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Thermal Response of Polymer Gel and Ultrasonic Velocity

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Dynamic light scattering, fluorescence spectroscopy, and ultrasonic velocity measurements of submicron sized N-normalpropyl acrylamide gel, which exhibits a unique thermal response (volume phase transition) around room temperature, were carried out in various solvent conditions to investigate the local structure inside the gel and the correlations among the volume change of the gel, local hydrophobicity, and hydrating structure. The radii of gel beads exhibit continuous volume phase transition. Transition temperature shifted to higher temperatures with copolymerization of acrylic acid and pH. Fluorescence spectra showed that the peak wavelength begins to decrease at the temperature where the size of gel beads becomes to decrease (a little lower temperature than the volume phase transition region). Ultrasonic velocity of aqueous solution of linear PNnPAM did not show any significant change below the transition temperature, but that of the aqueous suspension of gel beads showed a remarkable change around the volume phase transition temperature. Local structure of PNnPAM chains relating to the hydrophobic interaction was discussed.
Key words: Volume phase transition, Polymer gel, Dynamic light scattering, Fluorescence, Ultrasonic velocity

1. INTRODUCTION

Volume phase transition which polymer gels exhibit in response to the external conditions; e.g., temperature, solvent condition, pH, etc., is the most striking characteristics of the gel materials, and its mechanism and dynamics are the most important subject for the characterization of gel [1]. Since the swelling-shrinking process of gels obeys essentially to a diffusion process, the equilibration time for the macroscopic sized gel should be very long. Moreover, inhomogeneity of the monomer density and the crossbridging points inevitable to macroscopic gel smear out the detailed analyses of physicochemical behavior of gels. By using submicron sized gel beads the observation of swelling-shrinking behavior becomes much easier and those problems could be lowered very much. In this paper, we report the combined study of thermal response of N-normalpropyl acrylamide (NnPAM) gel beads with submicron size using dynamic light scattering (DLS), fluorescence, and ultrasonic velocity. Local hydrophobic hydrating structure was analyzed relating to the volume phase transition. In our previous study of dansyl-labelled linear PNnPAM (polyNnPAM), we found that local clustering of PNnPAM chains occurs due to hydrophobic interaction preceding to the coil-globule transition [2-7] of the whole chain (substantially below the transition temperature). This should be related to the abrupt coil-globule transition and to the marked discrete volume phase transition of NnPAM gel in aqueous media. In the present work, one of the typical hydrophobicity probe, ANS (1-anilino-8-naphthalene sulfonate), was mixed with NnPAM suspension instead. Ultrasonic velocity measurements combined with the density measurements gives the configurational information of water molecules and hydrating state of PNnPAM chains.

2. EXPERIMENTAL

NnPAM (N-normalpropyl acrylamide) monomer was synthesized from N-normalpropyl amine and acryloyl chloride by a standard method, and was used after thorough purification by successive recrystalization. Linear PNnPAM was polymerized in benzene with azobis(isobutyronitrile) as an initiator [8]. NnPAM submicron gel was polymerized by using the emulsion polymerization [9]. The pregel solution composed of 30g water, 1.875g NnPAM, 0.02g N,N'-methylenebis-acrylamide, 0.191g sodium dodecylbenzenesulfonate, and 2.5 mg of ammonium persulfate was degassed with being cooled down by ice, and was put into a 50ml vial equipped with a nitrogen bubbling tube and a magnetic stirrer. Pregel solution was heated at 60°C for 2hrs continuing agitating under nitrogen, and terminated by adding methanol into a reactor. After the reaction was stopped by adding methanol, the suspension was dialyzed for one week against methanol and distilled water to remove the residual monomers and surfactant. Copolymerization of gel beads with acrylic acid (AAc) was similarly performed with the molar ratio of 100/1 (S12) and 20/1 (S14) of [NnPAM]/[AAc]. Very monodispersed gel beads were obtained.

Dynamic light scattering measurement was carried out using a homemade spectrometer and an ALV-5000 multiple-tau digital correlator to obtain the correlation function of scattered light $g^{(2)}(\tau)$ [10]. Vertically polarized Ar ion laser operated at the wavelength of 488.0 nm was used as the incident beam. Hydrodynamic diameter was calculated by using the Einstein-Stokes equations.

Fluorescence measurements were done by HITACHI F-4010 fluorescence spectrometer. ANS was added to probe the local hydrophobic circumstances at 0.1mM near the PNnPAM chains. Emission from ANS changes from 520 nm (in water) to about 465 nm (in n-propanol) with the decrease of polarity around ANS molecules (hydrophobicity) [11]. Excitation wavelength of 356 nm was used. Temperature was controlled by circulating thermostatted water. Difference spectra were obtained in order to make the detail of fluorescence spectra clear,

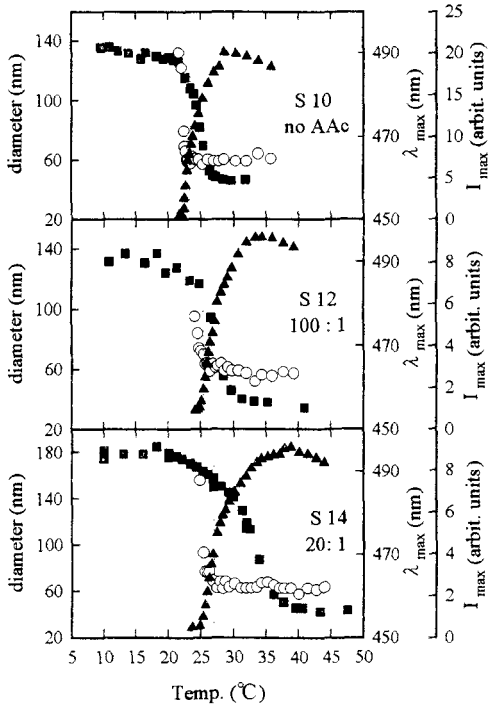

Fig.1 Acrylic acid composition dependence of the swelling curve. ■ is the diameter of gel beads determined by DLS, and ▲ and ○ are $I_{EM,max}$ and $\lambda_{EM,max}$ of the difference spectrum, respectively.

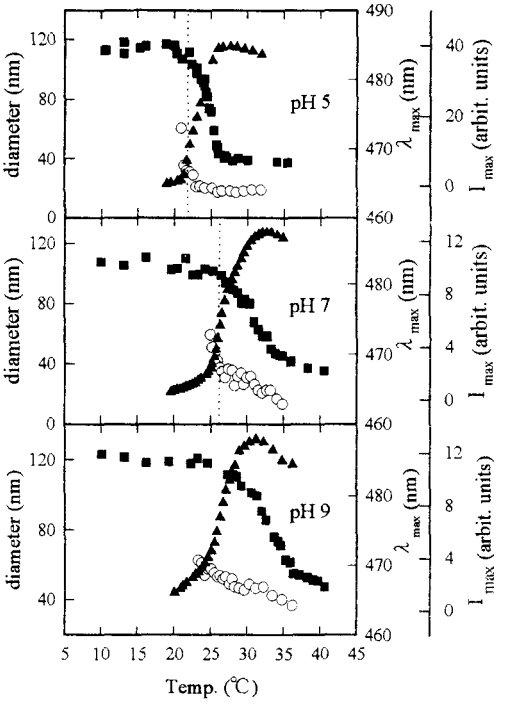

Fig.2. pH dependence of the swelling curve of NnPAM-co-AAc (S12) gel beads. ■ is the diameter of gel beads determined by DLS, and ▲ and ○ are $I_{EM,max}$ and $\lambda_{EM,max}$ of the difference spectrum, respectively.

which are the differences in fluorescence intensity between those at the measured temperatures and that at the lowest temperature (~10°C).

Ultrasonic velocities (resonant frequency = 3 MHz) were measured by a sequential pulse oscillation method developed from the sing-around method [12]. The time interval between the input and the output signal was directly measured by a universal counter with the time resolution of 0.1 ns. Velocimeter was calibrated using water. Density was obtained by vibrating densimeter (DMA602, Anton Paar), and the adiabatic compressibility β was calculated from the velocity V and density ρ as $\beta = 1/\rho V^2$.

Measurements were done with increasing temperature. In all the measurements, temperature was controlled with the constancy better than 0.01°C.

3. RESULTS AND DISCUSSION

Figure 1 shows the hydrodynamic diameter, and the peak wavelength and intensity of the difference spectra of fluorescence intensity as a function of temperature. The peak wavelength shifted rapidly towards the shorter wavelength (blue shift) near the temperature [13,14] where the diameter of gel beads begins to decrease slightly, although such a temperature is fairly lower than the main transition temperature region, and reached soon the final state showing a plateau behavior. On the other hand, fluorescence intensity at the peak wavelength starts to increase from those temperatures, and increase continuously until gel beads shrink enough. This fact suggests that microscopic environment inside the gel does not change continuously in the process of volume phase transition, but two states (locally clustered region by the hydrophobic interaction and the well hydrated region as that at low temperature) coexists and the quantity of clusters increases with the increase in temperature. Since the interchain interaction enhances such a cluster formation in case of gel, clear change in the fluorescence spectra was observed. For linear chains, only a weak clustering and formation of hydrophobic region occur, and the blue shift is much less.

In case of copolymerization gel with AAc (S12 and S14, [NnPAM]/[AAc] = 100/1 and 20/1, respectively), the transition temperature observed by DLS increases with AAc content and the size change is quite continuous. But fluorescence spectra showed only a little increase of transition temperature, and the sharpness of temperature dependence does not change. The plateau behavior of fluorescence peak wavelength (especially for S14) is observed around 25°C well below the transition region in the gel diameter. These features are in contrast that the size change of bulk gel with submillimeter dimension occurs discontinuously [15]. This fact indicates the importance of inhomogeneity of gel structure for the volume phase transition behavior. Electrostatic interaction caused by carboxyl group of AAc increases the swelling pressure, but inhomogeneity of charge density and the decrease of dissociation of

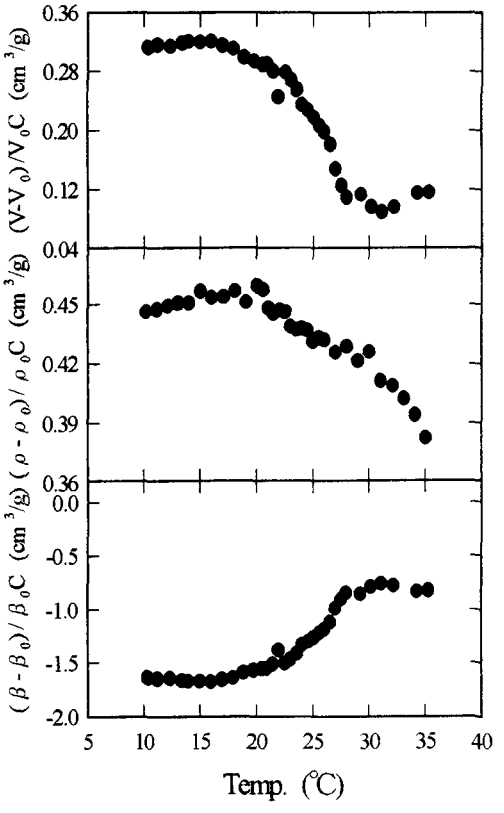

Fig.3. Temperature dependence of ultrasonic velocity [V], density[ρ], and compressibility[β] of aqueous suspension NnPAM gel beads. Concentration of gel beads is 1.51 mg/cm^3.

carboxyl group with increasing temperature results in a local mechanical strain in a macroscopic bulk gel. This effect plays an essential role in the discontinuous volume phase transition in such a case. However, such an effect should not be strong enough in the submicron sized gel, and continuous transition occurs.

Figure 2 shows the pH dependence of thermal response of AAc copolymerized gel beads (100/1) in the buffer solution. Temperature dependence of the hydrodynamic diameter shows more gentle transition at higher pH, and the volume phase transition occurs at higher temperature. However, the change in fluorescence response appears clearly in the lower temperature region compared to the temperature dependence of size change, especially in pH 7. Increase of pH affects the volume change with temperature similarly with the increase of AAc content. At pH 9, the change in fluorescence response appears at a lower temperature than that at pH 7. Those behaviors are reproducible enough, but the clear reason is at present open to the further study.

Figure 3 shows the temperature dependence of ultrasonic velocity, density, and compressibility of NnPAM gel beads (S10) in water displayed as the limiting number defined as $[V] = \lim_{c\to 0}(V - V_0)/V_0C$, where V_0 and C are the sound velocity in the solvent and concentration, respectively [16]. [V] and [ρ] are positive in the experimental temperature range, and decreases over the transition region. This is because water molecules are structured surrounding the hydrophobic n-propyl group, and therefore are stiffer with higher density than free water. Around the volume phase transition temperature, hydrophobic hydration is broken and structured water molecules are released (dehydration), then, [β] increases. At the higher temperature where the gel size becomes constant at the shrunken state, the temperature dependences of [V] and [ρ] are quite different. However, [β] becomes almost constant. Before the volume change of gel beads occurs, dehydration due to hydrophobic interaction starts to occur, which is consistent with the local cluster formation detected by fluorescence spectra. It is noteworthy that [β] increases, although slightly, around 18°C (the temperature where the fluorescent response in dansyl-labelled PNnPAM showed clear change indicating the formation of hydrophobic region). [V] of linear PNnPAM aqueous solution also showed slight wiggling behavior around 18°C suggesting the occurrence of weak dehydration. On the other hand, [V] of linear PNiPAM aqueous solution showed quite less temperature dependence below the transition temperature. (Above the transition temperature, the aggregation occurred and the measurements became impossible.) Local cluster formation could be enhanced by hydrophobic core (the case of dansyl-labelled linear PNnPAM) or high monomer density (the case of gel beads) in addition to stronger hydrophobic interaction of n-propyl groups than that of isopropyl groups. These points should be closely related to the inhomogeneity of gel structure and the discontinuous volume phase transition of bulk gels.

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