Hydration Behavior of Polymeric Gel revealed by Ultrasonic Velocity

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Thermal response and hydration behavior of linear polyacrylamide (PAAm) with molecular weight of 10 KDa were investigated by means of ultrasonic velocity and density measurements focusing on the hydration behavior and comparison with those of NiPAM gel particles that were obtained recently. Hydration number, defined as the number of water molecules bound to one monomer unit, was evaluated quantitatively. Hydration number of NiPAM gel decreased markedly near the volume phase transition temperature in good agreement with the temperature dependence of the size of gel beads determined by dynamic light scattering measurements, and becomes to coincide with that of PAAm at the higher temperature region than the transition regime. It was ascertained that the decrease of hydration number of NiPAM gel is responsible to the dehydration caused by the formation of hydrophobic bonding.
Key words: NiPAM gel, ultrasonic velocity, hydration, hydrophobic bonding, volume phase transition

1. INTRODUCTION

N-isopropylacrylamide (NiPAM) gel is the most widely investigated one among polymeric due to its unique thermal response, volume phase transition, and so many investigations have been reported so far especially relating to the functional fabrications [1,2]. Volume phase transition is brought about by the competitive actions of swelling pressure due to mixing entropy and deswelling pressure due to mixing interaction. Isopropyl group of each NiPAM monomer unit exhibits hydrophobic interaction with water [3]. A NiPAM monomer unit has not only isopropyl group, but also has amide bonding (CONH). Amide bond region is hydrophilic forming hydrogen bonding with surrounding water molecules. Those hydrophobic interaction and hydrophilic interaction interplay competitively, and hydrophobic bonding formed between adjacent NiPAM chains results in a coil-to-globule transition for NiPAM polymer chain at higher temperature than the threshold temperature [4,5]. In this process, the interaction of NiPAM monomers with water plays an essential role, and the characterization of hydration and dehydration is important. Because hydrophobic groups as isopropyl groups form hydrophobic hydration, clathrate, restricting water molecules around the hydrophobic groups when dispersed in water, formation of hydrophobic bonding between isopropyl groups results in the liberation of many water molecules. That is, hydrophobic interaction is the dominant factor in the volume phase transition of the hydrogels as well as coil-to-globule transition in a single chain, and the characterization of hydrophobic interaction and hydration behavior is quite important for the detailed analyses of those transitions.

Several studies about the hydration of NiPAM hydrogel have been reported. Suetoh et al. studied the non-uniform hydration in the thermal response of NiPAM gel by DSC measurements, and observed a unique dependence of thermal properties of NiPAM gel on the history of gel treatment [6]. Lele et al. studied the bound water content in NiPAM gel theoretically and obtained that the bound water content at the shrunken state (high temperature) is about 0.4 g/g (hydration number ~ 2.5), and becomes 3–4 times at the swollen state [7]. Sasaki et al. studied the salt effect on the elastic properties of shrunken NiPAM gel, and estimated the hydration number (number of water molecules hydrated with one monomer unit) from DSC data as ca. 2 at shrunken (dehydrated) state and ca. 14 at swollen state [8]. The difference 12 corresponds to hydrophobic hydration number. However, temperature dependence of hydro- phobic and hydrophilic hydration was not taken into account.

Recently, we examined the hydration number of NiPAM gel by use of ultrasonic sound velocimetry combined with density measurements, and obtained that the hydration number of ca. 3 at shrunken state (40°C) increases to ca. 7.5 at swollen state (20°C) taking the temperature dependence of hydration into account [9]. Submicron size NiPAM gel beads prepared at the temperature above the volume phase transition temperature were used there because of the dispersion stability even at the shrunken state. In the evaluation procedure, the structure of hydrophobically hydrated water was assumed to be the same as that of ice. In order to clarify that the hydration number of NiPAM chain at shrunken state can be attributed to hydrophilic hydration only and that the difference of the hydration number between shrunken and swollen states corresponds to

hydrophobic hydration, it is desirable to verify the hydration behavior of amide group independently. In this report, hydration behavior of linear polyacrylamide (PAAm) was examined to evaluate quantitatively the contribution of hydrophilic hydration. As a result, hydration and dehydration behavior of hydrophobic isopropyl group of NiPAM monomer unit could be demonstrated explicitly.

2. EXPERIMENTAL

The preparation of NiPAM gel particles has been described elsewhere [9]. The sample with the diameter at 20°C being ca. 700 nm was used in this work. Linear PAAm with nominal molecular weight 10 KDa was purchased from Aldrich, and was purified by recrystalization using aqueous methanol solution. Finely powdered acrylamide gel with micron order size was also prepared. Molar ratio of acrylamide and N,N'-methylene bisacrylamide was the same as that used for NiPAM gel particles. Polymerized acrylamide gel with the size of $(5cm)^3$ was crushed by homogeniser, dialyzed thoroughly by distilled water, freeze-dried, and grounded finely by a mortar.

Ultrasonic velocity was measured by a sequential pulse oscillation method developed from the sing-around method [10,11]. The details of apparatus has been described elsewhere [9]. Resonant frequency of the transducer was 3MHz. Time interval between the input and output signal was determined by a universal counter with the time resolution of 0.1 ns, and the obtained period is related to the ultrasonic velocity as,

$$\tau = L_{25} [1 + \alpha (T-25)] / v + \Delta\tau \qquad (1)$$

Here, τ, L_{25}, α, T, v, and $\Delta\tau$ are the period of the detected pulse sequence, cell length at 25 °C, thermal expansion coefficient of the cell, temperature, ultrasonic velocity, and the delay time due to the detecting circuit, respectively. Temperature was controlled within ± 1 mK, and the reproducibility of velocity measurements was within 5×10^{-3} m/s. Calibration of the system was achieved by measuring pure water.

Ultrasonic velocity in water in the experimental temperature range is about 1500 m/s. Since the resonant frequency is 3 MHz, the wavelength is about 0.5 mm being much larger than the size of sample particles, and the sample solutions can be regarded as continuous media, and the ultrasonic velocity is affected only by the state of water.

In order to represent the variation of ultrasonic velocity in the solution compared to that in the solvent, the limiting velocity number defined as,

$$[v] = \lim (v / v_0 - 1) / C \quad (C \to 0) \qquad (2)$$

was used. Here, v, v_0, and C are the ultrasonic velocity in the solution, that in the solvent, and the concentration

of the sample. As the concentration used in the present study is sufficiently low, the difference between the experimentally determined values of $(v / v_0 - 1) / C$ and $[v]$ is negligibly small.

Density of the sample solutions was measured by the vibrating densitometer (DMA602, Anton Paar) with the constancy of temperature ± 5 mK, and the reproducibility of density measurements was within 0.1 mg/cm^3. In order to represent the variation of the solution density, the limiting density number defined as,

$$[\rho] = \lim (\rho / \rho_0 - 1) / C \quad (C \to 0) \qquad (3)$$

was used. Here, ρ and ρ_0 are the density of the solution and of the solvent, respectively. Adiabatic compressibility β can be obtained from v and ρ by the well-known relation of $\beta = 1 / \rho v^2$.

The hydration number S has been formulated as [9],

$$S = -\rho_h (m_s / m_w)\{[\beta] + V_s'(1 - \beta_s / \beta_0)\}$$
$$/ [(1 - \beta_h / \beta_0) - (1 - \rho_h / \rho_0)(1 - \beta_s / \beta_0)] \qquad (4)$$

where ρ_h is the density of hydrated water, β_h, β_s, and β_0 the adiabatic compressibility of hydrated water, solute, and solvent (water), m_s and m_w the molecular weight of solute and water, $[\beta]$ the limiting compressibility number as defined as (2), V_s' the partial volume of solute, respectively. Because hydration might be caused by hydrogen bonding principally, the structure of hydrated (bound) water could be represented as that of ice without much error, and ρ_h and β_h can be approximated by those of ice. Remaining unknown variable is β_s. If S becomes 0 at some condition (all the hydrated water are excluded), β_s can be estimated. Then, the hydration number S is obtainable from the experimentally observed quantities.

3. RESULTS AND DISCUSSION

Temperature dependence of the size of present NiPAM gel particle is a continuous curve different from the discrete thermal response observed for macroscopic NiPAM gel prepared at low temperature. Marked decrease in the diameter occurred around 32 °C. This behavior corresponds to the volume phase transition observed in the macroscopic NiPAM gels [9].

Figure 1 illustrates the relationships of $(v / v_0 - 1) / C$ as a function of temperature. Similar to the swelling curve of Fig. 1, continuous curve was obtained for NiPAM gel sample, and that for PAAM is almost a straight decreasing curve with temperature. Marked decrease in $(v / v_0 - 1) / C$ was clearly observed near the volume phase transition temperature (ca. 32 °C) for NiPAM gel sample. It has been ascertained that indistinguishable curves of $(v / v_0 - 1) / C$ are obtainable for NiPAM gel particles with the same composition, even if the sizes of gel are largely different. No differences in the curve were observed between linear PAAm and finely powdered AAm gel samples.

Figure 2 illustrates the limiting density number. Continuous temperature dependence is again obtained and a weak decrease at about 32 °C is observed for NiPAM gel, and that for PAAm is almost constant. The magnitudes for NiPAM gel in the shrunken state are less than those in the swollen state. This fact means that the partial volume of NiPAM chain in the shrunken state is larger than that in the swollen state, even though the elementary NiPAM chain composing gel network shrinks. Dehydrated self-assembly of NiPAM chain due to hydrophobic bonding is more bulky than that in the hydrated state, and this behavior is similar to the micellar formation by hydrophobic interaction.

Adiabatic compressibility β is related to the ultrasonic velocity v and density ρ by the equation $\beta = 1 / \rho v^2$. Resultant $[\beta]$ calculated from $(v / v_0 - 1) / C$ and $(\rho / \rho_0 - 1) / C$ are shown in Fig. 3., in which the intrapolated data of $(\rho / \rho_0 - 1) / C$ were used. Negative $[\beta]$ was obtained in the experimental range increasing with temperature both for NiPAM gel and PAAm. Marked increase occurs for NiPAM gel near the transition temperature, although a monotonous increasing curve was obtained for PAAm.

In order to evaluate the hydration number, adiabatic compressibility of NiPAM gel was obtained using ethanol/water mixture [12,13]. NiPAM chain in aqueous ethanol solution (ca. 30 vol%) is known to be dehydrated. Resultant β_s was 4 ($\pm$ 0.4) x 10^{-10} Pa^{-1}. This magnitude is vary similar to that of water, 4.5 x 10^{-10} Pa^{-1}. Then, the hydration number S can be calculated by use of eq. 4.

The hydration number of NiPAM gel and PAAm thus obtained are shown in Fig. 4. Hydration number S of NiPAM gel is a decreasing function with temperature, and a marked decrease occurres at the volume phase transition region. Slope of the gradual decrease of S at higher temperature than the volume phase transition temperature seems to be the same as that in the lower temperature. Hydration number S of PAAm is depicted, too, and coincides well with that of NiPAM gel at higher temperature region than the volume phase transition temperature. Temperature dependence of S of NiPAM gel agrees quite well with the swelling curve. These facts clearly ascertain that the temperature dependent variation of S of NiPAM gel at higher temperature is due to the hydrophilic hydration in the amide group (and partly due to the hydrophobic hydration by the methylene chain). The magnitude of hydrophilic hydration depends on the temperature, due to the weakening of hydrogen bonding with temperature. Therefore, the difference between the hydration number of NiPAM gel and PAAm at lower temperature region should correspond to the extent of hydrophobic hydration and is about 3. Moreover, the slopes of S of
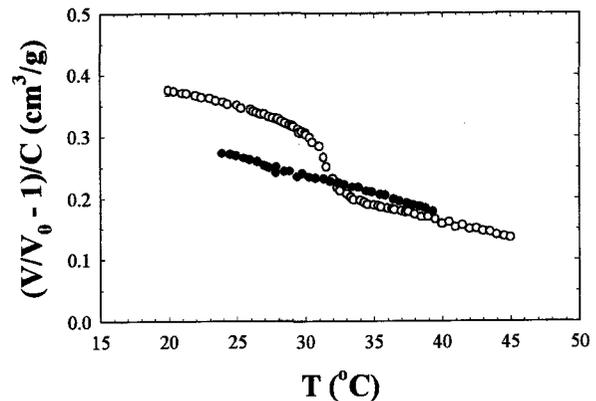
Fig. 1. Limiting velocity number of NiPAM gel (○) and PAAm (●) as a function temperature.
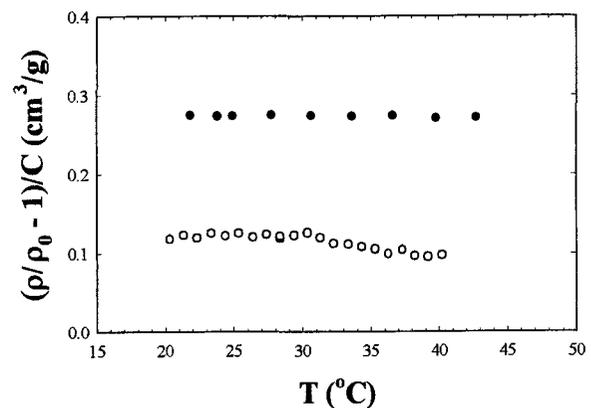
Fig. 2. Limiting density number as a function of temperature. Meanings of the symbols are the same as those in Fig. 1.
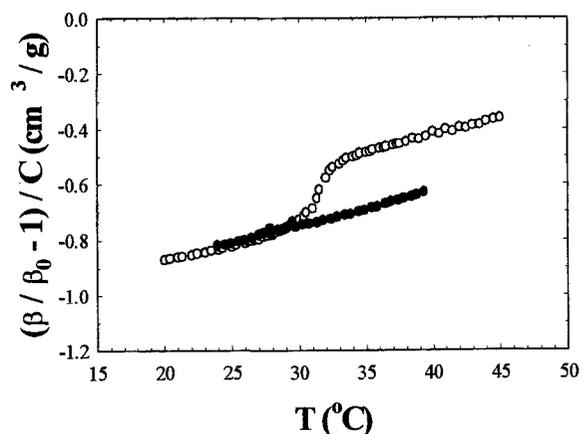
Fig. 3. Limiting compressibility number as a function temperature. Meanings of the symbols are the same as those in Fig. 1.

PAAm both at the higher and lower temperature regions are very similar. This fact suggests that the temperature dependence of hydrophobic hydration could be much less than hydrophilic hydration.

The magnitude 3 of hydrophobic hydration is a little less than the prediction by Lele (ca. 7) and the results of Sasaki (ca. 12). In the procedure evaluating S, it is assumed that hydrated water is restricted by hydrogen bonding and the structure of it can be represented by ice, and the compressibility of ice was used for β_h (1.8 x 10^{-10} Pa^{-1}). It should be noted that the magnitudes of S at 40°C and 20°C could become larger 4.2 and 10.2, respectively, if the bound water around hydrophobic group is more compressible than ice and a little larger value of β_h is assumed (say, 2.5 x 10^{-10} Pa^{-1}). On the other hand, the magnitude of ρ_h affects only a little.

CONCLUSION

Hydration behavior of PAAm was investigated and compared with that of NiPAM gel. At higher temperature region where NiPAM gel shrinks, both S of PAAm and NiPAM gel coincide well with each other. Hydrophobically hydrated water of NiPAM gel should be fully excluded and hydrophobic bonding between isopropyl groups in good agreement with the volume phase transition. The difference between the hydration number of NiPAM gel and PAAm at lower temperature region should correspond to the contribution of hydrophobically hydration, and was evaluated as ca. 3. The present results ascertains well the recent our results on the hydration behavior of NiPAM gel.

ACKNOWLEDGMENT

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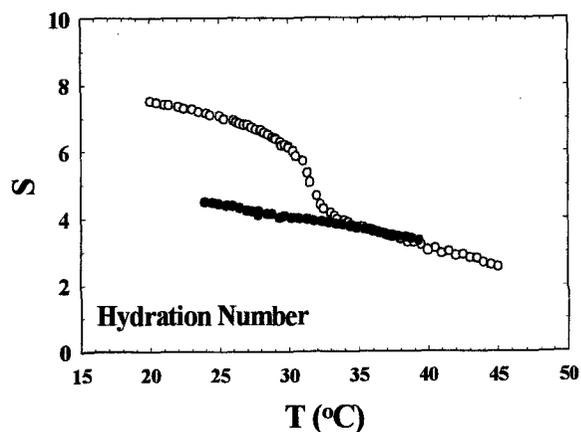
Fig. 4. Temperature dependence of the hydration number. Meanings of the symbols are the same as those in Fig. 1.

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