pyridine concentration as well as in pure water and shrinks by an addition of a small amount of pyridine, approximately $x = 0.1-0.2$. For the higher temperature, 40 °C, the reentrant transition shifts to a continuous volume transition from the shrunken state to the swollen state. For the lower temperature, 15 °C, the volume transition disappears and the swelling curve becomes flat. One can attribute these similarities between the swelling curves to that there are some similarities between the physical properties of the aqueous solutions of pyridine and that of methanol. Both the solutes are non-electrolyte substances which associate with water by hydrogen-bonding interaction and form complexes (the clathrate hydrate like local structure) in these aqueous solutions at low concentrations around $x = 0.1$ [12]. The result suggests that the formation of such complexes in the aqueous solutions intimately relates to the volume transition in the gel.

3.2. Depolarized Rayleigh scattering

A typical depolarized Rayleigh spectrum, I_{HV}, of the gel immersed in the aqueous solution of 80% pyridine at 40 °C is shown in Fig. 3. The spectrum consists of a sum of two spectral components with different half-widths and a constant background. One is the narrow component, $I_N(\omega)$, due to the I_{VV} light leakage into the I_{HV} component. The inhomogeneous distribution of polymer chains and the large difference between refractive indexes of the polymer and the solution cause a strong elastic scattering light and bring a strong narrow component. Another is the depolarized Rayleigh component, $I_{DR}(\omega)$, caused by the reorientational motion of pyridine molecules.

To decompose the obtained spectrum of the gel into these two components, we fit the following spectral functions to the spectrum. The spectral function of $I_N(\omega)$ is assumed to

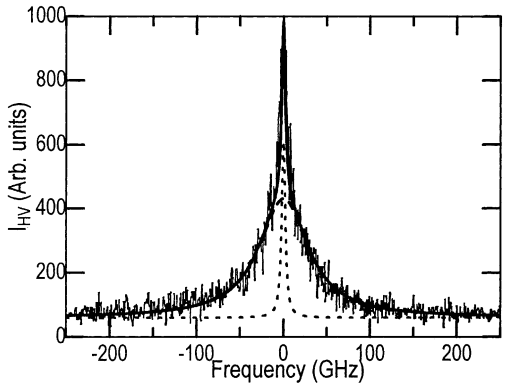

Fig. 3. A typical depolarized spectrum of the PNIPA gel in the aqueous solution of vol% pyridine at 40 °C. The dotted, dashed and solid curves are the calculated ones.

approximate to the following Lorentzian function

$$I_N(\omega) = I_{N,0}/(1 + (\omega/\Delta\omega)^2), \quad (1)$$

where $\Delta\omega$ is the half-width at half-height of the spectrum which is related to the apparatus half-width. The spectral function of $I_{DR}(\omega)$ is also assumed to be written in the following single Lorentzian function [17]

$$I_{DR}(\omega) = I_{DR,0}\Gamma/(\omega^2 + \Gamma^2), \quad (2)$$

where Γ is the half-width at half-height of the spectrum.

The measured spectrum consists of a sum of the spectra of $I_N(\omega)$ and $I_{DR}(\omega)$ and the background, I_B.

In Fig. 3, the dotted and dashed curves represent the spectra, $I_N(\omega)$ and $I_{DR}(\omega)$, calculated using the appropriate values for the parameters, $I_{0,N}$, $\Delta\omega$, $I_{0,DR}$, and Γ, in Eqs. (1) and (2). In the calculations, we used 2.7 GHz as the value of $\Delta\omega$, which is obtained by fitting Eq. (1) to the spectrum I_{HV} of the gel immersed in pure water. The values of other parameters, $I_{N,0}$, $I_{DR,0}$, I_B, and Γ, were chosen so that the sum of the calculated spectra and I_B fit the measured spectrum. The solid curve represents the spectrum of their sum. It is seen that the solid curve fits the experimental spectrum well. This spectrum fitting procedure does not bring a significant error in decomposing the spectrum into the depolarized Rayleigh spectrum since the half-width of the narrow component is much smaller than that of the depolarized Rayleigh spectrum. Carrying out the fitting procedure to measured spectra, we can decompose the spectra into the depolarized Rayleigh spectra and obtain their half-width Γ at half-height.

The Rayleigh reorientational relaxation time τ_{Ray} is calculated from the obtained Γ according to the relation:

$$\tau_{Ray} = (2\pi\Gamma)^{-1}. \quad (3)$$

The calculated values of τ_{Ray}, together with the values for the aqueous solutions of pyridine, are plotted as a function of concentration for three temperatures 15, 30, and 40 °C in Fig. 4. It is seen that there is no significant difference between the Rayleigh reorientational relaxation time of

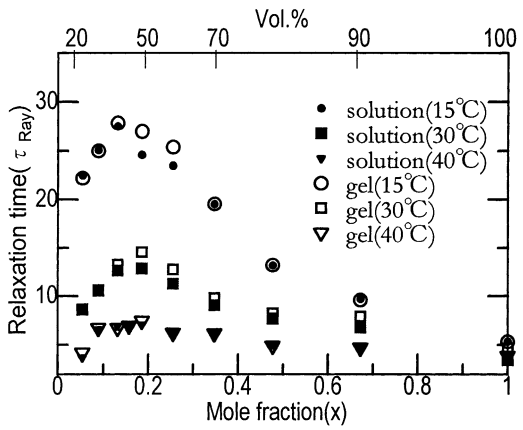

Fig. 4. Rayleigh relaxation time, τ_{Ray}, of pyridine in the PNIPA gels and in the aqueous solutions as a function of pyridine concentration (vol% and x) at 15, 30, and 40 °C.

pyridine in the gel and that in the solution in the whole concentration range. The τ_{Ray} varies with pyridine concentration and attains a maximum around $x = 0.1–0.2$. Comparing the result with the swelling curves shown in Fig. 2, one finds that the concentration at which τ_{Ray} attains the maximum coincides with that at which the gel undergoes the abrupt volume change from the shrunken state to the swollen state. This implies that the volume transition of the gel is related to some structure change of the solution. Wang and Whittenburg [11] measured the depolarized Rayleigh spectral width for an aqueous solution of pyridine at lower temperatures and reported that the relaxation time τ_{Ray} attains a maximum around $x = 0.2$, reflecting the extensive hydrogen-bond formation of the pyridine molecule with water. Also, Ito and Kato [12] pointed out that the local structure due to the hydrogen bond between them is formed at the low concentration and grows with temperature. For the volume phase transition in polymer gels, the polymer–solvent interaction parameter χ plays an important role through the osmotic pressure of a gel. As mentioned, for a mixing solvent, the parameter χ is related with the free energies of the association between solute and polymer segment, solvent and polymer segment, and solute and solvent. The formation of the hydrogen-bond structure in the solution affects these free energies, i.e. the osmotic pressure of the gel through the change in χ, and causes the volume transition in the gel.

Pyridine molecules in the network can be divided into two types in mobility. They have different reorientational relaxation times. One is bound pyridine of which mobility is restricted by the interaction with polymer chains. Another is free pyridine which is not immobilized in the network. One can suppose that the interaction is due to the hydrogen bond between N of pyridine and H–N of PNIPA chains. Then, the depolarized Rayleigh spectrum should be written in a sum of two Lorentzian functions with different half-widths, Γ_1 and Γ_2, for free and bound pyridines, corresponding to the different relaxation times, $\tau_{Ray,1}$ and $\tau_{Ray,2}$:

$$I_{DR}(\omega) = I_{DR,0,1}\Gamma_1/(\omega^2 + \Gamma_1^2) + I_{DR,0,2}\Gamma_2/(\omega^2 + \Gamma_2^2). \quad (4)$$

It has been reported that the mobility of bound water in polymer chains is restricted at 10^4 times compared with free water [18]. This implies that the Rayleigh reorientational relaxation time of bound pyridine is much longer than that of free pyridine, i.e. $\tau_{Ray,2} \gg \tau_{Ray,1}$. In this case, it is expected that the half-width of the spectrum of bound pyridine is much narrower than that of free pyridine, and the spectrum will be superimposed on the narrow central component. So, one can regard the obtained depolarized Rayleigh spectrum $I_{DR}(\omega)$ is described by a single Lorenzian as given by Eq. (2). So, the half-width of the measured spectrum represents Γ of free pyridine which is equal to the half-width of the spectrum of pyridine in the aqueous solutions, as shown in Fig. 4. It is difficult to separate the spectrum of the reorientational motion of bound pyridine from the narrow central component because of the presence of the strong elastic scattering. The intensity of the spectrum $I_N(\omega)$ at lower concentrations becomes much stronger than that at higher concentrations. Though the number of the bound pyridine is expected to increase as the gel shrinks, it does not affect the half-width of the spectrum because only the rorientational motions of free pyridine are reflected in the measured depolarized Rayleigh spectrum. However, the intensity of the spectrum is expected to decrease as the gel shrinks because the number of free pyridine will decrease relatively.

3.3. Intensity of the depolarized Rayleigh spectrum

The intensity ratios, I_G/I_S, were obtained for the depolarized spectra measured at 40 °C. They are plotted as a function of concentration in Fig. 5. For the ratio, I_G is the intensity of the depolarized Rayleigh spectrum of pyridine in the gel, which represents the number of free pyridine, and I_S the intensity in the aqueous solution with the same pyridine concentration, which does the total number of pyridine in the network. So, one can regard that the ratio represents the number fraction of free pyridine in the polymer network. The each intensity was obtained by integrating Eq. (2) for each Γ. In the calculation of the ratio, the intensity, I_G, was corrected for the change in volume fraction of the network. Fig. 5 shows that the ratio is approximately 1 for the swollen gel in the concentration region above $x =\sim 0.2$, and the value sharply decreases as the concentration is decreased, i.e. as the gel shrinks. It is found that in contrast to the relaxation time, τ_{Ray}, the intensity ratio, I_G/I_S, strongly reflects the volume change of the gel. As mentioned above, the intensity of the depolarized Rayleigh spectrum represents the number of free pyridine molecules. The result says that for the swollen gel, all the molecules in the gel are free from the interactions with the polymer chains, and the number of free molecules per unit

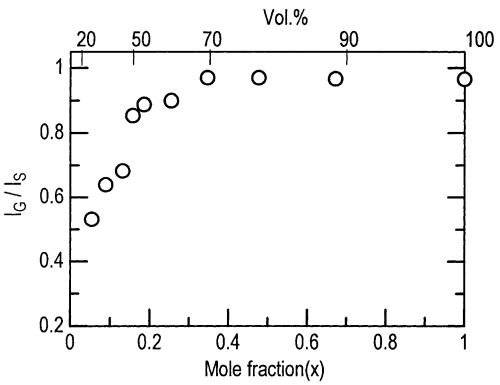

Fig. 5. The intensity ratio of the depolarized Rayleigh spectrum, I_G/I_S, at 40 °C as a function of pyridine concentration. I_G is the intensity of the spectrum of the gel and I_S, the intensity of the solution with the same concentration.

volume in the gel can be regarded to be equal to that in the solution. So, I_G/I_S is 1 as expected. As the gel shrinks, some of the molecules in the network will be bound to the PNIPA chains by the hydrogen-bonding interaction acting between them. This means that the number of the free pyridine decreases as the gel shrinks, and the intensity, I_G, namely, the ratio, I_G/I_S, decreases as shown in Fig. 5.

3.4. Raman scattering

Raman and infrared spectra of pyridine had been obtained by previous researchers [19–21]. It was reported that the vibration spectrum of pyridine in the frequency region from 3000 to 3100 cm^{-1} contains five C–H stretching fundamental vibrations and possibly five binary combinations [21]. In the present study, we measured Raman spectra of pyridine in the PNIPA gel network in this frequency region for various concentrations.

Fig. 6 shows the Raman spectra of PNIPA gels at 40 °C (a) together with the spectra of the aqueous solutions (b), for concentrations, 10, 30, 40, and 60 vol%. For the swollen gel at high concentrations above 60%, the spectral feature is almost the same as that of the solutions (Fig. 6(b)). The spectrum consists of two spectral band groups: one is the sharp band whose peak is at approximately 3060 cm^{-1}, and another is the broad one whose peak is at approximately 3400 cm^{-1}. This shows that pyridine molecules in the swollen gel are in the same circumstances as in the solutions and are free from the interactions with PNIPA chains. One can assign the former band to the C–H stretching vibrations of pyridine and the latter to the O–H stretching mode of water. As seen in Fig. 6(b), such a band profile of the spectrum does not change with concentration except the change in intensity. Meanwhile, for the spectra of the gel (Fig. 6(a)), it is seen that the new band group appears as the concentration is decreased, namely, the gel shrinks. The peak of this new band group occurs at approximately 2930 cm^{-1}, which shifts approximately by 130 cm^{-1} from the C–H stretching band of free pyridine. Such a new band

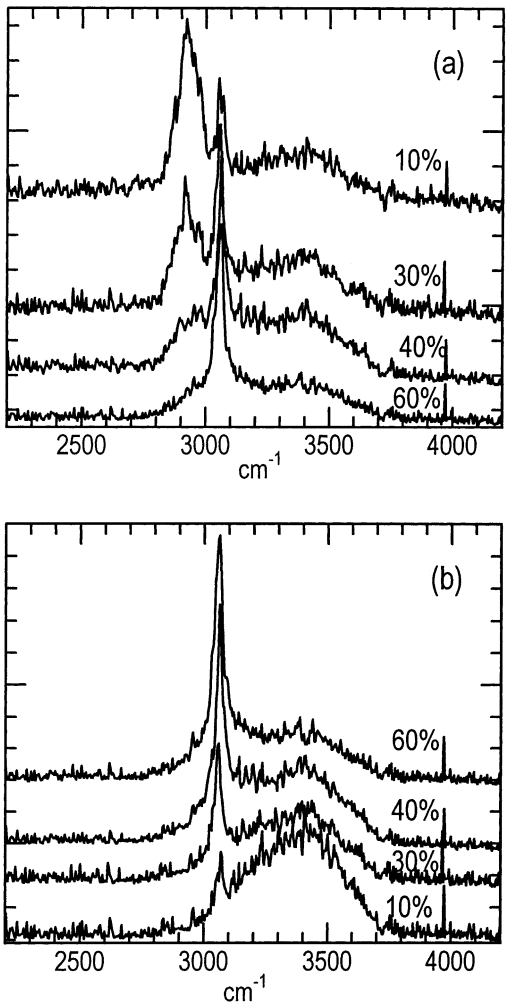

Fig. 6. Raman spectra of pyridine (a) in PNIPA gels and (b) in the aqueous solutions for 10, 30, 40, and 60 vol% at 40 °C.

group is not observed for the solutions. As the gel shrinks the peak intensity of the new band abruptly increases, but its frequency scarcely varies. For the concentration of 10%, the intensity of the new band becomes seven times as large as that of free pyridine. At low concentrations, these intensities are reversed and the band of the free pyridine disappears.

From the result, the new band should be assigned to the C–H stretching vibrations of pyridine bound to the PNIPA chains by the hydrogen-bonding interaction. The red shift of the band implies that the interaction weakens the force constants relating to these vibrations. The neighboring molecular environment is important to these vibrations, and it mainly depends on the polymer chain density, namely, the volume fraction of the network. This implies that the cross-link is not always necessary for the new band. But, the cross-links plays an important role in the volume phase transition in gels. The high polymer density state, the shrunken state, causing the new band can be realized by the phase transition to the shrunken state in the gels.

One can regard that the intensity, I_B, of the new band group represents the number of bound pyridine and the

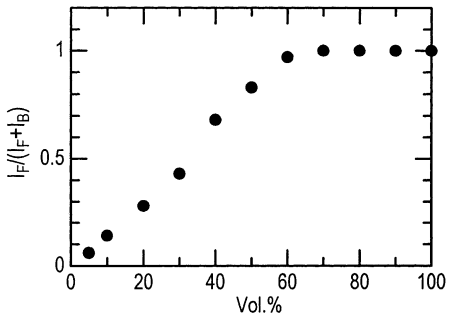

Fig. 7. The intensity ratio, $I_F/(I_F + I_B)$, of Raman spectrum of PNIPA gels at 40 °C as a function of pyridine concentration. I_F is the spectral intensity of free pyridine, and I_B, the intensity of bound pyridine.

intensity, I_F, of the other band group does the number of free pyridine. So, the intensity ratio of I_F to $I_B + I_F$ represents the number fraction of free pyridine in the network. By subtracting the spectrum of O–H stretching mode of water from the obtained Raman spectrum, one can calculate the intensity of the spectra, I_B and I_F, and the intensity ratio.

The obtained intensity ratio is plotted as a function of concentration in Fig. 7. The figure shows that the ratio is equal to 1 for the concentrations above 60%, but as the concentration decreases, namely, as the gel shrinks, abruptly decreases. This means that the solute pyridine in the swollen gel is free from the interactions with the polymer chains, but the solute in the shrunken gel is restricted by the hydrogen-bonding interactions with the polymer chains also. The abrupt decrease in the ratio reflects the abrupt decrease in the number of free pyridine molecules in the gel network. It is found that the result is consistent with that obtained from the intensity ratio of the depolarized Rayleigh spectrum.

The Raman intensity ratio, $I_F/(I_B + I_F)$, together with the depolarized Rayleigh intensity ratio, I_G/I_S, is plotted as a function of the swelling ratio in Fig. 8. Both the ratios represent the number fraction of free pyridine in the PNIPA network as mentioned. It is seen that the ratios excellently agree with each other in spite of different measurements. As the gel shrinks, namely, the network size becomes small, the ratio abruptly decreases. This means that the

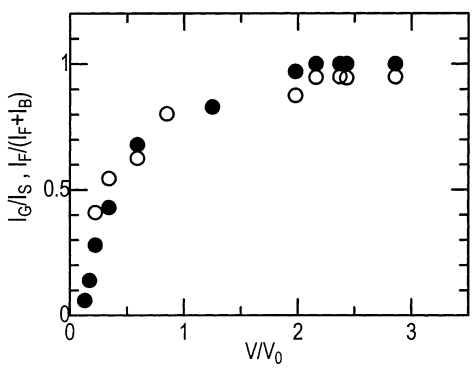

Fig. 8. The intensity ratios, I_G/I_S and $I_F/(I_F + I_B)$, as a function of the swelling ratio: (○) I_G/I_S, and (•) $I_F/(I_F + I_B)$.

number of free pyridine abruptly decreases and that of bound pyridine becomes dominant in the shrunken network relatively. This is the same result as obtained from the DSC measurement of freezable (free) water and non-freezable (bound) water content in the gels [22]. We think that the present result generally applies to hydrophilic solutes in PNIPA gels.

Such strong interactions between the hydrophilic solutes and the polymer chains will affect transport properties of the solutes in the gels, such as diffusion. Previously, we reported that the diffusion coefficient of rhodamine B in the shrunken PNIPA gels is extremely, $\sim 10^3$ times, lower than that in the swollen gel [23].

4. Conclusion

The volume phase transition of neutral PNIPA gels in aqueous solutions of pyridine was studied by means of depolarized Rayleigh and Raman scattering. The swelling curves of the gels in the aqueous solutions were measured as a function of pyridine concentration. The gels underwent the reentrant volume phase transition like the gels in methanol–water solutions. The Rayleigh relaxation time, τ_{Ray}, of pyridine in the gels was calculated from the half-width at half-height of the depolarized Rayleigh spectra for various pyridine concentrations. The τ_{Ray} attains a maximum at approximately $x = 0.2$ at which the gel undergoes the abrupt volume change. This suggests that a certain structure change, hydrogen-bond formation of pyridine with water, formed in the aqueous solutions of pyridine is associated with the volume transition of PNIPA gels. The intensity ratio of the depolarized Rayleigh spectrum, I_G/I_S, abruptly decreases as the gel shrinks. This suggests that the number of free pyridine in the gel network abruptly decreases as the gel shrinks because of the increase in the number of bound pyridine to PNIPA chains due to the hydrogen-bonding interaction.

The new Raman band group, which is assigned to the C–H stretching vibrations of pyridine bound to PNIPA chains by the hydrogen-bonding interaction, appears for the shrunken gel. The band shifts by 130 cm^{-1} from the band of free pyridine. As the concentration decreases, the gel shrinks, the intensity, I_B, of the new band group abruptly increases, on the contrary, the band intensity, I_F, of free pyridine decreases. The intensity ratio, $I_F/(I_B + I_F)$, which represents the number fraction of the free pyridine in the network, abruptly decreases as the gel shrinks. This intensity ratio excellently agrees with the intensity ratio of the depolarized Rayleigh spectrum, I_G/I_S, in spite of different measurements.

From the above results, it is found that the hydrophilic solutes such as pyridine in the PNIPA gels are immobilized by the hydrogen-bonding interaction between the solutes and the chains.

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